

GROWTH OF POLYELECTROLYTE ON LIGNOCELLULOSIC FIBRES: STUDY BY ζ -POTENTIAL, FTIR, AND XPS

Houssein Awada,^{a,*} Daniel Monplaisir, and Claude Daneault

A layer-by-layer (LbL) self-assembly technique using polyallylamine hydrochloride (PAH) and polyacrylic acid (PAA) was employed to build up polyelectrolyte multi-layers on pretreated thermomechanical pulp fibres. These pretreated fibres previously had been oxidized by means of a 4-acetamido TEMPO-mediated process in order to create carboxylic functions. These allow the subsequent formation of amide bonds between PAH and fibres. X-ray photo-electronic spectroscopy (XPS) analyses confirmed the formation of amide bonds between the carboxylic function on the fibres and the primary amine function of the PAH. Besides, the surface charge intensity of the coated fibres was determined by measuring the zeta potential after each treatment step.

Keywords: Thermomechanical pulp; XPS; Zeta potential; FTIR; TEMPO oxidization

Contact information : Centre de Recherche sur les Matériaux Lignocellulosiques (CRML), Université du Québec à Trois-Rivières 3351, Boulevard des Forges, Trois-Rivières (Québec), Canada, G9A 5H7;

* *Corresponding author:* houssein.awada@uqtr.ca, houssein_awada@hotmail.com

INTRODUCTION

Recently, lignocellulosic fibres are being increasingly used to reinforce polymer-matrix composite materials. Its advantages are that it is renewable, biodegradable, and biocompatible, and it can be derivatized to yield various useful products (Mohanty et al. 2002). The modification of individual lignocellulosic fibres with active substances represents an opportunity to develop new attractive materials with advanced bulky functionalities and to increase the interactions between the fibres.

The mechanical properties of paper, directly linked to the capability of its fibres to establish inter-and intra-fibre bonds, can be improved either by chemical modification (Montplaisir et al. 2006; Sang et al. 2009) or by physical adsorption of a cationic component (Gandini et al. 2012). Fahmy et al. (1974) reported that the physical addition of cellulose derivatives to cellulose pulps was more effective in improving paper properties than the chemical modification of cellulose pulp fibres, probably because of the unavoidable degradation side-processes in the latter case. Hubbe (2006) reported the influence of the polyelectrolytes adsorption on the fibres on the paper dry-strength. He reported that, though it is possible to achieve significant strength gains by optimal usage of individual polyelectrolytes, greater strength gains can be achieved by sequential addition of oppositely charged polyelectrolytes.

The recently discovered “layer-by-layer” (LbL) process, which was developed and applied first by Decher et al. (1992) on a planar surface, is based on the alternating adsorption of cationic and anionic species. The alternating adsorption of the polyelectro-

lytes on a charged surface is driven by the electrostatic interaction at each step of adsorption. A rinse step is included between each two adsorption processes to remove the unadsorbed excess of the polyelectrolyte. Multiple layers can be created by simply dipping the substrate in alternating anionic and cationic baths (Decher et al. 1997). Recently the LbL process has attracted considerable attention to the field of fibres modification.

The use of the LbL processing can allow for the improvement of the mechanical properties of the resulting paper. Wågberg et al. (2002) and Erikson et al. (2005, 2006) have studied the influence of the adsorption of the polyelectrolyte on paper strength. On the other hand, new properties have been introduced to paper by incorporating polyelectrolytes or nanoparticles with special function during the growth of the multilayers. Lu et al. (2007) adsorbed TiO_2 and SiO_2 nanoparticles on the fibre in order to increase the porosity of the paper. Electroconductivity has been introduced to the paper by adsorption of conductive polymer (Agrawal et al. 2006) or by adsorption of charged particles (Sarrazin et al. 2009) during the LbL process. Li et al. (2011) introduced hydrophobicity to the fibres surfaces by adsorption of lignosulfates during the LbL process. Pettersson et al. (2006) used this process to adsorb carboxymethylcellulose (CMC) on the fibres.

All of these cited studies have adsorbed the polyelectrolyte on the fibres surfaces using kraft fibres. To the best knowledge of the authors there has not been a study about the adsorption of the polyelectrolyte on the oxidised fibres of the thermomechanical pulp (TMP). In this case, due to the presence of a high amount of lignin, the chemical composition of the surface is totally different than the chemical composition of kraft pulp.

In the present study we have chosen to study the adsorption of polyelectrolyte on thermomechanical pulp (TMP) after increasing the number of the carboxylic function groups on the fibres surfaces by oxidation. In fact, the surface of such fibres contains mainly lignin, cellulose, and hemicellulose. Since the carboxylic acids on the fibres surface can be easily deprotonated to yield negative charges ($-\text{COO}^-$), we have performed LbL self-assembly of polyelectrolyte multilayers to modify the fibres surfaces. We have chosen the adsorption of poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) as polyelectrolytes, because carboxylic and amine groups of these couples could crosslink to improve the stability of the adsorbed layers on the fibres surfaces (Zhang et al. 2007).

In a first step the number of the carboxylic acid groups was increased through an oxidation process by TEMPO-mediation using a TEMPO-NaBr-NaOCl system. The term TEMPO refers to 2,2,6,6-tetramethylpiperidin-1-oxyl (4-acetamino TEMPO). Oxidation of the secondary alcohol groups (C6 in the cellulose chain) to carboxylate is the main objective of the TEMPO-NaBr-NaOCl treatments (De Nooy et al. 1995). After TEMPO oxidation, the adsorption of the polyelectrolyte on the fibres surfaces was verified by measuring the ζ -potential of the modified fibres during the LBL coating process. In fact, we measured the charge of the surface fibres after each adsorption step. X-ray photoelectron spectroscopy (XPS) was used to check the adsorption of the polyelectrolyte and also to verify the formation of the chemical bond between the polyelectrolyte and the fibres.

EXPERIMENTAL

Materials

A sample of unbleached TMP was taken after the twin-wire press at a Kruger mill in Trois-Rivieres (Quebec). Pulp consistency was approximately 32 to 38%. Reagent grade 4-acetamido-TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl), sodium bromide (NaBr), Poly(Allylamine Hydrochloride) (PAH, average molecular mass $M_w = 15000$) and Poly(Acrylic Acid) (PAA, average molecular mass $M_w = 5000$) were obtained from Sigma-Aldrich. Sodium chloride (NaCl) was purchased from Anachemia. A commercial Clorox bleach (source of sodium hypochlorite, NaOCl) solution was used. The concentration of NaOCl in this commercial solution was measured before use. All of these products were used as received.

Cellulose Oxidation

Oxidation experiments were conducted in a 4-L glass reactor. The reactor used for the oxidation experiments was placed in a bath of water in which the temperature was regulated at 25 °C. The oxidation was carried out in batch mode with 30 g of pulp (oven dried wt basis) in each batch. The pulp sample was first disintegrated for 20 min in deionised water at 1.5% consistency to obtain a uniform suspension of fibre and then transferred to a glass reactor. 50 mL of aqueous solution containing 4-acetamido-TEMPO (0.062 mmol per g cellulose fibre) and NaBr (0.415 mmol per g cellulose fibre) were added to the pulp suspension and stirred continuously for 5 min (Saito et al. 2006). The pH of the suspension was adjusted to 10.3 ± 0.3 with 1 M NaOH or 1 M HCl, depending on the situation, using a pH controller. The volume of NaOCl solution (5 mmol per g cellulose fibre) was then added dropwise to the mixture in approximately 30 min, while maintaining the pH at 10.3 ± 0.3 using 1 M NaOH or 1 M HCl solution. The reaction time, starting at the beginning of the NaOCl solution and the oxidation, was 90 min. The pulp suspension was continuously mixed with an electric stirrer. At the end of the predetermined reaction time, the oxidation was quenched by adding 50 mL of ethanol to the reaction mixture. The final pH of the solution was adjusted to 7.0 by adding 1 M HCl solution. The pulp suspension was filtered and washed three times with deionised water to remove any residual chemical products. The TEMPO-oxidized cellulose was stored at 4 °C for further treatment and analysis.

Determination of Carboxylate Contents

The carboxylate content of the oxidized and untreated cellulose was determined by an electric conductivity titration method (Katz et al. 1984). A Dosimat 765 (Metrohm) titrator and conductivity meter (Thermo Orion, model 150), supplied by Brinkmann Instruments Canada Ltd., was used to measure the carboxylate content. The measurement was carried out with 1.5 g of pulp sample (oven dried wt basis). Briefly, the quantity of pulp was first treated twice with 200 mL of 0.1 M HCl solution for 45 min and thoroughly washed and filtered three times with 100 mL of deionised water for each wash. This treatment converts the sodium carboxylate groups in the TEMPO-oxidized cellulose to the free carboxyl form. For titration, the filtered sample was suspended in 450 mL of 0.001 M NaCl solution followed by the addition of 5 mL of standardized 0.1 M

HCl solution for the titration process. At the end of titration the fibres were filtered, washed, and dried overnight in an oven at 105°C to determine the exact weight of the sample. The carboxylate content of the sample, expressed in mmol.kg^{-1} and repeated twice, was determined from the conductivity curve and processed by a computer.

Layer-by-Layer Process

The TEMPO-oxidized fibres were dispersed in deionised water. The concentration of the fibres suspension was kept at 2.5 g/L. The pH of this suspension was adjusted to 5.5. At this pH, Shiratori et al. (2000) reported that in the pH range of 5.5 to 6, the PAH chains are fully ionized. And the degree of ionization of the PAA chains varies from about 80 to 90%. Under this condition, they found a thick adsorbed layer of the polyelectrolyte. PAH (30 mg per g cellulose fibre) was dispersed in 10 L of deionised water, and the pH was adjusted to 5.5. The same condition was used for the PAA solution. NaCl (0.005 M) was added to all the solution to reduce the repulsion between the charges and the polyelectrolyte and facilitate its adsorption. The TEMPO-oxidized fibres (negatively charge) were first coated with PAH (positively charge) by adding the fibres solution to the PAH solution. The polyelectrolytes were allowed to adsorb for 20 min under continuous agitation by means of an electric stirrer. The pulp suspension was filtered and washed three times with deionised water to remove the non-adsorbed polyelectrolytes. PAA (negatively charge) was then coated onto the PAH treated fibres by the same process of the PAH coating. The process was repeated until the desired number of bilayer coating was reached. Figure 1 illustrates this process.

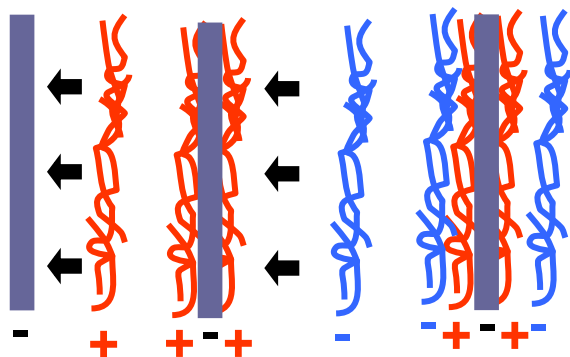


Figure 1. Layer-by-layer assembly via alternate adsorption of oppositely charged polyelectrolytes for coating on fibres substrates

In the discussion that follows, “one bilayer” means one combined step of PAH and PAA coating treatment. Handsheets of 80 g/m^2 for the surface analysis were prepared in a British sheet-mould according to the PAPTAC Standard Testing Methods. When the polyelectrolytes were adsorbed on the oxidized fibres, each handsheet was made from 50-50% mixtures of negative and positive fibres for each bilayer. For example a handsheet with one bilayer was made from a mixture of 50% of TEMPO oxidized fibres + 1 bilayers of PAH-PAA (negative fibres) and 50% of TEMPO oxidized fibres + (1 bilayers of PAH-PAA and one top layer of PAH (positive fibres)). Then, the suspension was disintegrated for 2 min before the formation of paper. All handsheets were pressed

respectively for 5 minutes on one side and 2 minutes on the other side with 343.238 kPa pressure. Then the handsheets were stocked in a conditional room with a temperature of 23 °C and 50% of relative humidity overnight before FTIR and XPS analysis.

ζ-potential Measurements

The surface charge of the fibres was evaluated using ζ-potential measurements (Nano-Zs, Malvern Instruments). During the LBL coating process the zeta potential of the surface fibres was measured after each adsorption step. After the dispersion of the fibres in deionised water (fibres concentration = 2.5 g/L, pH = 5.5 and NaCl concentration = 0.005 M), 20 mL from the suspension was used to measure the zeta potential of the surfaces fibres. The same process was repeated before the adsorption of the each new layer of polyelectrolyte. The reported value is an average of 5 measurements for each sample.

Fourier Transform Infrared spectrometry (FTIR)

Absorbance infrared spectra were recorded using a PerkinElmer 2000 Fourier Transform Infrared (FT-IR) spectrometer. 3 mg of handsheet material and 100 mg crystalline KBr were ground together using an alumina mortar and pestle and pressed to form discs. The discs were scanned over the range 4000 to 400 cm^{-1} with a total of 16 scans at a resolution of $\pm 4 \text{ cm}^{-1}$.

XPS Analysis

The X-ray photoelectron (XPS) method has been shown to be a useful tool for the study of chemical structure of fibres surface (Dorris and Gray 1978a). XPS spectra of the handsheet surfaces were obtained using an “AXIS Ultra” instrument from “Kratos Analytical”. A 225 W monochromatic aluminum source ($\text{Al}_{k\alpha}$) was used. Survey scans were taken with 1.0 eV step and 160 eV analyzer pass energy, while the high resolution regional spectra were recorded with 0.1 eV step and 40 eV pass energy. The pressure was typically 1×10^{-9} Torr. An area of 2 mm^2 at three different spots was analyzed in order to average over the heterogeneity of the sample. The position of the detector was at an angle of 90° to the sample surface. Deconvolution analysis was performed with a SUN Sparc Station IPX computer (Vision 2). The spectrum analysis was done with casa XPS 2.3.9.

RESULTS AND DISCUSSION

Carboxylic Acid Group Content

We measured the carboxylic acid contents by the electric conductivity titration method in the case of untreated fibres and of the TEMPO-oxidized fibres. The value in the case of TEMPO-oxidized fibres represents an average of 10 oxidation reaction. In the case of untreated fibres this value is the average of five measurements. For the untreated fibres, the carboxylic acid contents was 42 ± 3 (mmol/kg), and after TEMPO mediated oxidation this value become 474 ± 28 (mmol/kg).

We observed an increase in the value of the carboxylic acid group, indicating that the TEMPO-mediated oxidation is effective in generating carboxylic groups on TMP fibres.

ζ -potential Measurements

To perform the LbL coating of the fibres, PAH was used as polycation and PAA as polyanion. The adsorption of the polyelectrolyte on the fibres surfaces was verified by measuring the ζ -potential of the modified fibres. Figure 2 represents the variation of the ζ -potential for each step of the adsorption cycle. Cycle zero corresponds to the TEMPO-oxidized fibres.

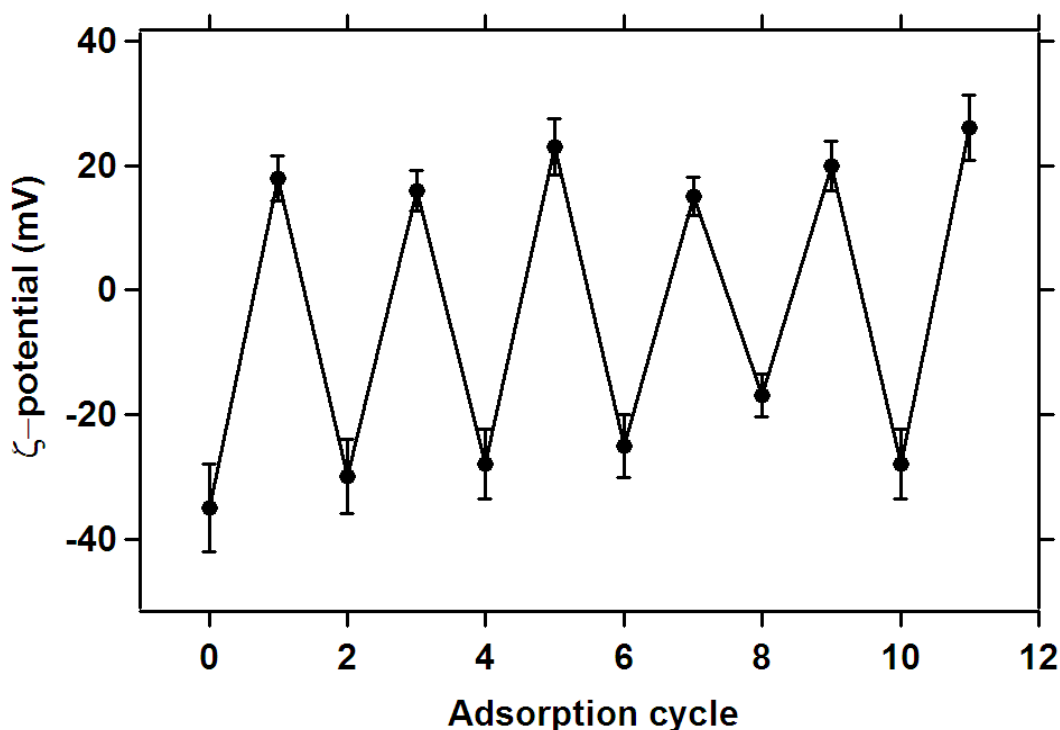


Figure 2. Evolution of the ζ -potential, as a function of layer number, during the LbL coating of positively (PAH) and negatively (PAA) polyelectrolyte ($n = 5$)

According to our experimental results, a negative ζ -potential (-35 mV) was measured for fibres after the TEMPO oxidation. Then, a positive ζ -potential ($+18$ mV) was observed in case after PAH was used, while a negative ζ -potential (-30 mV), in case PAA was used, indicating the successful adsorption of the first bilayer of polyelectrolyte. This phenomenon was observed for the subsequent bilayers, indicating that multilayer build-up takes place.

FTIR Experiments

The FTIR spectra of TEMPO-oxidized fibres before and after the adsorption of the polyelectrolytes are represented in Fig. 3 (for simplicity, we show only the case of 2, 4 and 5 bilayers). Spectrum (a) in Fig. 3 (a typical spectrum of the TEMPO-oxidized

fibres) shows two characteristics peaks at 1610 and 1740 cm^{-1} (Lasseguette 2008) corresponding to the carbonyl stretching vibration with strong intensity. These peaks represent respectively the COO^- and COOH . After the adsorption of the polyelectrolyte (PAH and PAA), we should observe an increasing of these two peaks due to the presence of the PAA. Moreover, one can observe a decreasing in these peaks at 1610 cm^{-1} and 1740 cm^{-1} (Fig. 3, b, c and d). This decreasing can be relate to an amide bound (CONH) formed between the acid group of the TEMPO-oxidized fibres and the amino group of the PAH for the first layer of the PAH and then between the acid group of the PAA and the amino group of the PAH for the following layers. According to the literature (Lasseguette 2008), the amide bound is characterised by the presence of two bands at 1644 cm^{-1} and 1567 cm^{-1} , corresponding respectively to the ($\text{C}=\text{O}$) stretching band and to the ($-\text{NH}$) bending vibration band. In Fig. 3 b, c, and d, we can clearly observe the presence of a new peak at 1635 cm^{-1} and the appearance of a small shoulder at 1560 cm^{-1} (Follain et al. 2008). Indeed, the carboxylic acid band is well separated from the amide group ($-\text{CONH}-$) bands at 1635 cm^{-1} . The presence of these two bands indicates that an amide bond has been formed.

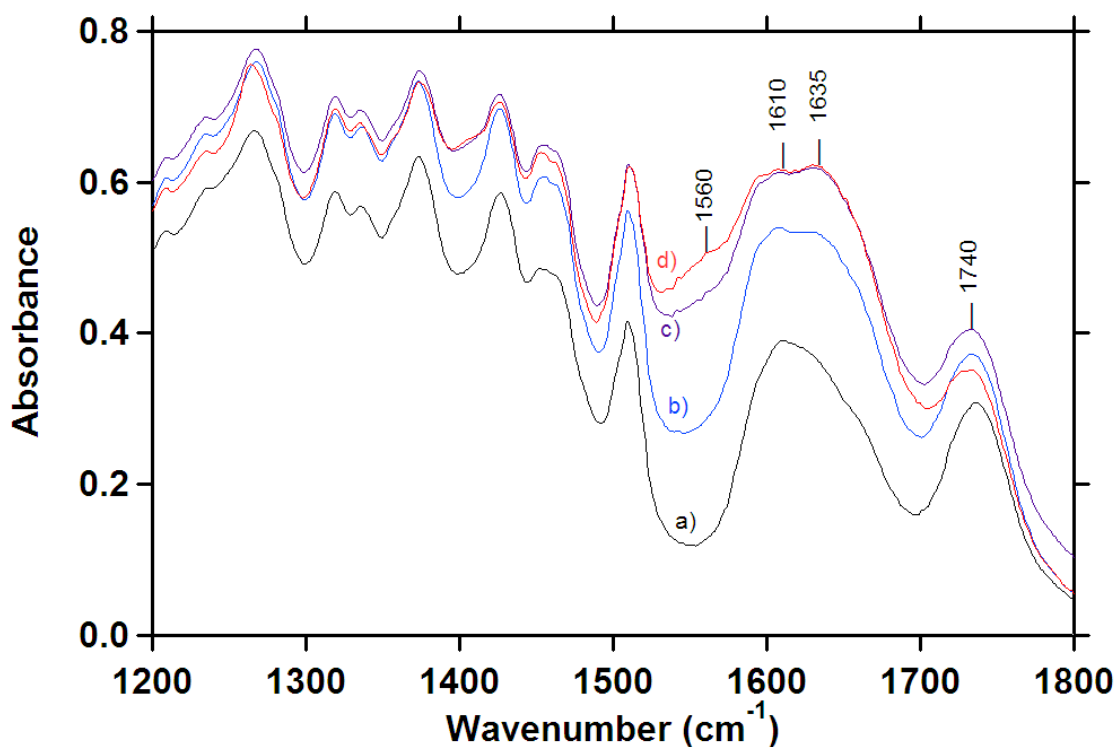


Figure 3. FTIR spectra of a) TEMPO-oxidized fibres and of TEMPO-oxidized fibres covered by. b) 2 bilayers, c) 4 bilayers and d) 5 bilayers of polyelectrolyte

The other FTIR absorption bands of all the samples were almost similar and are in good agreement with the literature data. We can observe mainly the presence of a peak at 3400 cm^{-1} representing the O-H vibration (strong intensity) and the peak at 2900 representing the C-H vibration (medium intensity).

XPS Analysis

The adsorption of the polyelectrolyte on the fibres surfaces was followed by XPS. In general, the surface of the TMP fibres contains mainly cellulose, hemicelluloses, lignin, and extractives. All of them consist mainly of carbon and oxygen. The O/C ratio, obtained from the low-resolution XPS spectrum, allows us to interpret the concentration of each component presented on the fibres surfaces. According to the literature (Toth et al. 2007) lignin has a ratio from 0.31 to 0.40. For the pure cellulose, the theoretical value is 0.83, since we have 5 oxygen atoms for 6 carbon atoms (Montplaisir et al. 2008).

Figure 4 shows a wide range XPS spectrum (also called a survey spectrum) for a handsheet made from TEMPO-oxidised fibres. For comparison, a typical spectrum for a handsheet made from 5 bilayers of polyelectrolyte on the TEMPO oxidised fibres is shown in Fig. 5. We also analysed representative samples of handsheet made from untreated fibres, fibres washed with acetone (in order to remove the extractives components), and a handsheet made from 50% of TEMPO-oxidised fibres (negatives fibres) and 50% of TEMPO-oxidised fibres covered by PAH (positives fibres).

Table 1 summarizes the data extracted from the survey XPS spectra and the experimental atomic ratio O/C.

Table 1. Atomic % of the Different Elements Presents in the Fibres Surfaces and O/C ratio

| | | Untreated fibres | Fibres washed with acetone | TEMPO oxidation | TEMPO oxidation + PAH | TEMPO oxidation + (PAH-PAA) ₅ |
|-----------|---------|------------------|----------------------------|-----------------|-----------------------|--|
| Name | Pos. | At% | At% | At% | At% | At% |
| C 1s | 285.00 | 68.554 | 67.9734 | 62.556 | 63.465 | 69.265 |
| O 1s | 531.00 | 31.446 | 32.025 | 36.145 | 35.210 | 24.683 |
| Br 3p | 182.00 | 0 | 0 | 0.426 | 0.322 | 0 |
| Na 1s | 1070.00 | 0 | 0 | 0.873 | 0.390 | 0 |
| N 1s | 400.00 | 0 | 0 | 0 | 0.612 | 6.052 |
| Cl 2p | 197.00 | 0 | 0 | 0 | 0 | 0.889 |
| O/C ratio | | 0.458 | 0.471 | 0.578 | 0.554 | 0.356 |

According to the survey spectra (c.f. data in Table 1) the fibres, before the adsorption of the polyelectrolyte (untreated, treated with acetone, and oxidized fibres), consisted mainly of carbon and oxygen. In the case of the oxidized fibres we observed the presence of a small amount of bromide and sodium coming from the reagent using during the oxidation process. The removal of the extractives by the acetone during 24 hours is observed by the slight modification in the O/C ratio. This small modification indicated the presence of a low concentration of the extractives on the fibres surfaces. For the oxidized fibres, the O/C ratio increases. Two reasons can explain this phenomenon: first, the removal of some lignin from the fibres surfaces and second, the creation of carboxylic functions on the fibres surfaces.

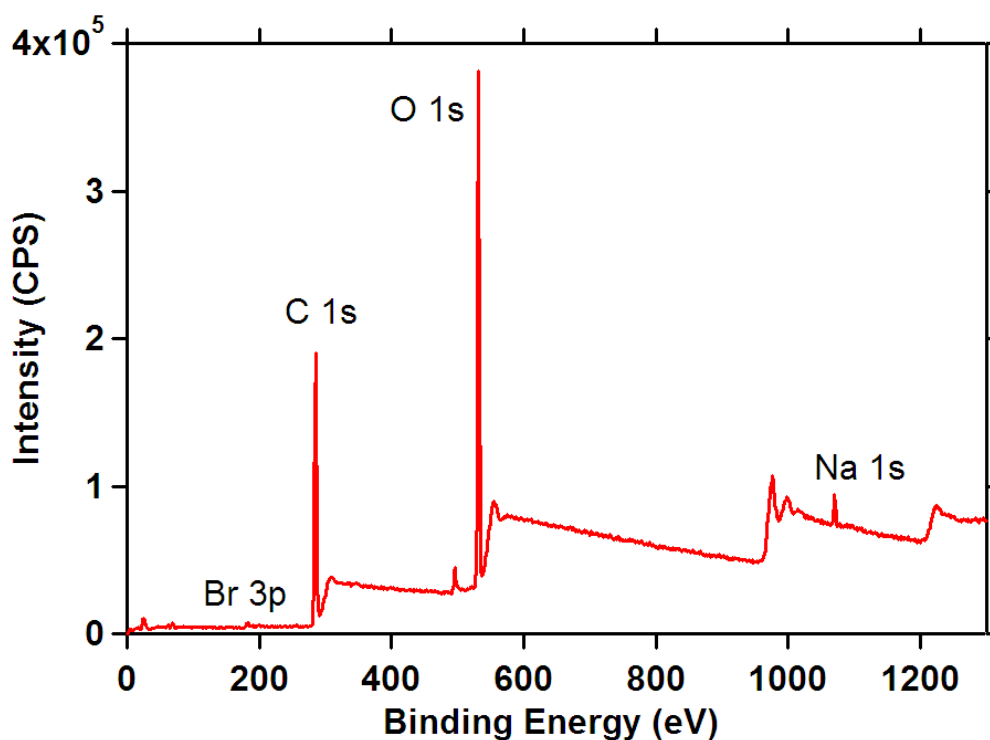


Figure 4. Survey XPS spectrum of fibres oxidised with TEMPO

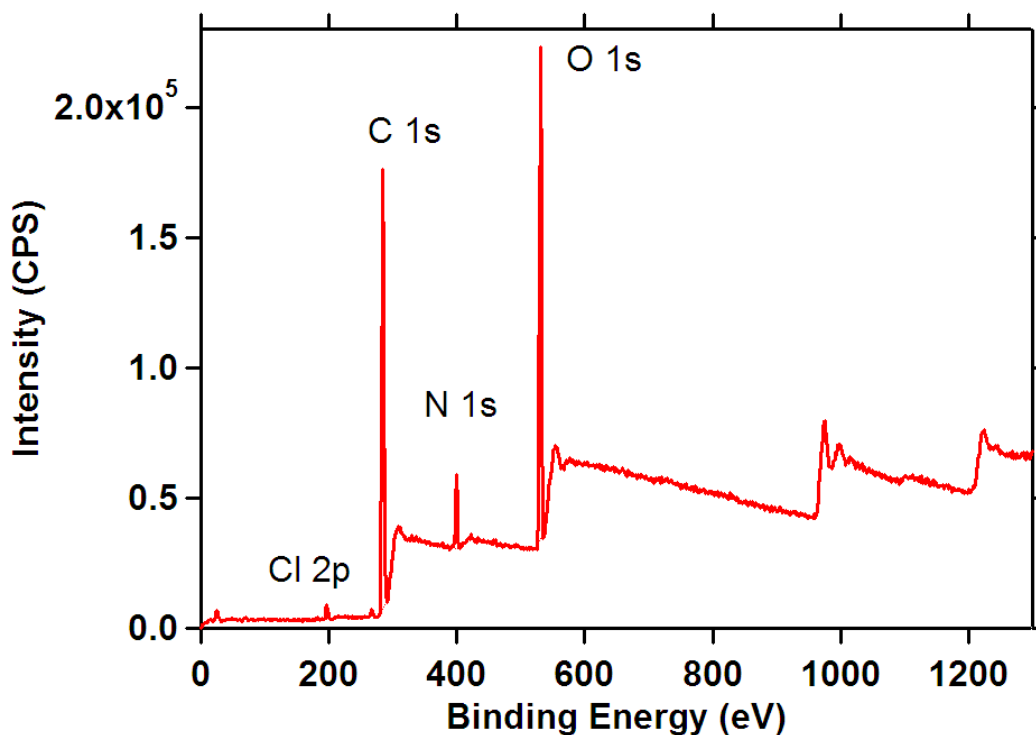


Figure 5. Survey XPS spectrum of fibres oxidised with TEMPO and covered by 5 bilayers of PAH-PAA

The comparison of the two spectra (Figs. 4 and 5) reveals that adsorption of the polyelectrolyte produced a distinctive N ($N 1s$) peak (from the nitrogen atoms in the PAH) and a relative decrease of the O/C signal due to the incorporation of the polyelectrolyte (PAH/PAA) on the fibres surface. From Table 1 we can clearly observe the increasing of the N when the number of the layer was increased. Moreover, it is apparent that after 5 bilayers of polyelectrolyte adsorption, the O/C ratio decreased due to the coverage of the fibres by the polyelectrolyte. In fact, the polyelectrolyte used in our case contains less O atom than the lignocellulosic polymers. Here, if we compare the O/C ratio we can clearly observe that before oxidation this ratio was 0.458. This value is in good agreement with the literature value (Montplaisir et al. 2008). After the adsorption of 5 bilayers this ratio became 0.356. This value is close to the theoretical ratio obtained for PAH-PAA ($O/C = 0.33$), indicating the coverage of almost all of the fibres surfaces by the polyelectrolytes. Finally, we notice the presence of small amount of Cl, due to the NaCl added during the polyelectrolyte adsorption process.

Carbon Signal Check

After the deposition of the polyelectrolyte, the percentage of the different classes of carbons appeared at different peaks. These will be influenced by the new functions contained in the polyelectrolyte and also with the amide groups created between the acid and the amines groups.

According to the literature data (Dorris and Gray 1978a) for the lignocellulosic fibres, and from our experimental spectra, it is possible to separate various carbons into four main classes:

C1: Carbon-Carbon or Carbon-Hydrogen bonding (C-C, C-H, peak at 285.0).

C2: Carbon having a simple bond with only one oxygen (C-O, peak at 286.48).

C3: Carbon that bonds only one oxygen carbonyl or two oxygen atoms, non-carbonyl (O-C-O, C=O, peak at 288.04). The carboxylate groups (COO^-) appears also at the same energy.

C4: Carbon that bonds an oxygen carbonyl and an oxygen non-carbonyl (COOH, peak at 288.94).

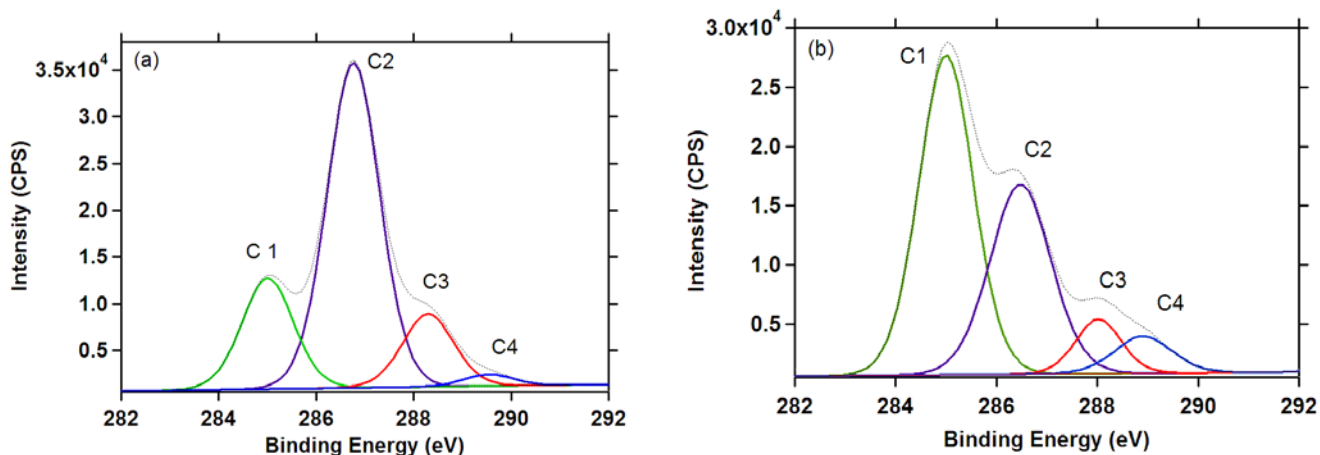


Figure 6. High-resolution XPS spectrum of a) the C1s for the TEMPO-oxidized fibres and b) the C1s for the fibres treated with TEMPO and covered with 5 bilayers of polyelectrolyte

Figure 6 represents two typical high resolution spectra of the C1s for the TEMPO-oxidized fibres and the fibres treated with TEMPO and covered with 5 bilayers of polyelectrolyte.

The other spectra (not represented here) had the same peaks with different atomic percentage. Table 2 summarizes the percentage of each class of carbon after each step of treatments.

Table 2. Atomic % of the Different Elements Presents in the Fibres Surfaces and O/C Ratio

| | | Untreated fibres | Fibres washed with acetone | TEMPO oxidized fibres | TEMPO oxidized fibres + PAH | TEMPO oxidized fibres + (PAH-PAA) ₅ |
|------|--------|------------------|----------------------------|-----------------------|-----------------------------|--|
| Name | Pos. | At% | At% | At% | At% | At% |
| C1 | 285.00 | 33.260 | 28.805 | 21.089 | 23.031 | 50.849 |
| C2 | 286.48 | 55.218 | 58.762 | 63.051 | 61.911 | 34.900 |
| C3 | 288.04 | 7.391 | 7.806 | 13.801 | 12.432 | 8.074 |
| C4 | 288.94 | 4.131 | 3.583 | 2.05 | 2.625 | 6.177 |

The C1 peak corresponds to the alkane-type carbon atoms, and, before the adsorption of the polyelectrolyte, it was attributed to the lignin and the extractive substances. After treatment with the acetone, we can clearly observe a slight decrease of this peak because of the removal of the extractive substances by acetone. Moreover, the C2 peak increased when the extractives were removed. C3 and C4 were quasi-unmodified. We observed the same phenomenon for C1 and C2 after TEMPO oxidation. In this case one can attribute this phenomenon to some removal of the lignin component. Moreover, the C3 peak increased due to the creation of the carboxylic function on the fibres surfaces. The adsorption of the polyelectrolyte induced a significant increase of the C1 peak (50.849 %), proving the adsorption of the polyelectrolyte. The percentage of the other peaks (C2, C3, and C4) was clearly changed, but at the same time we adsorbed new moieties that have binding energies very close to the C2, C3, and C4. For example C-N appears at 286.4; therefore C2 can be a mixture of C-O and C-N. The amide function appears at 288.9, which is very close to the carboxylic function. In order to check the formation of the amide function, we studied the high resolution spectrum of the nitrogen atoms.

Nitrogen Signal Check

The XPS nitrogen signal is distinctive of adsorbed polyelectrolytes on the fibres since this substrate does not have any nitrogen atom. The polyelectrolytes studied, on the other hand, carry nitrogen atoms in one functional group. Specifically, PAH carry cationic amine function (NH_3^+). The N 1s signal in the form of cationic amine groups appears as a peak at a binding energy of about 401 to 402 eV. The reaction between the carboxylate function and the cationic amine function induce the formation of amide groups, which appear as a peak at a binding energy about 399.85 eV (Jansen and Van Bekkum 1995). Figure 7 shows the high resolution spectrum of the nitrogen atom.

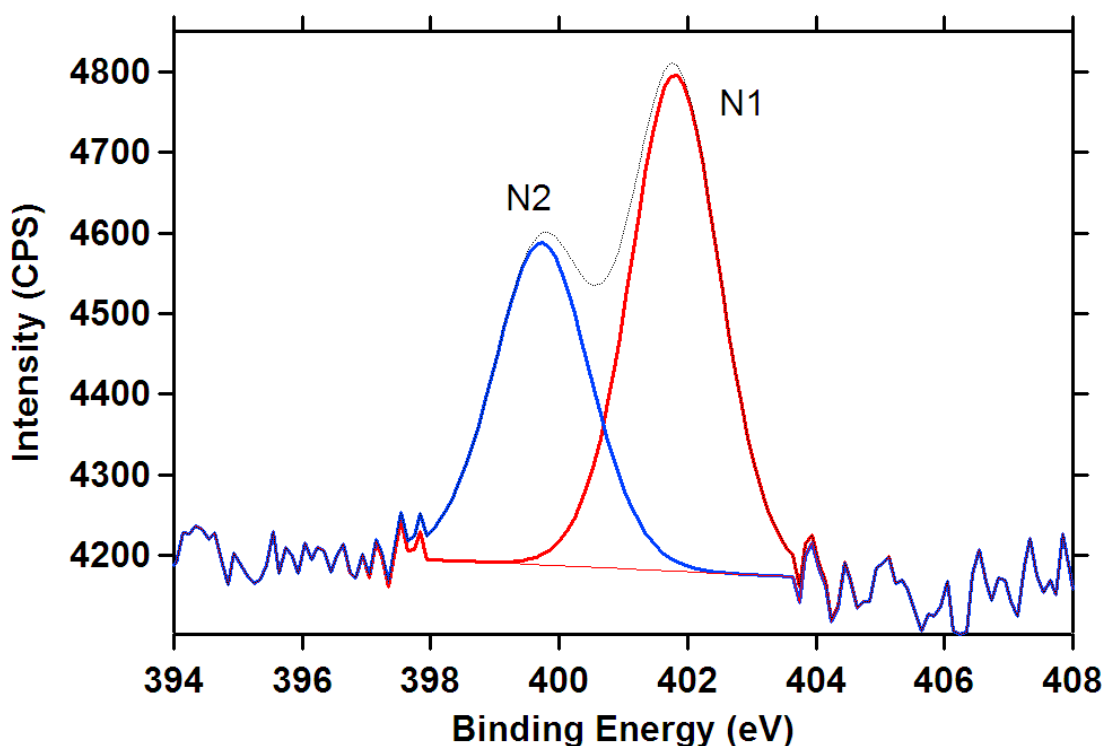


Figure 7. High-resolution XPS spectrum of the N1s for a blend of 50 % of fibres treated with TEMPO and 50 % of fibres covered by PAH

Figure 7 shows clearly the presence of two distinguishable peaks corresponding to nitrogen atoms. One peak (N1) was at a binding energy of about 401.80 (58.903 %). This peak is typical of protonated nitrogen (NH_3^+). Another peak (N2) appeared at about 399.73 eV (41.097%). This peak is characteristic of nonprotonated nitrogen (typical of amide group) (Jansen and Van Bekkum 1995). The presence of this peak proves the formation of chemical bonding between the polyelectrolyte and the fibres. This XPS analysis are in good agreement with the results obtained by the FTIR analysis and both confirm the formation of amide groups between the polyelectrolytes adsorbed on the TEMPO-oxidized fibres.

CONCLUSIONS

In this work the growth of polyelectrolyte on TMP was shown. The carboxylate function in the fibres surface was increased by TEMPO oxidation. The adsorption of the layers was followed by ζ -potential measurement. The FTIR and the XPS analysis were used to show the creation of chemical bonding (amide group) between the fibres and the polyelectrolyte on one hand and between the polyelectrolyte itself on the other hand. Finally, by this method one can create a three-dimensional network between the fibres on the basis to the chemical bonding between the polyelectrolyte and the fibres.

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