ALKALINE SOLUTION SWELLING OF FATTY ACIDS-MODIFIED
SOFTWOOD KRAFT PULP FIBERS UNDER
COLD PLASMA CONDITIONS

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The swelling behavior of unbleached and bleached softwood Kraft pulp modified with butyric acid and oleic
acid in cold plasma conditions, in alkaline solutions, has been studied comparatively with pristine polymers,
by gravimetric measurements and optical microscopy. It has been established that the swelling degree
depends on the type of cellulose fiber, on the solvent and concentration of the alkaline solution. The treated
samples present higher susceptibility in NaOH solutions, in comparison with KOH solutions. Both cellulose
fibers modified with oleic acid present a higher swelling degree than those treated with butyric acid.
FT-IR spectroscopy of the swollen fibers showed that the modified celluloses present some modifications
after swelling in alkaline solutions.

Keywords: softwood Kraft pulp fibers, swelling, alkaline solutions, grafting

INTRODUCTION

Due to its crystalline nature, cellulose is insoluble in most solvents, albeit the limited
solubility of the cellulose fibers comes only from the amorphous segments of cellulose
and non-cellulose components, such as lignin; however, both intra- and inter-
crystalline swelling is possible in certain solvents. The action of a mild swelling agent
is confined entirely to the amorphous portion of the fiber. As the fiber swells,
intermolecular bonds are broken as a result
of the internal stresses produced by swelling.
The degree of order within the fiber is
reduced and an increase in the surface area of
the fiber occurs. Also, with very strong
cellulose swelling agents, it is possible to
reach a critical point where the entire
crystalline structure of the fiber is disrupted
and the fiber structure is lost.1

Many processes, such as the organosolv
pulping,2 chemical pulping,3 etherification,
esterification of dissolving grade pulp4 and
acetylation of wood5 are controlled by the
solubility and permeability of organic
solvents and water into cellulose materials.

Therefore, strong interacting solvents are
required to penetrate such lignocellulose
materials. The extent and nature of cellulose
fiber–solvent interactions are important for a
complete understanding of solvent
penetration and diffusion processes.6

Generally, the interactions of solvents
with cellulose materials are investigated by
measuring the swelling volume. Robertson7
studied the cellulose–liq uid interactions and
interpreted the swelling results based on
molar volume and solubility parameters of
various solvents. It was concluded that the
molar volume is important in the swelling of
cellulose and also that the solubility
parameter correlates with swelling among
solvents which are proton acceptors, but not
with those with proton donor characteristics.

Mantanis and coworkers, who
investigated the swelling of cellulose fiber
webs1 and wood8−11 in water and organic
solvents, concluded that the hydrogen
bonding parameter is the most important
factor in the swelling of cellulose fiber
webs.1 The maximum swelling degree in

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water was correlated with wood density, while the removal of extractives enhanced the rate and maximum swelling of wood.\textsuperscript{8} Liquids with a molar volume greater than 100 ml/mol or with a small hydrogen solubility parameter caused very little wood swelling in organic solvents.\textsuperscript{1,8} Based on statistical analysis solvent basicity, the solvent molecular volume and wood density were the most important parameters for the swelling of wood into organic solvents.\textsuperscript{10}

A previous work of ours reported\textsuperscript{12} the results on grafting in cold plasma conditions of unbleached (UBP) and bleached (BP) pulp fibers with two fatty acids, namely butyric (BA) and oleic acid (OA), on also showing that the grafting degree is higher for oleic acid (9-56\%) than that obtained with the use of butyric acid (3-15\%), and higher on unbleached than on bleached pulp fibers, under cold plasma conditions. Grafting was observed as occurring differently on the two pulp samples, so that the assumption was made that their behavior will be different on swelling, as well. The use of cold plasma grafting was realized to increase the wet-strength of paper.

The present study brings new insights into the modification, through grafting, of softwood Kraft pulp fibers, by following the swelling behavior in alkaline solutions. The modifications that occurred after the swelling process, in comparison with the unswollen samples, were investigated by FT-IR spectroscopy and optical microscopy.

**EXPERIMENTAL**

**Materials**

Two types of softwood pulp fibers – unbleached (UBP) and bleached (BP) –, provided by Södna Cell Värö, Sweden, have been used. Bleaching was achieved with oxygen. For details, see Popescu et al.\textsuperscript{13}

The average properties of the unbleached and bleached softwood Kraft pulp fibers are presented in Table 1.

Cold plasma grafting of pulp fibers took place under the following conditions: in a typical experiment, after several washing cycles with inert gas (nitrogen) from the metal gas reservoir, the working pressure (0.3 mm Hg) was established in the cylindrically shaped vacuum plasma reactor, after which the R.F. power was transferred to the reactor through the semi-cylindrical, external, silver-coated electrodes. The R.F. power was dissipated to the electrodes from an R.F. generator able to generate 50-300 W. The support used for the sample was a 20 x 2.3 cm\textsuperscript{2} glass plate, with a circular aperture of 1-2 mm in diameter.

The UBP and BP fibers were treated in plasma at a $P = 300$ W, frequency – 13.56 MHz, pressure – 0.3-0.5 mm Hg, for 5 or 10 min, at room temperature. Prior to the treatment, the samples were impregnated with solutions of fatty acid in the case of oleic acid (20\% solutions, in acetone); butyric acid was continuously distilled from the monomer flask into the plasma reactor. After plasma treatment, the samples were Soxhlet-extracted for 6 h, to remove any physically adsorbed unreacted acids. After the extraction, the samples were dried before being characterized.

The modification degrees estimated both from ATR-FT-IR and XPS data were of about 15 and 56\% for UBP + BA and UBP + OA, and of about 3 and 9\% for BP+BA and BP+OA, respectively. These results, presented in a previous paper,\textsuperscript{12} can be explained by the plasma chemistry of the system. Actually, plasma treatment generates mainly radical species by gas fragmentation. These radicals evolve to more stable species by reorganization, decomposition or reactions with other molecules, present in the reaction vessel. The main reactions with other species are the typical reactions of radicals: recombination, transfer by abstraction of hydrogen, hydroxyl or other groups, and addition to unsaturated bonds. Particularly, if vinyl groups are present, usually polymerization takes place by a radical mechanism. Under the experimental conditions here adopted, grafting of oleic acid is expected to occur mainly by grafting polymerization initiated by radicals, on the pulp surface or by polymer chain transfer. Grafting of oleic acid as a single molecule may also occur, thus it may be a subject for research. However, grafting by esterification is not the main reaction pathway. This basic concept is also proved by our data, as the butyric acid (BA), having no vinyl groups, was only scarcely or perhaps not at all grafted to pulp – a single molecule, difficult to identify, was attached.

The parameters related to the crystalline fraction, which influence the swelling behavior, were obtained by X-ray diffraction analysis. XRD measurements were performed on a Bruker diffractometer equipped with a Kristalloflex 760 sealed-tube copper anode generator and a two-dimensional position-sensitive wire-grid detector pressured with xenon gas. The diffracted intensity of CuKα radiation ($\lambda = 0.1542$ nm, 40 kV and 40 mA) was measured in a 20 range, between 2º and 45º. The samples were placed in sealed Mark-Röhrchen 1.0 mm inner diameter glass capillaries (Charles Supper) and for each sample 1200 scans were done. The diffractograms were deconvoluted using Gaussian and mixed Gaussian-Lorenzian profiles. After deconvolution, several parameters can be
calculated and compared, e.g., the crystalline
index proposed by Hermans:14
\[
CrI = \frac{A_{\text{cryst}}}{A_{\text{total}}} \quad (1)
\]
where \(CrI\) = crystalline index, \(A_{\text{cryst}}\) = sum of
crystalline peak areas and \(A_{\text{total}}\) = total area of the
diffractogram curve.

The apparent crystallite size was estimated by
Scherrer equation:15
\[
L = \frac{K \cdot \lambda}{\beta \cdot \cos \theta} \quad (2)
\]
where \(K\) is a constant (0.94), \(\lambda\) is X-ray
wavelength (0.1542 nm for Cu Kα radiation), \(\beta\) is
the half-height width of the diffraction peak and \(\theta\)
is the Bragg angle corresponding to the (002)
plane.

Surface chains occupy an approximately 0.57
nm thick layer, so that the ratio of the crystallite
inner chains is the following:
\[
X = \frac{(L-2h)^2}{L^2} \quad (3)
\]
where \(L\) = apparent crystallite size for the (002)
reflection and \(h = 0.57\) nm is the thickness of the
surface chain layer.

The mass fraction of the cellulose content
(cell content) in wood may be estimated:16
\[
\text{cell content} = \frac{CrI'}{CrI_{\text{cell}}} \quad (4)
\]
where \(CrI_{\text{cell}} = 70\%\)

The values of these parameters for the
samples under study are given in Table 2.

Swelling has been achieved at room
temperature, in NaOH and KOH solutions of
different concentrations (5, 10 and 40 wt%).
NaOH and KOH of analytical purity were
purchased from S.C. Chemical Company S.A.
Twice distilled water was used in all experiments.

Table 1
Properties of softwood Kraft pulp fibers

<table>
<thead>
<tr>
<th>Property</th>
<th>UBP</th>
<th>BP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wall thickness (μm)</td>
<td>8.2</td>
<td>7.8</td>
</tr>
<tr>
<td>Intrinsic viscosity (mL/g)</td>
<td>1109</td>
<td>728</td>
</tr>
<tr>
<td>Kappa number</td>
<td>26.8</td>
<td>3.2</td>
</tr>
<tr>
<td>Dry matter content (%)</td>
<td>32.3</td>
<td>32.8</td>
</tr>
<tr>
<td>Water retention value (g/g)</td>
<td>1.59</td>
<td>1.43</td>
</tr>
<tr>
<td>Thickness (μm)</td>
<td>122</td>
<td>113</td>
</tr>
<tr>
<td>Bulk density (cm³/g)</td>
<td>1.9</td>
<td>1.79</td>
</tr>
<tr>
<td>Tensile strength (kN/m)</td>
<td>1.92</td>
<td>1.74</td>
</tr>
<tr>
<td>Stretch (%)</td>
<td>2.1</td>
<td>3.4</td>
</tr>
<tr>
<td>Tensile energy absorption (J/m²)</td>
<td>30.9</td>
<td>47.3</td>
</tr>
<tr>
<td>Tensile stiffness (kN/m)</td>
<td>296</td>
<td>241</td>
</tr>
<tr>
<td>Modulus of elasticity (N/mm²)</td>
<td>2420</td>
<td>2129</td>
</tr>
<tr>
<td>Ln, Lw, Lww</td>
<td>1.52; 2.65; 3.17</td>
<td>1.11; 2.23; 2.85;</td>
</tr>
<tr>
<td>Fine %; Fine % Lw</td>
<td>29.96; 2.67</td>
<td>38.05; 4.83</td>
</tr>
<tr>
<td>kink index; kink angle; kink/mm</td>
<td>0.99; 31.86; 0.45</td>
<td>1.17; 40.56; 0.68</td>
</tr>
</tbody>
</table>

Table 2
Crystalline parameters for UBP and BP untreated and plasma-treated samples with fatty acids

<table>
<thead>
<tr>
<th>Parameters</th>
<th>UBP</th>
<th>UBP+ BA</th>
<th>UBP+ OA</th>
<th>BP</th>
<th>BP + BA</th>
<th>BP+OA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr. I. (%)</td>
<td>60</td>
<td>59</td>
<td>57</td>
<td>61</td>
<td>61</td>
<td>59</td>
</tr>
<tr>
<td>L101 (nm)</td>
<td>3.25</td>
<td>3.24</td>
<td>3.29</td>
<td>3.36</td>
<td>3.36</td>
<td>3.39</td>
</tr>
<tr>
<td>L101 (nm)</td>
<td>5.56</td>
<td>5.58</td>
<td>5.96</td>
<td>5.85</td>
<td>5.84</td>
<td>5.97</td>
</tr>
<tr>
<td>L002 (nm)</td>
<td>4.07</td>
<td>4.08</td>
<td>4.76</td>
<td>4.18</td>
<td>4.19</td>
<td>4.36</td>
</tr>
<tr>
<td>X</td>
<td>0.52</td>
<td>0.52</td>
<td>0.57</td>
<td>0.53</td>
<td>0.53</td>
<td>0.55</td>
</tr>
<tr>
<td>Cellulose fraction (%)</td>
<td>86</td>
<td>84</td>
<td>81</td>
<td>88</td>
<td>87</td>
<td>84</td>
</tr>
</tbody>
</table>

Investigation methods

Optical microscopy images were obtained on
a LEICA DM 2500M microscope, in polarized
light, at 200x magnification.

The swelling degree \((Q)\) was determined by
measuring fiber diameter with an optical
microscope and by the following equation:
\[
Q_{\text{max}} = \frac{(d - d_0)/d_0}{d} \times 100\% \quad (5)
\]
where \(d_0\) – diameter of the dry sample (g) and \(d\) –
diameter of the wet sample (g).

The FT-IR spectra have been recorded with a
Bruker VERTEX 70 spectrometer, in absorbance
mode. Background and sample spectra were
obtained in the 600 to 4000 cm⁻¹ wavenumber
range. Spectra processing was achieved with the
SPECVIEW program. The following spectral
characteristics have been evaluated:

- energy of H-bonds, calculated using the
  following equation:17
\[
E_{HH} (kJ) = \frac{1}{k} \left[ \frac{\nu_o - \nu}{\nu_o} \right] \quad (6)
\]
where: $v_o$ – standard frequency corresponding to the free –OH groups (3650 cm$^{-1}$); $v$ – frequency of bonded –OH groups; $k = 4 \times 10^{-3}$ kJ$^{-1}$

- enthalpy of H-bond formation, evaluated with the formula: $\Delta H$ (kJ/mole) = 0.0672 $\Delta \nu_{OH}$ + 2.646 (7)

where: $\Delta \nu_{OH}$ – OH wave number shift (cm$^{-1}$) – H-bounding distance (R) (Å), obtained by the Sederholm equation: $\Delta \nu (\text{cm}^{-1}) = 4.43 \times 10^3 (2.84 - R)$ (8)

where: $\nu = \nu_o - \nu$ : $\nu_o$ – OH monomeric stretching frequency = 3600 cm$^{-1}$; $\nu$ – OH stretching frequency in the sample IR spectrum;

- relative value of optical density (RVOD) from FT-IR spectrum, calculated by the following relation:
$$\text{RVOD} = \frac{E_C(\nu_j)}{E_C(\nu_s)}$$ (9)
where: $E_C(\nu_j) = \lg \frac{T_C(\nu_j)}{T(\nu_j)}$ (10)

$T(\nu_j)$ transmission at $\nu_j$ frequency when the component content is 0; $T_C(\nu_j)$ – transmission at $\nu_j$ frequency; $\nu_s$ – standard frequency = 1425 cm$^{-1}$

- asymmetrical index (a/b) – the ratio between peak full width at half height of the OH absorption band.

RESULTS AND DISCUSSION

Swelling of pulp samples in alkaline solutions at room and low temperatures was previously achieved, to observe the structural and morphological modifications and obtain a higher swelling degree. In order to clarify some aspects concerning the swelling process, the unbleached and bleached Kraft pulp fibers were subjected to swelling with an 8.5% NaOH solution, at low temperature. Resuming the study in this field, the present paper is devoted to a similar investigation, yet involving two substrates, unbleached (UBP) and bleached (BP) Kraft pulps modified with butyric (BA) and oleic acid (OA), swollen in two alkaline solutions (NaOH and KOH) of different concentrations.

Optical microscopy

Figure 1 provides the images of both dry samples and of samples swollen in a 10% KOH solution.

All samples (both unswollen and swollen in alkaline solutions) were left in a desiccator (75% humidity), for 72 h. The increase in the percentage of the diameters of the swollen pulp fibers and of the wet fibers, as determined from the optical microscopy images presented in Figure 1, and the relative increase in the diameter of the fibers, are given in Tables 3 and 4.

A higher increase in diameter is observed for BP in comparison with UBP, in all solvents.

After grafting, a higher increase in diameter is observed for the samples modified with OA, in comparison with those modified with BA. Swelling in a KOH solution increases the swelling degree with increasing solution concentration while, for the NaOH solution, the variation of the swelling degree with concentration is not significant.
### Table 3
Percentage increase (wt%) in diameters of softwood Kraft pulp fibers after swelling in alkaline solutions

<table>
<thead>
<tr>
<th>Sample</th>
<th>KOH solution</th>
<th>NaOH solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5%</td>
<td>10%</td>
</tr>
<tr>
<td>UBP</td>
<td>8.82</td>
<td>35.29</td>
</tr>
<tr>
<td>UBP+BA</td>
<td>19.35</td>
<td>54.83</td>
</tr>
<tr>
<td>UBP+OA</td>
<td>32.14</td>
<td>67.85</td>
</tr>
<tr>
<td>BP</td>
<td>10.71</td>
<td>42.85</td>
</tr>
<tr>
<td>BP+BA</td>
<td>72.00</td>
<td>84.00</td>
</tr>
<tr>
<td>BP+OA</td>
<td>76.19</td>
<td>152.38</td>
</tr>
</tbody>
</table>

For the samples swollen in KOH, a higher increase in diameter is observed when using a 10% solution while, in the case of NaOH, a higher increase in diameter is observed when using 5 and 40% solutions.

After grafting, a higher increase in the diameter of UBP is observed for the samples modified with BA while, in the case of BP, a higher increase in diameter is observed for the samples modified with BA for 5% and 10% solutions of KOH and NaOH while, for the 40% KOH and NaOH solutions, a higher increase is seen in the samples modified with OA.

Generally, a decrease in average diameter with increasing solution concentration is noted for all samples.

### Table 4
Percentage increase (wt%) in diameters of Kraft softwood pulp fibers after swelling in alkaline solutions

<table>
<thead>
<tr>
<th>Sample</th>
<th>KOH solution</th>
<th>NaOH solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5%</td>
<td>10%</td>
</tr>
<tr>
<td>UBP</td>
<td>100</td>
<td>80.64</td>
</tr>
<tr>
<td>UBP+BA</td>
<td>119.21</td>
<td>138.09</td>
</tr>
<tr>
<td>UBP+OA</td>
<td>38.70</td>
<td>41.93</td>
</tr>
<tr>
<td>BP</td>
<td>100</td>
<td>78.57</td>
</tr>
<tr>
<td>BP+BA</td>
<td>84.00</td>
<td>88.00</td>
</tr>
<tr>
<td>BP+OA</td>
<td>100</td>
<td>116.00</td>
</tr>
</tbody>
</table>

Determination of swelling degree

The swelling degree represents the quantity of water or solvent absorbed by a substance without dissolution. The swelling properties are controlled by two factors that act in different ways. On the one hand, the free mixing energy between solvent and the polymeric chains determines an increase in the cellulose volume; on the other, the elastic response of the macromolecular network opposes swelling. At equilibrium, cellulose reaches the maximum swelling degree.24

During cellulose fiber–alkaline solution interactions, an increase in the diameter of the fiber (through swelling) and a decrease in its length (contraction) take place. Due to the well-known cellulose structural heterogeneity (crystalline structure, amorphous unordered zone and semicrystalline zone), swelling can be inter- and intra-crystalline. Under a 12 wt% alkaline solution, swelling prevails in amorphous and unordered zones; when increasing concentration above 12 wt% alkaline solution, swelling becomes intramicellar, with network modifications visible on X-rays.25

Aqueous solutions of NaOH (5-40 wt% NaOH) are formed from ionic dissolved pairs (Na⁺HO⁻, nH₂O). NaOH is fixed on cellulose, forming mixed hydrates: Na⁺HO⁻ * (n-3)H₂O * 3HO-Cel, in which three H₂O molecules of the compound hydrated by a NaOH in solution are molecules with 3 OH groups of cellulose. Fixing of NaOH is done in a 1:1 ratio, with the C₆H₁₀O₅ unit. After removing NaOH by water wash, the zigzag structure of the cellulose chains is stabilized by H networks, which make the secondary structure tougher in a reduced form, through mercerization.25

The swelling behavior of fibers was determined by immersing dried samples into NaOH and KOH solutions of different concentrations (5, 10 and 40 wt%), at room temperature. After 72 h, the samples were removed from the swelling medium, the excess of solution was gently removed and the progress of swelling was monitored.
gravimetrically. The swelling degree \((Q_s)\) of the samples was calculated with the following relation:

\[
Q_s = \frac{(W_S - W_D)}{W_D} \times 100 \ (	ext{%) (11)}
\]

where \(W_S\) is the weight of the swollen test sample after 72 h of process, and \(W_D\) is the weight of the dried test sample.

Table 5 presents the maximum swelling degree of unbleached, bleached and modified pulp fibers as a function of the solvent used.

As seen from Table 5, the swelling degree in both NaOH and KOH solutions is higher for UBP than for BP in all solvents, because of the high water retention capacity of the first pulp fibers (Table 1).

After grafting, the swelling degree is higher for all samples. In all cases, the maximum swelling degree increases with increasing solution concentration.

Nenitescu\(^26\) determined the hydration energies: \(\Delta H_{Na^+} = -411.6\) kJ/mole and \(\Delta H_{K^+} = -323.4\) kJ/mole. As known, the hydration energies of ions decrease with increasing ionic volume, that is why for the samples swollen in 40 wt% solutions, a slightly higher swelling degree is observed when using a NaOH solution.

It may be also remarked that the swelling degree rises with the increase in solution concentration for all studied samples. The equilibrium swelling degree is higher for the samples modified with oleic acid than that for the samples modified with butyric acid, because the oleic acid has a longer chain, thus creating a looser structure.

As expected, the variation in the swelling degree is similar to that found for the increase in the diameter of the pulp fibers.

**FT-IR spectra results**

The FT-IR spectra of both unbleached and bleached softwood Kraft pulp fiber samples after swelling in alkaline solutions are plotted in Figures 2 and 3.

As previously shown,\(^12\) in the sample modified with butyric acid, the FT-IR spectral contour is approximately the same as that for the untreated sample – indicating that a low amount of butyric acid was modified on the Kraft pulp fiber surface. The spectra of the plasma-treated samples with oleic acid are different from those of the untreated pulp fibers. Spectral modification occurs both in the 3000-2700 cm\(^{-1}\) region, assigned to different stretching vibrations of the CH groups, as well as in the 1800-500 cm\(^{-1}\) range – the “fingerprint region”, assigned to different stretching or bending vibrations of the functional groups from the pulp fiber components. The IR spectra of unbleached and bleached pulp fibers modified with oleic acid present a shift and splits of the bands found at 2901 cm\(^{-1}\), in two bands located at 2850 cm\(^{-1}\) and 2923 cm\(^{-1}\), assigned to asymmetrical and symmetrical CH\(_2\) vibrations. Moreover, evidence on the ester bonds in plasma-modified samples becomes obvious at 1715 and 1610 cm\(^{-1}\). The presence of spectral bands located at 1715, 2850, and 2923 cm\(^{-1}\) indicates that oleic acid was efficiently modified on the Kraft pulp fiber surface.

Tables 6 and 7 present the most significant absorbance bands in the IR spectra for bleached and unbleached cellulose fibers, unmodified and modified with different fatty acids, after swelling in alkaline solutions.

The bands in the 3400-3300 cm\(^{-1}\) region are assigned to the stretching modes of the OH groups (intramolecular H bonds). After swelling, a shift of these bands to higher wavenumbers takes place. The shift increases with increasing solution concentration, being more obvious in the case of the samples (unbleached and bleached) swollen in 40 wt% KOH and NaOH solutions.

### Table 5

<table>
<thead>
<tr>
<th>Sample</th>
<th>KOH 5%</th>
<th>KOH 10%</th>
<th>KOH 40%</th>
<th>NaOH 5%</th>
<th>NaOH 10%</th>
<th>NaOH 40%</th>
</tr>
</thead>
<tbody>
<tr>
<td>UBP</td>
<td>212.92</td>
<td>261.07</td>
<td>288.23</td>
<td>247.85</td>
<td>371.31</td>
<td>420.34</td>
</tr>
<tr>
<td>UBP+BA</td>
<td>340.81</td>
<td>371.53</td>
<td>403.33</td>
<td>418.58</td>
<td>461.13</td>
<td>502.38</td>
</tr>
<tr>
<td>UBP+OA</td>
<td>440.81</td>
<td>475.78</td>
<td>539.40</td>
<td>541.35</td>
<td>561.00</td>
<td>641.89</td>
</tr>
<tr>
<td>BP</td>
<td>164.87</td>
<td>207.35</td>
<td>212.07</td>
<td>197.29</td>
<td>292.86</td>
<td>351.37</td>
</tr>
<tr>
<td>BP+BA</td>
<td>205.24</td>
<td>245.65</td>
<td>300.27</td>
<td>284.95</td>
<td>398.13</td>
<td>453.08</td>
</tr>
<tr>
<td>BP+OA</td>
<td>284.34</td>
<td>319.41</td>
<td>355.28</td>
<td>353.37</td>
<td>430.32</td>
<td>530.13</td>
</tr>
</tbody>
</table>
The bands from the 2910-2850 cm\(^{-1}\) region are assigned to the symmetrical CH\(_2\) valence vibrations. For the bleached cellulose samples, after swelling, a shift of bands to lower wavenumbers takes place, which is more evident with an increasing solution concentration, the most pronounced values being found for the samples swollen in 40 wt% KOH and NaOH solutions.

The bands from the 1650-1640 cm\(^{-1}\) region are assigned to C=O stretching. For bleached pulp fibers, one may observe that, after swelling, a shift of the bands occurs towards lower wavenumbers for the pulp fibers modified with butyric acid while, in the case of unmodified cellulose and of the cellulose modified with oleic acid, the shift appears at higher wavenumbers.

The absorbencies from the 1430-1004 cm\(^{-1}\) region, also called the “fingerprint region”, evidenced in both spectra, are associated with different stretching vibrations or deformations in cellulose and hemicelluloses.

All these observations are related to changes in the inter- and intra-molecular interactions in the samples as estimated from the spectral characteristics – Tables 8-11.

The changes in the spectral features after alkaline treatment could be caused by the breaking of some inter- and intra-molecular bonds and by the re-organizing of macromolecular chains in a more ordered structure.

The decrease of the H-bond energy after swelling of both 10 and 40 wt% alkaline solutions shows that the structural order has been disturbed, as also demonstrated by the increase of the hydrogen bonding distances.

The high values of absorbancies corresponding to the crystalline bands of cellulose and the increased \(\Delta_{\text{OH}}/\Delta_{\text{CH}}\) ratio indicate that the treated samples have an ordered structure, as also supported by the increased values of hydrogen bonding enthalpy – Tables 10, 11.

The low values of relative optical density show that some fragments of lignin from the samples are removed.

For the samples modified with BA, variations similar to those found for the samples modified with OA were observed (not shown) in the spectral characteristics.
### Table 6
Position and assignments of the main bands from IR spectra of UBP and UBP+OA samples, before and after swelling in alkaline solutions

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Band assignment</th>
<th>Reference</th>
<th>10% KOH</th>
<th>40% KOH</th>
<th>10% NaOH</th>
<th>40% NaOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>3375-3330</td>
<td>O₃-H₃-O₅ intra-molecular H bonds</td>
<td>3335</td>
<td>3338</td>
<td>3340</td>
<td>3341</td>
<td>3347</td>
</tr>
<tr>
<td>1365-1335</td>
<td>OH in-plane bending in cellulose</td>
<td>1335</td>
<td>1336</td>
<td>1336</td>
<td>1340</td>
<td>1335</td>
</tr>
<tr>
<td>1278-1248</td>
<td>C=O stretching</td>
<td>1281</td>
<td>1269</td>
<td>1279</td>
<td>1265</td>
<td>1272</td>
</tr>
<tr>
<td>1215-1200</td>
<td>OH in-plane bending in cellulose, C-O symmetrical stretching in pyranose ring</td>
<td>1203</td>
<td>1203</td>
<td>1205</td>
<td>1213</td>
<td>1213</td>
</tr>
<tr>
<td>1120-1115</td>
<td>asymmetrical in phase stretching ring</td>
<td>1105</td>
<td>1107</td>
<td>1107</td>
<td>1109</td>
<td>1119</td>
</tr>
<tr>
<td>1070-1015</td>
<td>C-O valence vibration mainly from C(3)-O(3)H; stretching C-O in cellulose I</td>
<td>1043</td>
<td>1054</td>
<td>1030</td>
<td>1046</td>
<td>1022</td>
</tr>
</tbody>
</table>

### Table 7
Position and assignments of the main bands from IR spectra of BP and BP+OA samples, before and after swelling in alkaline solutions

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Band assignment</th>
<th>Reference</th>
<th>10% KOH</th>
<th>40% KOH</th>
<th>10% NaOH</th>
<th>40% NaOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>3375-3330</td>
<td>O₃-H₃-O₅ intra-molecular H bonds</td>
<td>3335</td>
<td>3335</td>
<td>3334</td>
<td>3340</td>
<td>3340</td>
</tr>
<tr>
<td>2910-2850</td>
<td>symmetrical CH2 valence vibration</td>
<td>2920</td>
<td>2900</td>
<td>2904</td>
<td>2894</td>
<td>2899</td>
</tr>
<tr>
<td>1650-1640</td>
<td>C=O stretching H-O-H from H₂O</td>
<td>1639</td>
<td>1642</td>
<td>1641</td>
<td>1645</td>
<td>1650</td>
</tr>
<tr>
<td>1430-1406</td>
<td>H-O-C in-plane bending of the alcohol groups</td>
<td>1428</td>
<td>1428</td>
<td>1428</td>
<td>1419</td>
<td>1422</td>
</tr>
<tr>
<td>1278-1248</td>
<td>C=O stretching</td>
<td>1281</td>
<td>1281</td>
<td>1280</td>
<td>1275</td>
<td>1276</td>
</tr>
<tr>
<td>1215-1200</td>
<td>OH in-plane bending in cellulose I, C-O symmetrical stretching in pyranose ring</td>
<td>1202</td>
<td>1204</td>
<td>1204</td>
<td>1212</td>
<td>1199</td>
</tr>
<tr>
<td>1047-1004</td>
<td>stretching C-O in cellulose I</td>
<td>1031</td>
<td>1029</td>
<td>1030</td>
<td>1020</td>
<td>1020</td>
</tr>
</tbody>
</table>
Table 8
Spectral characteristics of UBP and UBP+OA samples before and after swelling in alkaline solutions

<table>
<thead>
<tr>
<th>Sample</th>
<th>OH band position (cm⁻¹)</th>
<th>a/b ratio</th>
<th>E_H (kJ)</th>
<th>ΔH (kJ/mol)</th>
<th>R (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UBP</td>
<td>UBP+OA</td>
<td>UBP</td>
<td>UBP+OA</td>
<td>UBP</td>
</tr>
<tr>
<td>Reference</td>
<td>3335</td>
<td>3335</td>
<td>1.023</td>
<td>1.012</td>
<td>21.57</td>
</tr>
<tr>
<td>KOH, 10%</td>
<td>3336</td>
<td>3340</td>
<td>0.971</td>
<td>0.934</td>
<td>21.51</td>
</tr>
<tr>
<td>KOH, 40%</td>
<td>3339</td>
<td>3347</td>
<td>0.754</td>
<td>0.722</td>
<td>21.30</td>
</tr>
<tr>
<td>NaOH, 10%</td>
<td>3338</td>
<td>3344</td>
<td>1.000</td>
<td>1.000</td>
<td>21.37</td>
</tr>
<tr>
<td>NaOH, 40%</td>
<td>3341</td>
<td>3350</td>
<td>0.920</td>
<td>0.893</td>
<td>21.16</td>
</tr>
</tbody>
</table>

Table 9
Spectral characteristics of BP and BP+OA samples before and after swelling in alkaline solutions

<table>
<thead>
<tr>
<th>Sample</th>
<th>OH band position (cm⁻¹)</th>
<th>a/b ratio</th>
<th>E_H (kJ)</th>
<th>ΔH (kJ/mol)</th>
<th>R (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BP</td>
<td>BP+OA</td>
<td>BP</td>
<td>BP+OA</td>
<td>BP</td>
</tr>
<tr>
<td>Reference</td>
<td>3335</td>
<td>3332</td>
<td>1.000</td>
<td>1.031</td>
<td>21.644</td>
</tr>
<tr>
<td>KOH, 10%</td>
<td>3336</td>
<td>3334</td>
<td>0.958</td>
<td>0.974</td>
<td>21.507</td>
</tr>
<tr>
<td>KOH, 40%</td>
<td>3339</td>
<td>3340</td>
<td>0.944</td>
<td>0.943</td>
<td>21.301</td>
</tr>
<tr>
<td>NaOH, 10%</td>
<td>3337</td>
<td>3336</td>
<td>0.969</td>
<td>1.028</td>
<td>21.438</td>
</tr>
<tr>
<td>NaOH, 40%</td>
<td>3340</td>
<td>3346</td>
<td>0.953</td>
<td>0.967</td>
<td>21.233</td>
</tr>
</tbody>
</table>

Table 10
Different absorbance ratios and relative value of optical density (RVOD) of UBP and UBP+OA samples before and after swelling in alkaline solutions

<table>
<thead>
<tr>
<th>Sample</th>
<th>χR (%)*</th>
<th>A_1370/A_2900</th>
<th>A_1420/A_900</th>
<th>A_1315/A_1370</th>
<th>A_1315/A_2900</th>
<th>RVOD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UBP</td>
<td>UBP+OA</td>
<td>UBP+OA</td>
<td>UBP</td>
<td>UBP</td>
<td>UBP+OA</td>
</tr>
<tr>
<td>Reference</td>
<td>0.656</td>
<td>0.627</td>
<td>1.158</td>
<td>1.178</td>
<td>0.780</td>
<td>0.860</td>
</tr>
<tr>
<td>KOH, 10%</td>
<td>0.760</td>
<td>0.709</td>
<td>1.320</td>
<td>1.241</td>
<td>0.960</td>
<td>0.930</td>
</tr>
<tr>
<td>KOH, 40%</td>
<td>0.892</td>
<td>0.827</td>
<td>1.751</td>
<td>1.714</td>
<td>1.147</td>
<td>1.189</td>
</tr>
<tr>
<td>NaOH, 10%</td>
<td>0.739</td>
<td>0.654</td>
<td>1.168</td>
<td>0.896</td>
<td>0.813</td>
<td>0.883</td>
</tr>
<tr>
<td>NaOH, 40%</td>
<td>0.796</td>
<td>0.750</td>
<td>1.500</td>
<td>1.291</td>
<td>1.122</td>
<td>1.138</td>
</tr>
</tbody>
</table>

* these ratios are proportional with crystallinity index
CONCLUSIONS
The pulp fiber samples were subjected to swelling in KOH and NaOH solutions of different concentrations (5, 10 and 40 wt%), for 72 h, at room temperature.

The swollen pulp fibers were investigated by FT-IR spectroscopy and optical microscopy. The swelling behavior depends both on the type of alkaline solutions and their concentration, and on the nature of the samples.

The pulp fibers present higher susceptibility in NaOH solutions, in comparison with the KOH ones, while the samples modified with OA in cold plasma conditions have a higher swelling capacity than those modified with BA, because of the long chain of OA and of a higher modification degree.

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REFERENCES