RADICAL FORMATION ON CTMP FIBERS BY ARGON PLASMA TREATMENTS AND RELATED LIGNIN CHEMICAL CHANGES

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The changes at molecular level induced by cold argon plasma treatments on fibers obtained from chemi-thermo-mechanical pulp (CTMP) fibers were investigated. The radicals formed on CTMP fibers after treatments were identified and quantified by Electron Paramagnetic Resonance (EPR) spectroscopy. The plasma conditions which maximize the formation of radicals on fibers were assessed: after treatment with 0.4 mbar Ar pressure and 75 W radiofrequency power, phenoxy radicals triple their concentration in only 60 s and reach a value 4 times higher than that reported for laccase-catalyzed lignin oxidation. It was found that in plasma-treated fibers, the formation of radicals competes with their coupling. This latter result leads to cross-linkages of the lignin monomeric units and formation of new intermonomeric C-C and C-O bonds, for the first time assigned to specific molecular interactions through Heteronuclear Single Quantum Coherence (2D-HSQC) spectroscopy and Nuclear Magnetic Resonance spectroscopy of carbon (^{13}C-NMR). These results were confirmed by Nuclear Magnetic Resonance spectroscopy of phosphorous (^{31}P-NMR). The lack of evidences of inter-fiber bond interactions, deduced from Gel Permeation Chromatography (GPC) data, suggests the possible application of plasma treatments for the production of wood fiber-based composites.

Keywords: Lignocellulosic fibers; EPR; NMR; phenoxy radicals; plasma treatment

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INTRODUCTION

The radicalization of lignocellulosic fibers is a first step in order to modify their properties for specific applications. For instance, radical centers were used as initiators for the grafting of synthetic polymers onto the fiber surface and the production of composites (Cai et al. 2005); on the other hand, the formation of lignin phenoxy radicals leads to an increased bonding strength in fibers, which allows the production of medium density fiberboards without the addition of synthetic adhesives (Lund and Felby 2001; Felby et al. 2002).

The formation of radicals at the surface of wood fibers is conventionally performed by enzymatic treatment or by chemical means. Phenoxy radicals were pro-

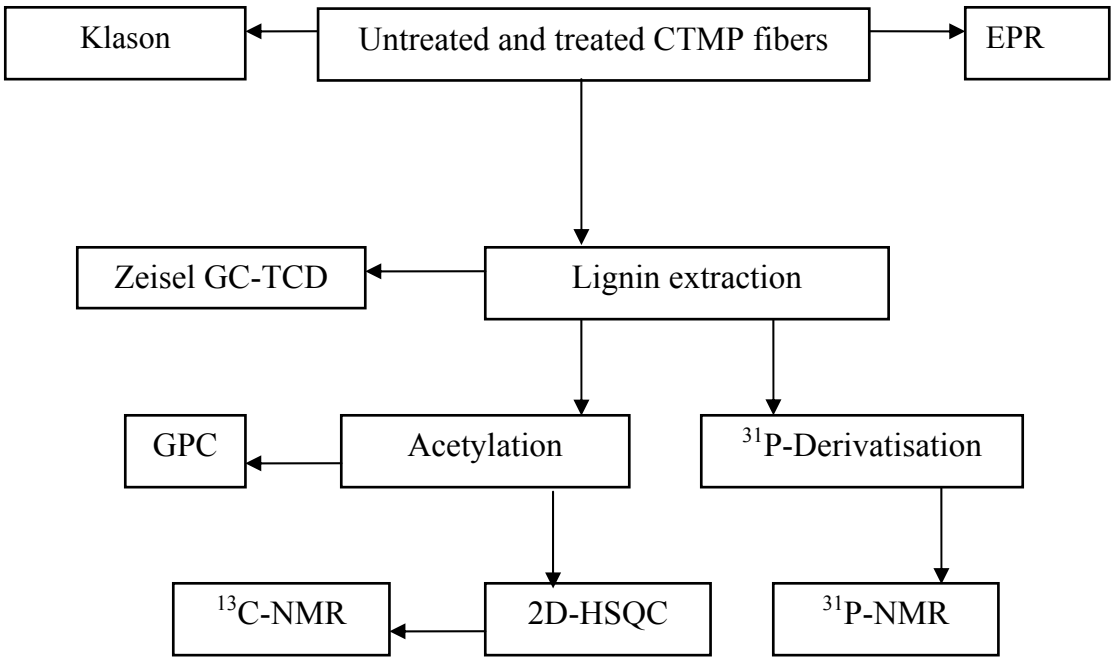
duced on thermo-mechanical pulp (TMP) fibers, by treatment with molecular oxygen, using laccase as a catalyst (Lund and Felby 2001). Formation of phenoxy radicals on TMP fibers and on fibers from chemi-thermo-mechanical pulp (CTMP fibers) can also be obtained by treatment with molecular oxygen, in the presence of N,N'-ethylenebis-(salicylideneiminato) cobalt(II), [Co(salen)], as catalyst (Canevali et al. 2002; Canevali et al. 2005; Zoia et al. 2008). The concentration of radicals in both TMP and CTMP fibers, when using [Co(salen)] as a catalyst, reaches values 10 times higher than those obtained after enzymatic treatment, and it was assessed that when the higher concentration of radicals are formed on a fiber, deeper structural and morphological changes are induced (Canevali et al. 2005). Unfortunately, for both enzymatic and chemical treatments, large amounts of solvent and catalyst are generally required, and the time needed to maximize the radical concentration is rather long, being about one hour for both methods.

A promising alternative technique for obtaining high amounts of radicals in fibers employs plasma, which makes it possible to avoid long reaction times and the use of solvents; this technique is already used for the surface modification of many polymeric materials, being fast, clean, and environmentally safe (Toriz et al. 2004; Inagaki 1995; Wan-Ling et al. 2003; Chi-Yuan et al. 2003). Radicals formed at the surface of jute lignocellulosic fibers after cold Ar plasma treatments were studied (Sabharwal et al. 1993; Young et al. 1995), and it was demonstrated that lignin is the primary molecular site of radical formation. In a preliminary study (Zanini et al. 2005), we showed that Ar plasma treatment of fibers obtained from chemical pulp (softwood kraft fibers) and of CTMP fibers forms a higher concentration of phenoxy radicals than enzymes, leading to a modification of the lignin chemical structure, as assessed by Nuclear Magnetic Resonance spectroscopy (^{13}C-NMR) and Gel Permeation Chromatography (GPC).

In order to clarify the possible applications of plasma-treated fibers, in the present paper the chemical changes at molecular level induced by cold Ar plasma treatments on CTMP fibers were investigated. Scheme 1 summarizes the analytical protocol used to evaluate the changes in CTMP fibers after Ar plasma treatments with respect to the untreated fibers.

The radicals formed on CTMP fibers by Ar plasma treatments were identified and quantified by Electron Paramagnetic Resonance (EPR) spectroscopy; the plasma conditions (treatment time, source power and argon pressure) that maximize the formation of radicals on fibers were assessed.

After a preliminary evaluation of lignin amount in fibers by the Klason method (Dence 1992), the changes in chemical structure, achieved by lignin units under plasma treatments, were investigated by Heteronuclear Single Quantum Coherence (2D-HSQC) spectroscopy, Nuclear Magnetic Resonance of carbon and phosphorus (^{13}C-NMR and ^{31}P-NMR), Gel Permeation Chromatography (GPC), and the Zeisel method (Girardin and Metche 1983). The lignin changes due to Ar plasma treatment were related to radical formation and compared with those produced by chemical or enzymatic treatments.



Scheme 1

EXPERIMENTAL

Reagents

Acetic anhydride, pyridine, 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, n-hydroxynaphthalimide, deuterated DMSO-d_6, deuterated chloroform, and tetrahydrofuran (THF) were supplied by Fluka Inc. and used without any further purification. Mill-Q water was used.

Fibers

Commercial lignin-rich softwood fibers, obtained from chemi-thermo-mechanical pulp (hereafter CTMP fibers), were examined. The lignin content in untreated fibers was 27.5 %, as evaluated by the Klason method (Dence 1992).

Before any characterization and any treatment, fibers were dried in an oven at 353 K for one night.

Plasma Treatments of Fibers

The details of the employed cold plasma reactor were reported elsewhere (Riccardi et al. 2001, 2003). Briefly, it consists of three parts: a) a reactor chamber connected to a pumping system; b) a plasma production system, composed of a radiofrequency (RF) power generator operating at 13.56 MHz and a capacitive cylindrical electrode axially located into the reactor chamber; and c) a sample holder consisting of 3 aluminum plates (7 cm x 5 cm) horizontally placed at a vertical distance of 3 cm one from the other and at a distance of 10 cm from the cylindrical electrode.

Before operating discharges, the reactor was evacuated up to a residual pressure of 2×10^{-5} mbar. Then, Ar was injected into the reactor by means of a micrometric valve,

and plasma treatments were carried out in the 0.1-0.8 mbar pressure range; the RF power input was varied between 35 W and 125 W. As a technical choice, plasma treatments were carried out through pulses of 30 s, repeated from 1 to 4 times, with 1 s of delay between two successive pulses; thus total exposure times ranged between 30 s and 2 min. In all cases, plasma treatments were performed on about 1 g of fiber. In order to normalize the results, fibers were weighed both before and after plasma treatments. The data are the average of three experiments.

Characterization

Fibers were characterized by EPR spectroscopy, while 2D-HSQC, ^{13}C-NMR, ^{31}P-NMR and GPC investigations were performed on lignin extracted from fibers. In all cases, both untreated and plasma-treated samples were characterized.

EPR characterization of fibers

Samples of fibers were treated by plasma under the above-described conditions, then the chamber was opened in the air, a suitable aliquot of fiber was withdrawn, immediately inserted in the EPR tube, and cooled in liquid nitrogen, in order to minimize both the decay and any other reactions of the radical species.

In order to determine whether the EPR data were affected by the interaction with molecular oxygen, fibers treated by argon plasma (0.4 mbar argon pressure, 75 W RF power, 4 pulses of 30 s) were kept under argon in the plasma reactor chamber, which was kept hermetically closed, and transferred inside a glove box. There, the chamber was opened in an Ar atmosphere, and the fibers were transferred into an EPR tube that was hermetically closed. The EPR tube was then extracted from the glove box, left at room temperature for the following times (expressed in minutes): 0, 5, 10, 15, 20, 30 and 120, then cooled in liquid nitrogen. As a comparison, another aliquot of fibers treated by plasma under the same conditions, was exposed to air and left at room temperature for the same times, then cooled in liquid nitrogen.

CW EPR spectra were recorded at 123 K on a Bruker EMX spectrometer working at the X-band frequency, equipped with a variable temperature BVT 2000 unit. Spectra were acquired using microwave power of 5 mW, modulation amplitude of 2.0 G, modulation frequency of 100.0 kHz, and resolution of 5 points/G. The g values were determined by standardization with α,α'-diphenyl-β-picryl hydrazyl radical (DPPH). The concentrations of paramagnetic species, expressed as spin/g of fibers, were calculated after subtraction of the cavity signal by double integration of the resonance lines (precision ± 10 %). The areas under the absorption lines were referred to a calibration curve (R^2 = 0.996), which plots the areas of standard DPPH solutions (toluene/Nujol 2:1 v/v) *vs.* the number of spins per cm. Since 1 cm is the sensitive part of the cavity, the weight of every sample filling 1 cm length of the EPR tube was always accurately determined.

2D-HSQC and ^{13}C-NMR investigation of lignin

NMR analyses were performed on lignin extracted from CTMP fibers by a modification of the acidolysis method reported in the literature (Gellerstedt et al. 1994; Canevali et al. 2005). The yield of lignin evaluated as extracted lignin relative to the

initial lignin in fibers (w/w %) was around 35-40%. In order to evaluate whether demethylation occurred during plasma treatments, the average number of methoxyl groups per aromatic ring on extracted lignin was evaluated by the Zeisel method (Girardin and Metche 1983).

2D-HSQC and ^{13}C-NMR spectra were run in DMSO on acetylated samples, to avoid the fractionation of the material before NMR analysis and to increase both solubility and chemical shift dispersion of the side chain units (Adler et al. 1987). As the analyzed lignin samples were obtained from both untreated and plasma-treated fibers, the structure modifications due to plasma treatment could be clearly distinguished from those due to the lignin isolation method. Thus, before NMR analyses, the extracted lignin (0.1 g) was acetylated with acetic anhydride/pyridine 1:1 v/v (2 ml), then 60 mg of acetylated lignin were dissolved in 0.75 ml DMSO-d_6.

The inverse detected ^{1}H-^{13}C correlation spectra (2D-HSQC) were recorded at 283 K using a Varian Inova 300 MHz instrument. The spectral width was set to 6 kHz in F2 and 25 kHz in F1. The polarization transfer delay was set at the assumed coupling of 140 Hz, and a relaxation delay of 2 s was used to obtain the spectra.

The 1D-^{13}C spectra were recorded at 333 K using a Varian Mercury 400 MHz instrument. Chemical shifts were referred to the solvent signal at 39.5 ppm. To obtain quantitative ^{13}C-NMR spectra, a relaxation delay of 10 s (45° pulse angle) was used between the scans (Landucci 1985; Robert and Brunow 1984). Line broadening of 2-5 Hz was applied to FIDs before Fourier transform. For each spectrum, typically about 16000 scans were accumulated.

^{31}P-NMR investigation of lignin

In order to characterize and quantify all the different functional groups with labile OH, Nuclear Magnetic Resonance analysis of phosphorus (^{31}P-NMR) of lignins extracted from CTMP fibers was performed. Before analysis, the extracted lignins were derivatized with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, as reported in the literature (Jiang et al. 1995; Granata and Argyropoulos 1995; Saake et al. 1996). Thus, the phospholane (100 μl) was added to 20 mg of extracted lignin, together with solutions of n-hydroxynaphthalimide as internal standard and tris(acetylacetonate)chromium(III), [Cr(acac)$_3$], as relaxation reagent (100 μl each). Accurately weighed derivatized lignin samples (30 mg) were dissolved in a solvent mixture composed of pyridine and deuterated chloroform 1.6:1 v/v ratio (0.5 mL), then the ^{31}P-NMR spectra were recorded at 333 K using a Varian Mercury 400 MHz instrument. The ^{31}P-NMR data reported in this article are averages of three experiments. The maximum standard deviation of the reported data was 2×10^{-2} mmol/g, while the maximum standard error was 1×10^{-2} mmol/g.

GPC investigation of lignin

Investigations were carried out on acetylated lignin samples dissolved in THF. Analyses were performed using a Waters 600 E liquid chromatograph connected with an HP 1040 ultraviolet diode array (UV) detector set at 280 nm. The GP-column was an Agilent PL 3 μm mixed gel E MW 220-400W. The acetylated lignin samples were analyzed at a flow rate of 0.8 ml/min. Polymer standards of polystyrene (PS) from

Polymer Laboratories were used for calibration. The PS-calibration curve was tested using acetylated dimeric, tetrameric, and hexameric lignin model compounds.

The evaluation of both the number-average molecular weight (M_n) and the weight-average molecular weight (M_w) was performed following the methodology developed in the literature (Himmel et al. 1989).

RESULTS AND DISCUSSION

Radicalization of Fibers

CTMP fibers were analyzed by EPR before plasma treatment in order to verify the presence of radicals. Spectra showed an isotropic signal (Fig. 1, line a) which, due to its position (g = 2.004) and line width (ΔH_{pp} = 10.7 G), can be attributed to phenoxy radicals (Hon 1992). These probably resulted from thermal, mechanical, and chemical pulp treatments or were photo-chemically induced (Hon 1987). The concentration of these radicals resulted to be 1.0×10^{16} spin/g.

The plasma conditions that maximize the formation of radicals on fibers were assessed by changing i) the treatment time, ii) the RF source power, and iii) the argon pressure. In all experiments, only the signals of phenoxy radicals were detected.

i) The dependence of the concentration of phenoxy radicals on the treatment time for CTMP fibers was investigated at an argon pressure of 0.4 mbar and a 75 W RF source power, by repeating the plasma pulse of 30 s, from 1 to 4 times. Within a short period of time (2 pulses of 30 s), the spin concentration rose to 3.4×10^{16} spin/g (Fig. 1, line b), thus it increased about 3 times with respect to the untreated fibers; even when continuing the plasma treatment, no further increase was observed. This trend is in agreement with that reported for jute lignocellulosic fibers (Young et al. 1995) and suggests that, after 60 s from the onset of treatment, the phenoxy radical formation competes with their coupling. The obtained results show that for CTMP fibers the maximum concentration of radicals is reached after a treatment of 60 s, a much shorter time than that required in the case of wet methods (about one hour) (Lund and Felby 2001; Canevali et al. 2005; Zoia et al. 2008).

ii) The concentration of phenoxy radicals vs. plasma RF power (35, 75, and 125 W) was evaluated in CTMP fibers treated at the argon pressure of 0.4 mbar for 2 min (4 pulses of 30 s). By using 35 W power, the concentration of phenoxy radicals reached the value of 3.3×10^{16} spin/g, then slightly decreased (Fig. 2). The obtained results show that at RF power greater than 35 W, the radical quenching prevails over the radical formation, as already observed for the Ar plasma treatment of jute (Sabharwal et al. 1993).

iii) The dependence of the concentration of phenoxy radicals on the argon pressure was assessed by treating CTMP fibers at 75 W RF power for 2 min (4 pulses of 30 s), at the following pressures: 0.1, 0.2, 0.4, 0.6, and 0.8 mbar. It was observed that the concentration of phenoxy radicals increased about 3 times at 0.1 mbar with respect to the untreated fibers, after which it kept a constant value, within experimental error.

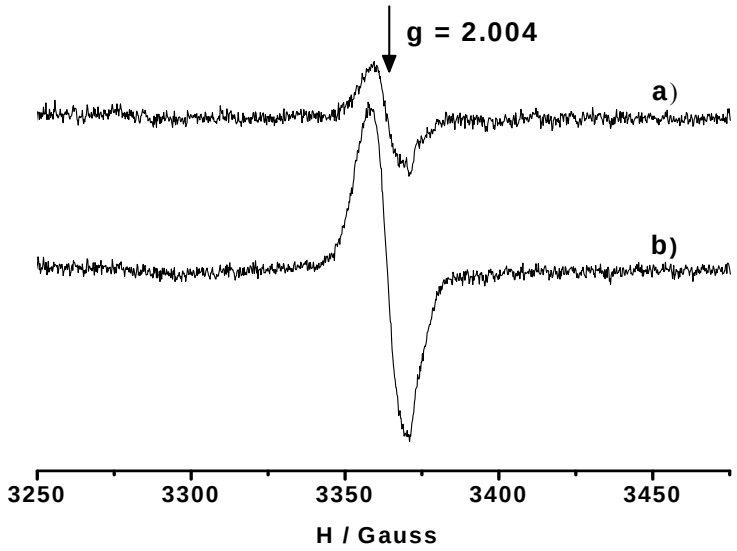


Fig. 1. X-band EPR spectra recorded at 123 K on CTMP fibers a) untreated and b) after plasma treatment at 0.4 mbar pressure, 75 W RF power and 2 pulses of 30 s.

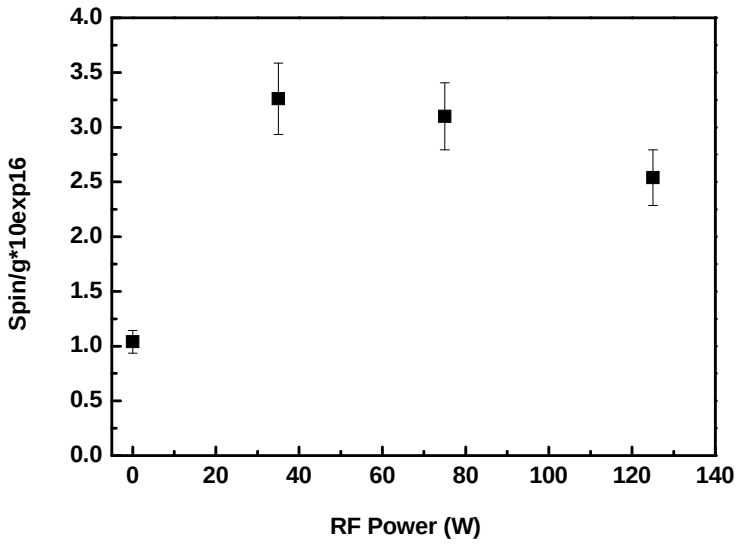


Fig. 2. Concentration of phenoxy radicals in CTMP fibers as a function of RF power, at 0.4 mbar Ar pressure, 4 pulses of 30 s.

In order to determine whether the EPR data were affected by the interaction of formed radicals with molecular oxygen, after plasma treatment (0.4 mbar argon pressure, 75 W RF power, 4 pulses of 30 s), an aliquot of fiber was maintained under argon, and

the concentration of radicals was monitored as a function of time. As a comparison, another aliquot of fibers treated by plasma under the same conditions was exposed to air and maintained at room temperature for the same times (see Experimental). Results show that the effects of molecular oxygen on radicals generated by plasma were negligible in the first 15 min (Fig. 3), which is a time longer than that required for the sample preparation and the EPR spectrum recording. Thus, the above reported EPR data and their interpretation in terms of radical stability were not affected by the presence of molecular oxygen. If the plasma treated fibers remains two hours in air, a strong decay of phenoxy radical concentration is detected, in comparison with the value observed at the same time under argon.

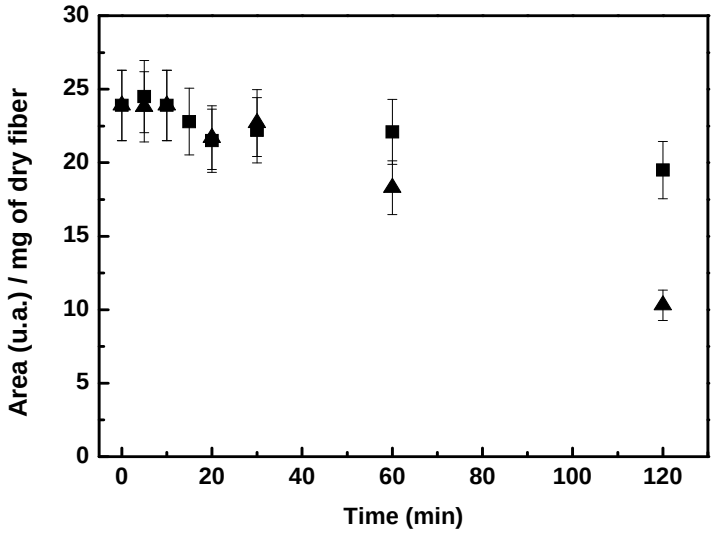


Fig. 3. Concentration of phenoxy radicals, reported as areas of the EPR resonances divided by the fiber weight, as a function of time for CTMP fibers in air (▲) and in argon (■).

Comparing the results obtained with different plasma conditions, the maximum obtained radical concentration was 3.4×10^{16}spin/g, formed at 0.4 mbar Ar pressure and at 75 W RF power, after 2 pulses of 30 s. This value is 68% of that obtained by chemical methods on the same fibers (Canevali et al. 2005), while it is 4 times higher than those reported in the literature (Felby et al. 1997; Ferm et al. 1972) for the oxidation of TMP and of milled wood lignin with molecular oxygen respectively, in the presence of laccase. Thus, cold Ar plasma treatment was shown to be a suitable method in order to activate fiber surface through the formation of a high radical concentration, as an alternative to enzymatic and chemically-catalyzed oxidation treatments.

Lignin Chemical Modifications after Plasma Treatment

The chemical changes in CTMP fibers after Ar plasma treatment in the experimental conditions that maximize the radical formation (0.4 mbar Ar pressure, 75 W RF

power and 2 pulses of 30 s) were evaluated as summarized in Scheme 1 (see Introduction). Samples were analyzed both before and after the radicalization treatment.

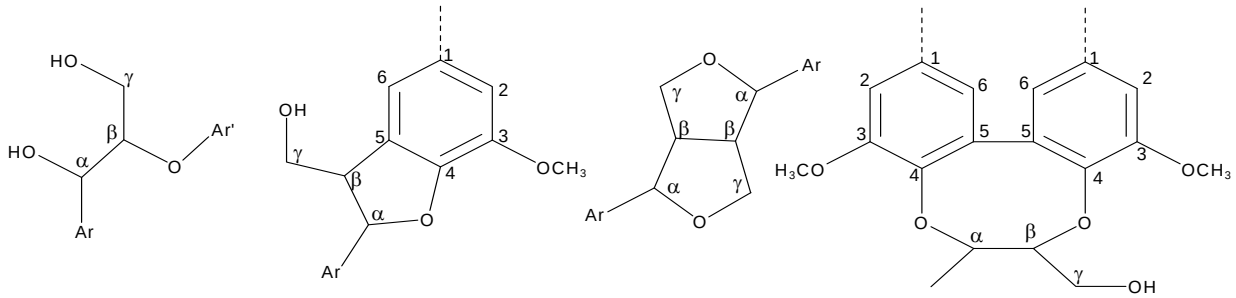
After plasma treatment, the recovery of the fiber was 92%, and a preliminary evaluation by the Klason method (Dence 1992) of the lignin content in fibers, 27.5% before and 27.0% after plasma treatment, allowed us to exclude relevant delignification effects.

The average number of methoxyl groups per aromatic ring on the extracted lignin was calculated by the Zeisel method (Girardin and Metche 1983) and gave 1.06 OCH_3 groups per C_6 unit on CTMP, both before and after plasma treatment. This result allowed us to exclude significant demethylation effects due to plasma treatment.

2D-HSQC and ^{13}C-NMR investigation

The knowledge of the lignin structure of untreated CTMP fibers, fully characterized by ^{13}C-NMR spectroscopy (Canevali et al. 2005), allowed us to evaluate and quantify the effects of plasma treatment under the conditions of maximum radicalization.

Samples were analyzed by 2D-HSQC spectroscopy to identify the principal intermonomeric units in lignin and to evaluate the changes in the CTMP lignin structure after plasma treatment. Assignments of the predominant 2D-HSQC signals were based on the chemical shift data of lignin model compounds and of milled wood lignin reported in the literature (Ede and Brunow 1992; Ralph 1996; Galkin et al. 1997; Canevali et al. 2005). The predominant intermonomeric units present in softwood milled wood lignin (MWL), taken as reference (Holmbom 2000), are reported in Scheme 2: arylglycerol-β-arylether (β-O-4), phenylcoumaran (β-5), pinoresinol (β-β), and dibenzodioxocine (5-5'-O-4).



β-O-4 β-5 β-β 5-5'-O-4

Scheme 2

The comparative evaluation of 2D-HSQC spectra of acetylated lignins extracted from CTMP, both untreated and plasma treated, shows that both lignins were rich in β-O-4 units (Figs. 4 a and b). In the case of lignin extracted from untreated CTMP fibers (Fig. 4a), the ^{1}H-^{13}C signal at 4.29-3.91/71.8, characteristic of γ carbons in β-β intermonomeric units, and the ^{1}H-^{13}C correlation at 4.85/83.7 ppm, typical of β carbons in 5-5'-O-4 intermonomeric units, were absent. Thus the structural assembly of lignin extracted from

untreated CTMP fibers is slightly different from that of softwood MWL, since the β-β and 5-5'-O-4 structures are absent or only present in traces.

Instead, the ^{1}H-^{13}C correlation corresponding to β-β and 5-5'-O-4 units was well observable from the expansion of the 2D-HSQC spectrum of acetylated lignin after plasma treatment (Fig. 4b).

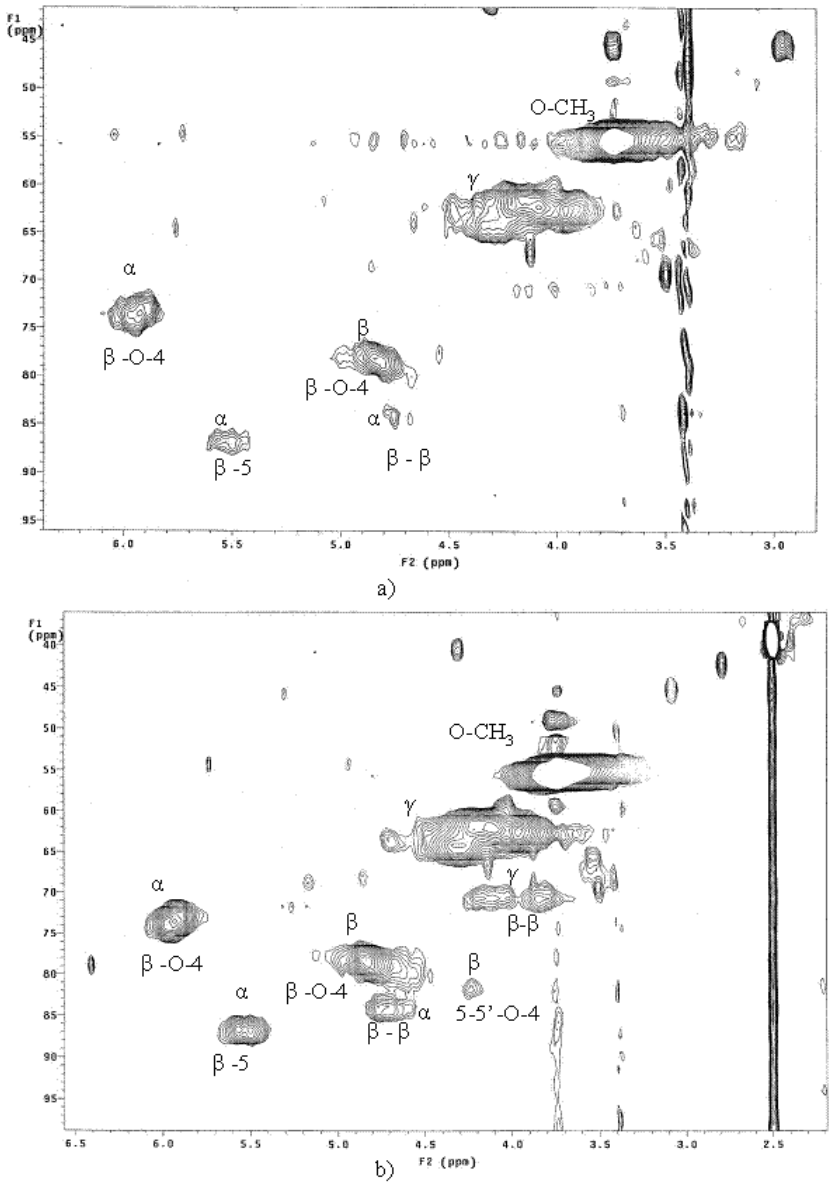


Fig. 4. 2D-HSQC spectra of acetylated lignin from CTMP fibers a) untreated and b) after plasma treatment (0.4 mbar Ar pressure, 75 W RF power and 2 pulses of 30 s).

In order to better evaluate the changes in the intermonomeric units of CTMP fibers, a quantitative analysis of ^{13}C-NMR spectra was performed, referring the intensity of each ^{13}C-β signal to that of the methoxyl signal (56.0 ppm) and multiplying this by the average number of methoxyl groups per aromatic ring (Canevali et al. 2005). The relative

amounts of the predominant intermonomeric units in MWL and in lignin from CTMP fibers are reported in Table 1, expressed as "+" marks, where each "+" mark means 0.06-0.09 the intensity of methoxyl signal multiplied by the average number of methoxyl groups per aromatic ring.

Table 1. Relative Amounts of the Predominant Intermonomeric Units in MWL and Lignin from CTMP Fibers.

Structural Units	MWL	Lignin from CTMP Fibers	
		Untreated	Plasma Treated
β-O-4	++++	++++	+++
β-5	++	+	+
β-β	+	Traces	+
5-5'-O-4	+	Not Detected	+

Results show that the relative amount of β-O-4 units, evaluated from the β carbon peak at 79.6 ppm, decreased after plasma treatment. Instead the signals corresponding to β-β and 5-5'-O-4 intermonomeric units became clearly observable after plasma treatment. Thus, it can be estimated that more than 20% of intermonomeric bonds in lignin are modified after plasma treatment and the interpretation of these data agrees with the tendency of radicals to couple in lignin, suggested on the basis of EPR results.

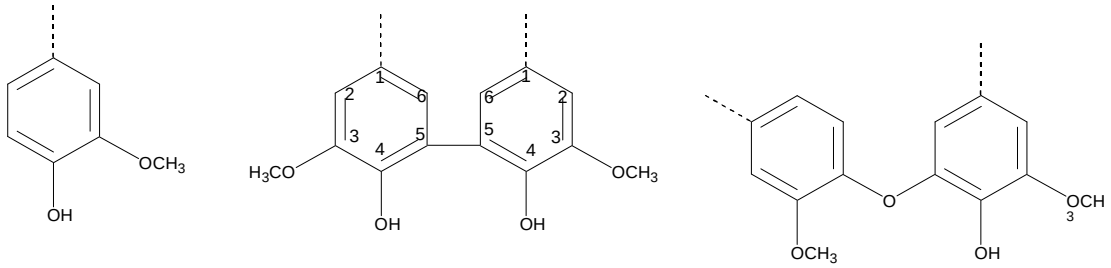
^{31}P-NMR investigation

Nuclear Magnetic Resonance of phosphorus (^{31}P-NMR), performed after derivatization of extracted lignins with phosphorus markers, makes it possible to characterize and quantify all the different OH groups with labile protons, such as aliphatic carboxylic acids, alcoholic groups, and the guaiacylic units. In addition, it is possible to quantify condensed aromatic structures bearing phenolic hydroxyl groups such as 5-5' and 4-O-5 (Crestini and Argyropoulos 1998), reported in Scheme 3.

Table 2 shows the absolute amounts of the different labile protons present in lignin, expressed as mmol/g of lignin.

Results show that after plasma treatment the concentration of free phenolic groups decreased by 13%, from 1.64 to 1.42 mmol/g, and in particular the concentration of guaiacyl unit decreased by about 11%, from 1.39 to 1.24 mmol/g (Argyropoulos 1995; Crestini et al. 2003). Also the concentration of phenolic 5-5' decreased after plasma treatment. These results are in agreement with those observed after 2D-HSQC and ^{13}C-NMR analyses, since phenolic 5-5' is one of the precursors of 5-5'-O-4 (Scheme 2), which ^{13}C-NMR demonstrated to increase after plasma treatment.

The concentration of carboxylic groups in lignin after plasma treatment was 0.16 mmol/g, a value three times higher than before plasma treatment. This is attributed to the oxidation of phenoxy radicals in lignin by molecular oxygen, already suggested by EPR measurements.



Guaicyl OH **5-5' -OH** **4-O-5-OH**

Scheme 3

Table 2. Concentrations (mmol/g of Lignin) of the Different Labile Protons in Lignin from CTMP Fibers.

Type of Labile Protons	Lignin from CTMP Fibers	
	Untreated	Plasma Treated
Aliphatic OH	5.62	5.56
Total Phenolic OH	1.64	1.42
Guaiacyl OH	1.39	1.24
5-5'-OH	0.12	0.10
4-O-5-OH	0.05	0.07
Acidic-OH in COOH	0.05	0.16

GPC investigation

The effects of plasma treatments on lignin structure were also evaluated through the changes of molecular weight distribution (MWD) in the extracted acetylated lignin under the conditions of maximum radicalization (0.4 mbar Ar pressure, 75 W RF power and 2 pulses of 30 s). Results showed that the differences in M_n, M_w, and polydispersity of acetylated lignin, before and after plasma treatments, were not relevant (Table 3).

Table 3. GPC Data of Lignin from CTMP Fibers.

	Lignin from CTMP Fibers	
	Untreated	Plasma Treated
M_n	9400 ± 500	8600 ± 500
M_w	31400 ± 1000	26900 ± 1000
Polydispersity	4.1	3.1

Thus in the plasma treated CTMP fibers the cross-linking deduced from 2D-HSQC and ^{13}C-NMR measurements induces intra-fibers modifications, while a relevant increase in inter-fiber lignin cross-linkages can be excluded. This result excludes the use of plasma treatment for the increase of bonding strength in fibers, while it suggests the possible application of this technique for the fixing of monomers onto the fiber surface and the production of wood fiber-based composites.

CONCLUSIONS

1. Phenoxy radicals in CTMP fibers triple their concentration after cold Ar plasma treatment in only 60 s at 0.4 mbar Ar pressure and 75 W RF power, reaching the value of 3.4×10^{16} spin/g. This radical concentration is 68 % of that obtained after [Co(salen)]-catalyzed oxidation, while it is 4 times that reported in the literature (Felby et al. 1997; Ferm et al. 1972) for the oxidation of TMP and of milled wood lignin with molecular oxygen respectively, in the presence of laccase. Thus, cold Ar plasma treatment is revealed to be a suitable method in order to activate fiber surface through the formation of a high radical concentration, alternative to enzymatic and chemically-catalyzed oxidation treatments.
2. After 60 s of treatment, the concentration of radicals does not change any more, suggesting that the formation of phenoxy radicals competes with their coupling. This leads to cross-linkages of the lignin monomeric units, with formation of new inter-monomeric C-C and C-O bonds, for the first time assigned to specific molecular interactions through 2D-HSQC and ^{13}C-NMR measurements, and confirmed by ^{31}P-NMR. The cross-linking induces intra-fiber modifications, as suggested by GPC data.
3. The lack of evidences of inter-fiber bond interactions excludes the use of plasma treatments for the increase of bonding strength in fibers, while it suggests the possible application of this technique for the fixing of monomers onto the fiber surface, which may be useful for the production of wood fiber-based composites.

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