CELLULOSE CHEMISTRY AND TECHNOLOGY

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 pulp[4] and acetylation of wood[5] 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. Robertson[7] studied the cellulose–liquid 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 webs[1] and wood[8-11] 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 water was correlated with wood density, while the removal of extractives enhanced the rate and maximum swelling of wood.[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.[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.[10]

A previous work of ours reported[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.* [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^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,[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 2θ range, between 2° and 45°. 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]

$$CrI = A_{crist}/A_{total} \quad (1)$$

where CrI = crystalline index, A_{crist} = sum of crystalline peak areas and A_{total} = total area of the diffractogram curve.

The apparent crystallite size was estimated by Scherrer equation:[15]

$$L = K*\lambda/\beta*\cos\theta \quad (2)$$

where K is a constant (0.94), λ is X-ray wavelength (0.1542 nm for Cu Kα radiation), β is the half-height width of the diffraction peak and θ 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:

$$X = (L-2h)^2/L^2 \quad (3)$$

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]

$$\text{cell content} = CrI'/CrI_{cell} \quad (4)$$

where CrI_{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

Property	UBP	BP
Wall thickness (µm)	8.2	7.8
Intrinsic viscosity (mL/g)	1109	728
Kappa number	26.8	3.2
Dry matter content (%)	32.3	32.8
Water retention value (g/g)	1.59	1.43
Thickness (µm)	122	113
Bulk density (cm^3/g)	1.9	1.79
Tensile strength (kN/m)	1.92	1.74
Stretch (%)	2.1	3.4
Tensile energy absorption (J/m^2)	30.9	47.3
Tensile stiffness (kN/m)	296	241
Modulus of elasticity (N/mm^2)	2420	2129
Ln, Lw, Lww	1.52; 2.65; 3.17	1.11; 2.23; 2.85;
Fine %; Fine % Lw	29.96; 2.67	38.05; 4.83
kink index; kink angle; kink/mm	0.99; 31.86; 0.45	1.17; 40.56; 0.68

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

Parameters	UBP	UBP+ BA	UBP+ OA	BP	BP + BA	BP+OA
Cr. I. (%)	60	59	57	61	61	59
L101 (nm)	3.25	3.24	3.29	3.36	3.36	3.39
L$10\bar{1}$ (nm)	5.56	5.58	5.96	5.85	5.84	5.97
L002 (nm)	4.07	4.08	4.76	4.18	4.19	4.36
X	0.52	0.52	0.57	0.53	0.53	0.55
Cellulose fraction (%)	86	84	81	88	87	84

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:

$$Q_{max} = (d - d_0)/d_0 * 100\ (\%) \quad (5)$$

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]

$$E_H\ (kJ) = 1/k\ [(\nu_o - \nu)/\nu_o] \quad (6)$$

where: ν_o – standard frequency corresponding to the free –OH groups (3650 cm^{-1}); ν – frequency of bonded –OH groups; $k = 4*10^{-3}$ kJ^{-1}

- *enthalpy of H-bond formation*, evaluated with the formula:[18]

$$\Delta H \text{ (kJ/mole)} = 0.0672\ \Delta \nu_{OH} + 2.646 \qquad (7)$$

where: $\Delta \nu_{OH}$ – OH wave number shift (cm^{-1})

- *H-bounding distance (R)* (Å), obtained by the Sederholm equation:[19]

$$\Delta\nu\ (cm^{-1}) = 4.43*10^{3}\ (2.84 - R) \qquad (8)$$

where: $\nu\Delta = \nu_o - \nu : \nu_o$; –OH monomeric stretching frequency = 3600 cm^{-1} [20]; ν – OH stretching frequency in the sample IR spectrum;

- *relative value of optical density (RVOD)* from FT-IR spectrum,[21] calculated by the following relation:

$$RVOD = E_C(\nu_j) / E_C(\nu_s) \qquad (9)$$

where: $E_C(\nu j) = \lg T_C(\nu_j) / T(\nu_j) \qquad (10)$

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

- *asymmetrical index (a/b)* – the ratio between peak full width at half height of the OH absorption band.[22]

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.[23] 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.

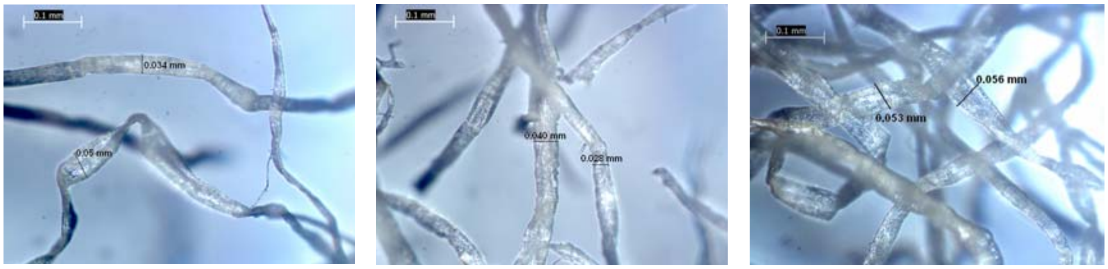
Optical microscopy

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

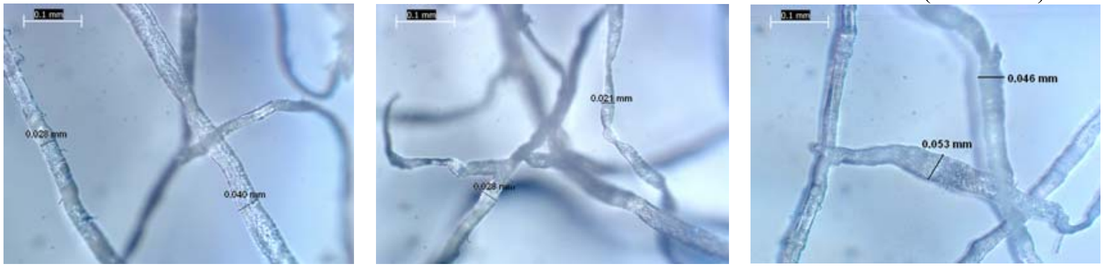
All samples (both unswollen and swollen in alkaline solutions) were left in a desiccator (75% humidity), for 72 h. The increase in the percentage of the diameters of the swollen pulp fibers and of the wet fibers, as determined from the optical microscopy images presented in Figure 1, and the relative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



UBP UBP + AO UBP + AO (10% KOH)



BP BP + AO BP + AO (10% KOH)

(a) (b)

Figure 1: Optical microscopy images: (a) blank samples and (b) samples in 10% KOH solution

Table 3
Percentage increase (wt%) in diameters of softwood Kraft pulp fibers
after swelling in alkaline solutions

Sample	KOH solution			NaOH solution		
	5%	10%	40%	5%	10%	40%
UBP	8.82	35.29	19.35	35.29	26.47	35.29
UBP+BA	19.35	54.83	47.35	38.70	29.03	61.29
UBP+OA	32.14	67.85	53.57	71.42	64.28	64.28
BP	10.71	42.85	32.14	53.57	50.00	64.28
BP+BA	72.00	84.00	80.00	72.00	60.00	68.00
BP+OA	76.19	152.38	138.09	104.76	71.42	85.71

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

Sample	KOH solution			NaOH solution		
	5%	10%	40%	5%	10%	40%
UBP	100	80.64	61.29	70.96	51.61	80.64
UBP+BA	119.21	138.09	76.19	180.95	166.66	104.76
UBP+OA	38.70	41.93	38.70	80.64	51.61	48.38
BP	100	78.57	53.57	53.57	42.85	57.14
BP+BA	84.00	88.00	84.00	100	60.00	72.00
BP+OA	100	116.00	72.00	112	60.00	60.00

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.

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 cellulosic 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 heterogenity (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^-, nH_2O). NaOH is fixed on cellulose, forming mixed hydrates: Na^+HO^- * (n-3)H_2O * 3HO-Cel, in which three H_2O 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 $C_6H_{10}O_5$ 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:

$Q_S = (W_S - W_D)/W_D * 100$ (%) (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.

Neniţescu[26] determined the hydration energies: ΔH_{Na+} = -411.6 kJ/mole and ΔH_{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.

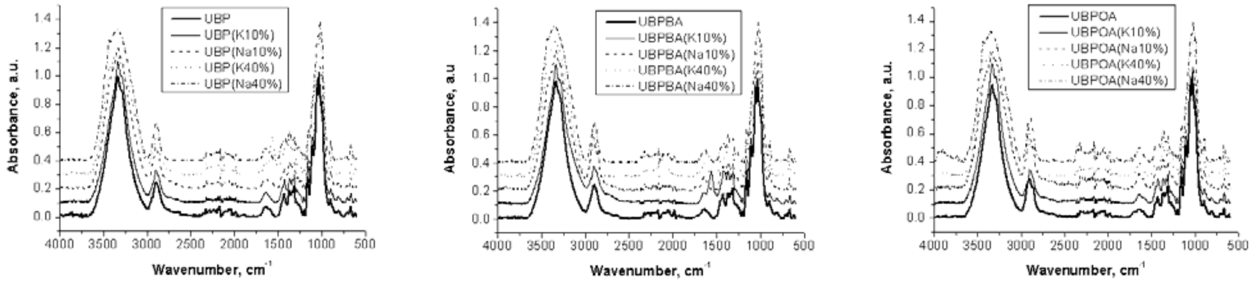
As previously shown,[12] in the sample modified with butyric acid, the FT-IR spectral contour is approximately the same as that for the untreated sample – indicating that a low amount of butyric acid was modified on the Kraft pulp fiber surface. The spectra of the plasma-treated samples with oleic acid 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.

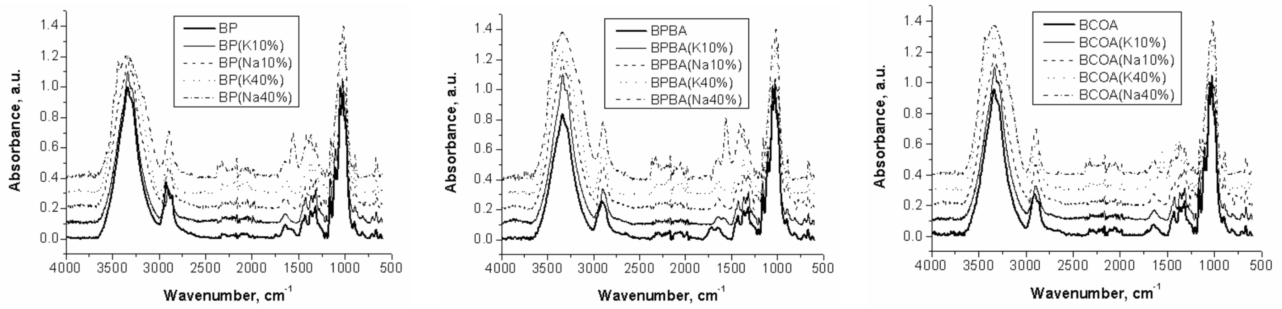
Table 5
Maximum swelling degree (wt %) in alkaline solutions of the unbleached, bleached and modified softwood kraft pulp fibers

Sample	KOH			NaOH		
	5%	10%	40%	5%	10%	40%
UBP	212.92	261.07	288.23	247.85	371.31	420.34
UBP+BA	340.81	371.53	403.33	418.58	461.13	502.38
UBP+OA	440.81	475.78	539.40	541.35	561.00	641.89
BP	164.87	207.35	212.07	197.29	292.86	351.37
BP+BA	205.24	245.65	300.27	284.95	398.13	453.08
BP+OA	284.34	319.41	355.28	353.37	430.32	530.13



(a) (b) (c)

Figure 2: FT-IR spectra for unbleached softwood Kraft pulp fibers after swelling in alkaline solution



(a) (b) (c)

Figure 3: FT-IR spectra for bleached softwood Kraft pulp fibers after swelling in alkaline solution

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 A_{OH}/A_{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

Wavenumber (cm^{-1})	Band assignment	Band position – wavenumber (cm^{-1})								
		Reference	10% KOH		40% KOH		10% NaOH		40% NaOH	
			UBP	UBP+OA	UBP	UBP+OA	UBP	UBP+OA	UBP	UBP+OA
3375-3330	O3-H3-O5 intramolecular H bonds	3335	3338	3340	3341	3347	3336	3344	3339	3350
1365-1335	OH in-plane bending in cellulose	1335 1368	1336 1370	1336 1370	1340 1371	1335 1367	1337 1368	1336 1372	1339 1368	1335 1368
1278-1248	C=O stretching	1281	1269	1279	1265	1272	1267	1277	1263	1273
1215-1200	OH in-plane bending in cellulose, C-O symmetrical stretching in pyranose ring	1203	1203	1205	1213	1213	1201	1204	1212	1212
1120-1115	asymmetrical in phase stretching ring	1105	1107	1107	1109	1119	1107	1107	1110	1119
1070-1015 1047-1004	C–O valence vibration mainly from C(3) –O(3)H; stretching C–O in cellulose I	1043	1054	1030	1046	1022	1053	1025	1045	1022

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

Wavenumber (cm^{-1})	Band assignment	Band position – wavenumber (cm^{-1})								
		Reference	10% KOH		40% KOH		10% NaOH		40% NaOH	
			BP	BP+OA	BP	BP+OA	BP	BP+OA	BP	BP+OA
3375-3330	O3-H3-O5 intra-molecular H bonds	3335	3335	3334	3340	3340	3336	3336	3340	3346
2910-2850	symmetrical CH_2 valence vibration	2920	2900	2904	2894	2899	2902	2901	2893	2898
1650-1640	C=O stretching H-O-H from H_2O	1639	1642	1641	1645	1650	1644	1641	1651	1649
1430-1406	H-O-C in-plane bending of the alcohol groups	1428	1428	1428	1419	1422	1428	1427	1411	1423
1278-1248	C=O stretching	1281	1281	1280	1275	1276	1280	1280	1277	1277
1215-1200	OH in-plane bending in cellulose I, C-O symmetrical stretching in pyranose ring	1202	1204	1204	1212	1199	1206	1205	1213	1200
1047-1004	stretching C–O in cellulose I	1031	1029	1030	1020	1020	1028	1029	1020	1020

Table 8
Spectral characteristics of UBP and UBP+OA samples before and after swelling in alkaline solutions

Sample	OH band position (cm^{-1})		a/b ratio		E_H (kJ)		ΔH (kJ/mol)		R (Å)	
	UBP	UBP+OA	UBP	UBP+OA	UBP	UBP+OA	UBP	UBP+OA	UBP	UBP+OA
Reference	3335	3335	1.023	1.012	21.57	21.57	46.9	47.88	2.780	2.780
KOH, 10%	3336	3340	0.971	0.934	21.51	21.23	47.9	48.43	2.780	2.780
KOH, 40%	3339	3347	0.754	0.722	21.30	20.75	48.9	49.39	2.781	2.782
NaOH, 10%	3338	3344	1.000	1.000	21.37	20.96	47.6	48.26	2.780	2.779
NaOH, 40%	3341	3350	0.920	0.893	21.16	20.55	48.4	48.68	2.779	2.785

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

Sample	OH band position (cm^{-1})		a/b ratio		E_H (kJ)		ΔH (kJ/mol)		R (Å)	
	BP	BP+OA	BP	BP+OA	BP	BP+OA	BP	BP+OA	BP	BP+OA
Reference	3335	3332	1.000	1.031	21.644	21.781	46.914	46.872	2.780	2.779
KOH, 10%	3336	3334	0.958	0.974	21.507	21.644	47.586	47.838	2.780	2.779
KOH, 40%	3339	3340	0.944	0.943	21.301	21.233	48.174	48.930	2.781	2.781
NaOH, 10%	3337	3336	0.969	1.028	21.438	21.507	47.292	47.502	2.780	2.780
NaOH, 40%	3340	3346	0.953	0.967	21.233	20.822	47.922	48.174	2.781	2.783

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

Sample	χ_{IR} (%)*				A_{OH}/A_{CH} ratio				RVOD	
	A_{1370}/A_{2900}		A_{1420}/A_{900}		A_{1315}/A_{1370}		A_{1315}/A_{2900}		A_{1505}/A_{1425}	
	UBP	UBP+OA	UBP	UBP+OA	UBP	UBP+OA	UBP	UBP+OA	UBP	UBP+OA
Reference	0.656	0.627	1.158	1.178	0.780	0.860	0.634	0.546	0.180	0.153
KOH, 10%	0.760	0.709	1.320	1.241	0.960	0.930	0.696	0.711	0.093	0.121
KOH, 40%	0.892	0.827	1.751	1.714	1.147	1.189	0.880	0.854	0.129	0.137
NaOH, 10%	0.739	0.654	1.168	0.896	0.813	0.883	0.648	0.667	0.088	0.111
NaOH, 40%	0.796	0.750	1.500	1.291	1.122	1.138	0.869	0.800	0.097	0.129

* these ratios are proportional with crystallinity index

Table 11
Different absorbance ratios and relative value of optical density (RVOD) of BP and BP+OA samples before and after swelling in alkaline solutions

Sample	χ_{IR} (%)				A_{OH}/A_{CH} ratio				RVOD	
	A_{1370}/A_{2900}		A_{1420}/A_{900}		A_{1315}/A_{1370}		A_{1315}/A_{2900}		A_{1505}/A_{1425}	
	BP	BP+OA	BP	BP+OA	BP	BP+OA	BP	BP+OA	BP	BP+OA
Reference	0.682	0.703	0.912	1.143	0.810	0.969	0.586	0.700	0.210	0.133
KOH, 10%	0.800	0.782	1.291	1.230	1.052	1.166	0.740	0.833	0.088	0.076
KOH, 40%	0.935	0.838	1.633	1.307	1.222	1.194	0.877	0.960	0.161	0.100
NaOH, 10%	0.723	0.716	0.965	1.182	0.863	1.037	0.690	0.745	0.075	0.062
NaOH, 40%	0.853	0.823	1.416	1.250	1.194	1.184	0.758	0.934	0.098	0.084

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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