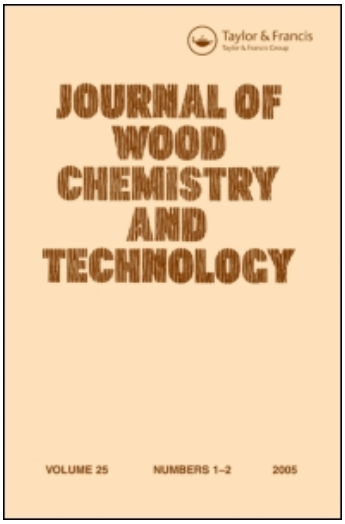

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Photoyellowing of milled Wood Lignin and Peroxide-Bleached Milled Wood Lignin in Solid 2-Hydroxypropylcellulose Films After Sodium Borohydride Reduction and Catalytic Hydrogenation in Solution: a Fluorescence Spectroscopic

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PHOTOYELLOWING OF MILLED WOOD LIGNIN AND PEROXIDE- BLEACHED MILLED WOOD LIGNIN IN SOLID 2-HYDROXYPROPYLCELLULOSE FILMS AFTER SODIUM BOROHYDRIDE REDUCTION AND CATALYTIC HYDROGENATION IN SOLUTION : A FLUORESCENCE SPECTROSCOPIC *STUDY*

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SUMMARY

Fluorescence spectra and emission quantum yields of 2-hydroxypropyl-cellulose films, incorporating milled wood lignin that had been treated in solution by H_2O_2/NaOH and/or $NaBH_4$ and/or H_2 (Pd/C), were measured before and after irradiation by UV light (λ>300 nm). Bleaching, reduction ($NaBH_4$), and hydrogenation (H_2, Pd/C) increase the quantum yield of fluorescence and emission in the blue region (400 nm). The destruction of carbonyl chromophores (α-carbonyl, coniferaldehyde, and quinones), which quench the fluorescence of biphenyl groups, the main structures emitting in this part of the spectrum, appeared to be mainly responsible for this increase. Irradiation restores i) emission in the long wavelength part of the spectra (maximum emission: 500 nm, maximum excitation: 400 nm), and ii) quenching of the fluorescence in the blue part (400 nm) of the spectra, even for hydrogenated films. These results are interpretated in relation to the formation, under irradiation, of coniferaldehyde groups and also the generation of complex structures formed by photooxidation of phenolic biphenyls.

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INTRODUCTION

The fluorescence technique has been applied to a study of the photobleaching and photoyellowing of paper containing lignin[1] (softwood CTMP). It was shown that peroxide bleaching of this paper, increased the fluorescence in the 420-450 nm wavelength region. It was also observed that impregnation of high-yield pulp (HYP) with ascorbic acid and thioglycerol enhanced the fluorescence. This latter observation was ascribed to the reduction of quinoid and carbonyl structural elements of lignin, giving phenols which fluoresce in the blue region and offset the natural yellow color of the paper. Moreover, irradiation of bleached HYP paper increased the fluorescence produced in the long wavelength region (400-450 nm) an effect attributed to the formation of hydroxyquinones included in condensed aromatic structures having low lying $\pi\pi^*$ excited electronic states.

In a preceding paper[2], we described an UV/Vis absorption study of the *photoyellowing of milled wood lignin (MWL) and peroxide-bleached milled wood lignin* (LHO) in solid hydroxypropylcellulose (HPC) films. The chromophores were characterized by UV absorption spectroscopy[2]. Extensive reduction with hydride ($NaBH_4$) and catalytic (Pd/C) hydrogenation, in the liquid phase, were also performed to eliminate carbonyl groups and aromatic conjugated double bond repectively, since they are involved in the photoyellowing of high-yield pulps[2]. The kinetics of discoloration and aromatic ring destruction showed the importance of phenolic biphenyl chromophores and among others, phenolic phenylcoumaran structures.

In the present report, we describe a parallel study using a fluorescence technique performed on the previously studied MWL and LHO samples[2] incorporated into HPC. With this procedure, we obtain transparent films very suitable for quantitative fluorescence investigations because the carbohydrate matrix is identical in all measurements. This was not the case in the investigation of CTMP papers[1] where cellulose (without the presence of hemicelluloses) was chosen as the carbohydrate background for comparison.

EXPERIMENTAL

The experimental details of the isolation, reduction, and hydrogenation of lignin (MWL and LHO) and the film-making procedures have been described previously[2]. The correspondance between the designation of the sample and nature of the chemical treatment is the same as in the absorption study[2] and is as follows: MWL= unbleached milled wood lignin; LHO= bleached milled wood lignin; BL= sodium borohydride reduced MWL; PBL= sodium borohydride reduced and hydrogenated (Pd/C) MWL; HOBL= sodium borohydride reduced LHO; HOPBL= sodium borohydride reduced and hydrogenated LHO. The films studied by fluorescence were

the same as used previously[2]. Irradiated samples were exposed for 15 hours to the light emited by a medium-pressure mercury lamp that was filtered by a borosilicate glass filter to eliminate wavelengths below 300 nm.

Corrected fluorescence and excitation spectra were obtained with a Spex Fluorolog fluorimeter equipped with a data station and set up so that the fluorescence emission could be observed at 90° with respect to the excitation light from behind the sample. The excitation and emission slit bandwiths were equal and fixed at 2 nm for the emission and at 1 nm for the excitation fluorescence spectra. The integration time was 0.5 s and the wavelength increment: 0.5 nm. Details on the fluorescence technique are avalaible in Parker's book[3].

The fluorescence quantum yields ($\lambda_{excitation}$= 330 nm) of the lignin samples (Φ_{lignin}) in HPC films were measured relative to quinine sulfate and calculated using the following formula:

$$\Phi_{lignin} = \Phi_{qs} \times A_{lignin} \times (1 - 10^{-Abs\ qs}) / A_{qs} \times (1 - 10^{-Abs\ lignin})$$

where:

A_{lignin} is the area under the emission curve of the lignin-containing film.

A_{qs} is the area under the emission curve of quinine sulfate incorporated in the HPC film.

Φ_{qs} is the fluorescence quantum yield of quinine sulfate in HPC film. It was assumed to be equal to that determined in ethanol. The latter was measured by comparing the emission of quinine sulfate in ethanol and in 1N sulfuric acid (Φ_f= 0.55 [3]), the absorbance of the solutions being adjusted to the same value (0.1).

Abs_{lignin} and Abs_{qs} are the absorbance of the lignin and quinine sulfate-containing films measured at 330 nm; they are, on average, around 0.2.

Both the emission and the absorption of the samples were corrected for the contribution of the HPC matrix.

RESULTS AND DISCUSSION

The fluorescence properties of the various films (MWL, LHO, BL, PBL, HOBL, and HOPBL) before and after irradiation were examined. The spectra are reported in Figures 1-6 and the quantum yields, in Table 1. The spectra presented in the figures are corrected for the contribution of HPC. Three wavelengths were chosen for fluorescence excitation, one in the UV (330 nm) and two in the visible region (400 and 450 nm) to compare with the experiments performed previously with HYP[1]. Excitation spectra were systematically recorded for two emission wavelengths: 420 nm, near the maximum emission, and 520 nm in the yellow region of the spectrum.

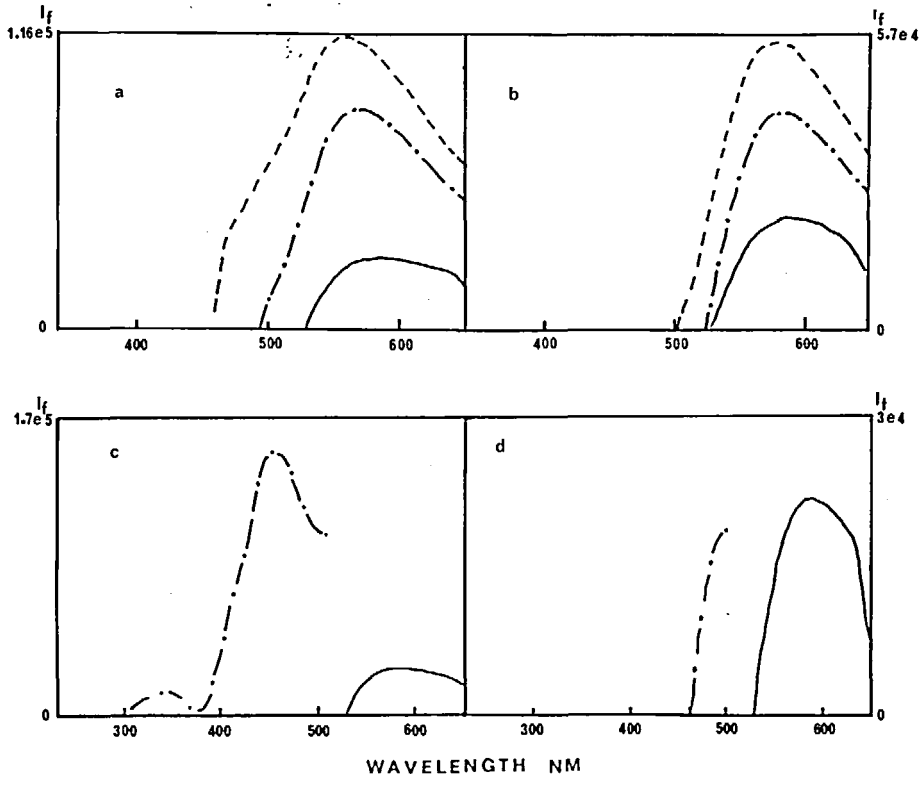

Figure 1: Fluorescence spectra of MWL in HPC films. The emissions are corrected for the contribution of HPC.
(a) and (c) are non-irradiated films; (b) and (d) are films irradiated for 15h
(a) and (b): emission spectra (——): excitation wavelength 330 nm; (– • –): excitation wavelength 400 nm; (- - -): excitation wavelength 450 nm
(c) and (d): excitation spectra (– • –): emission wavelength 520 nm; (- - -): emission wavelength 420 nm; emission spectra (——): excitation wavelength 330 nm

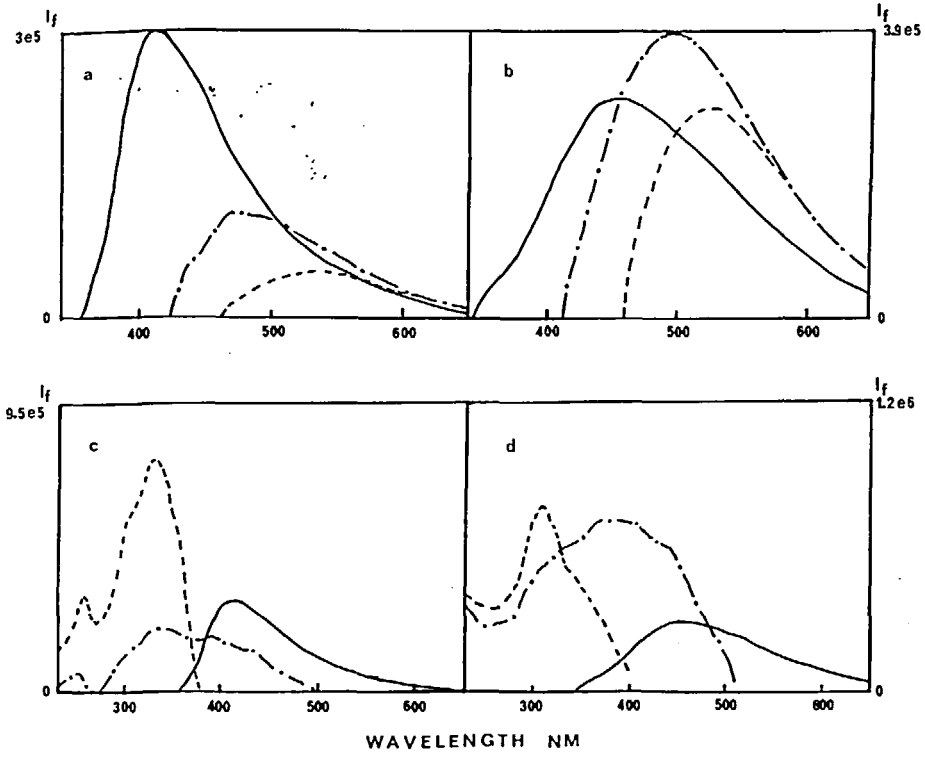

Figure 2: Fluorescence spectra of LHO in HPC films. The emissions are corrected for the contribution of HPC. (a), (b), (c) and (d) have the same legends as in Figure 1.

a) Non-irradiated films

- MWL and LHO

Analysis of the chromophores present in MWL by ionization difference UV spectroscopy[2] showed the presence of significant quantities of phenolic and etherified α-carbonyl and coniferaldehyde chromophores: 13.5 and 4.5/100C_9, respectively, values higher than those found for LHO: 7.2 and 1.1/100 C_9. Lundquist et al[4] have studied the fluorescence properties of several lignin models and milled wood lignin in solution; and the results obtained by the authors are of great value for

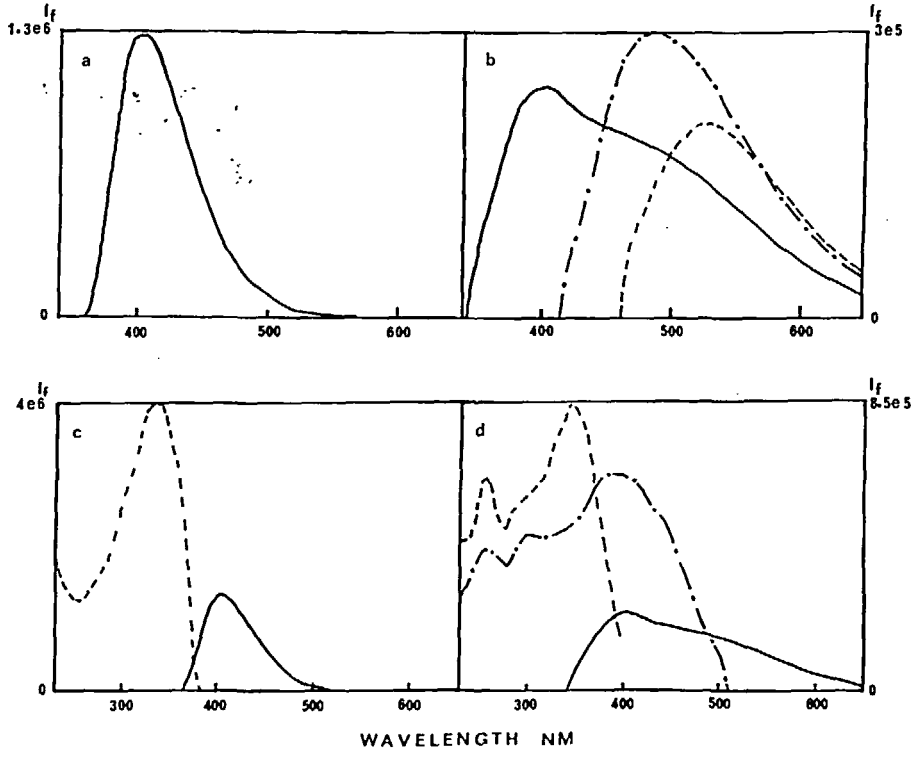

Figure 3: Fluorescence spectra of BL in HPC films. The emission are corrected for the contribution of HPC. (a), (b), (c) and (d) have the same legends as in Figure 1.

the interpretation of the present fluorescence data. Lundquist[4] has shown that lignin models with carbonyl groups emit very weakly. He found an emission maximum at 410-420 nm and an excitation maximum at 310 nm for the α-carbonyl structures, and maxima at 465 nm (emission) and 340 nm (excitation) for the coniferaldehyde molecules. Moreover, open stilbenoid models such as diguaiacylstilbene, emit intensely near 400 nm (excitation maximum: 338 nm)[4]. For phenylcoumarone derivatives, Lundquist[4] observed an increase in emission intensity and a shift to shorter wavelengths (emission maximum: 355 nm, excitation maximum: 310 nm). Aromatic conjugated double bond structures, such as isoeugenol and coniferyl alcohol, display fluorescence emission centered near 340 nm (excitation maxima: 265

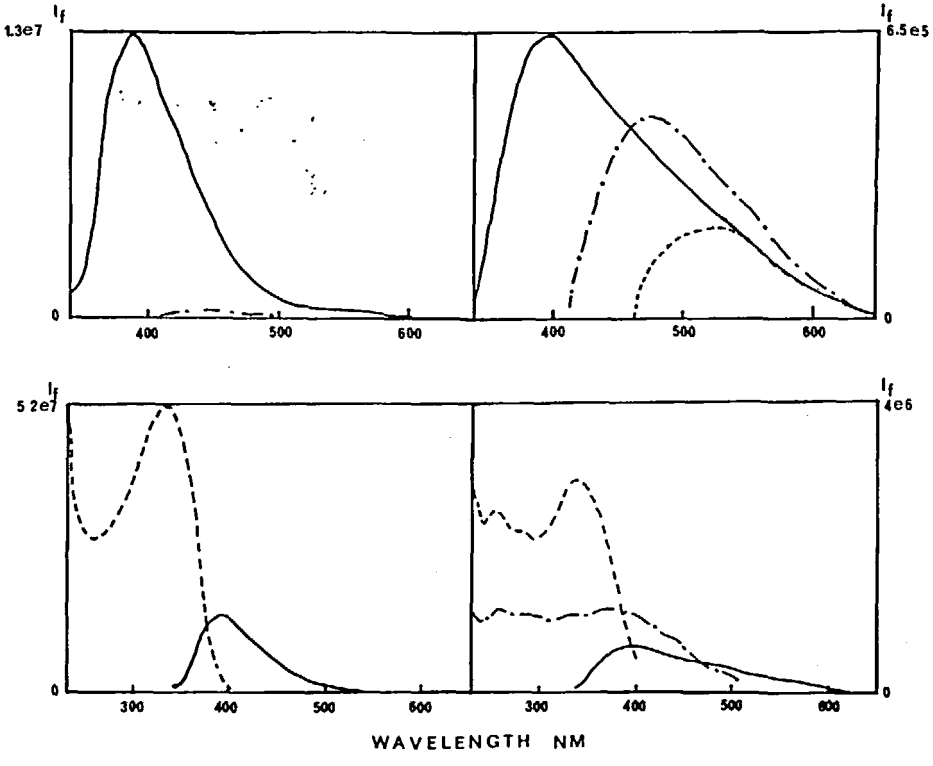

Figure 4: Fluorescence spectra of HOBL in HPC films. The emission are corrected for the contribution of HPC. (a), (b), (c) and (d) have the same legends as in Figure 1.

and 302 nm) with an emission intensity comparable to that of stilbene[4]. A strong bathochromic shift is noted in the case of ferulic acid which presents a maximum emission at 421 nm (excitation maximum: 327 nm). 5,5'-Biphenyl chromophores show an intense bathochromic shift in the emission of fluorescence (emission maximum: 420 nm, excitation maximum: 290 nm) compared to that of the guaiacol group substituted in position 4 by a saturated chain (emission maximum: 315 nm, excitation maximum: 280 nm)[4].

MWL emits very weakly ($\Phi_f = 1.2 \times 10^{-4}$) when the excitation wavelength is set in the UV region (330 nm) (Table 1). The residual emission has a maximum centered at 585 nm (Fig. 1). The emission increases slightly when the material is excited at 400

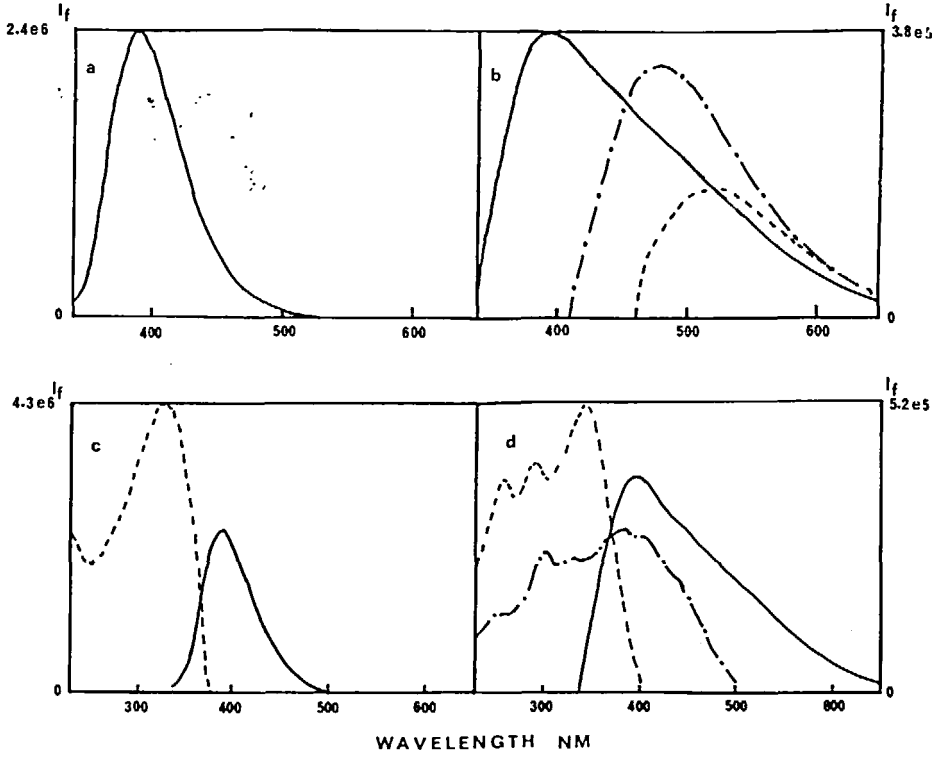

Figure 5: Fluorescence spectra of PBL in HPC films. The emission are corrected for the contribution of HPC. (a), (b), (c) and (d) have the same legends as in Figure 1.

and 450 nm with a maximum situated at 570 and 560 nm, respectively; however the excitation specta (maximum: 450 nm) recorded at 520 nm is very weak. The presence of α-carbonyl, and coniferaldehyde groups, and quinones, which quench the fluorescence, probably accounts for this low emission, quenching being very efficient in the solid where these chromophores in lignin act as an energy sink. The phosphorescence of benzoquinone has been observed[5] near 535 nm, although quinones are normally non-fluorescent because of the $n\pi^*$ character of their lowest excited singlet state. However, when the quinone moiety is included in a condensed aromatic structure with hydroxy substituents hydrogen-bonded with the quinone

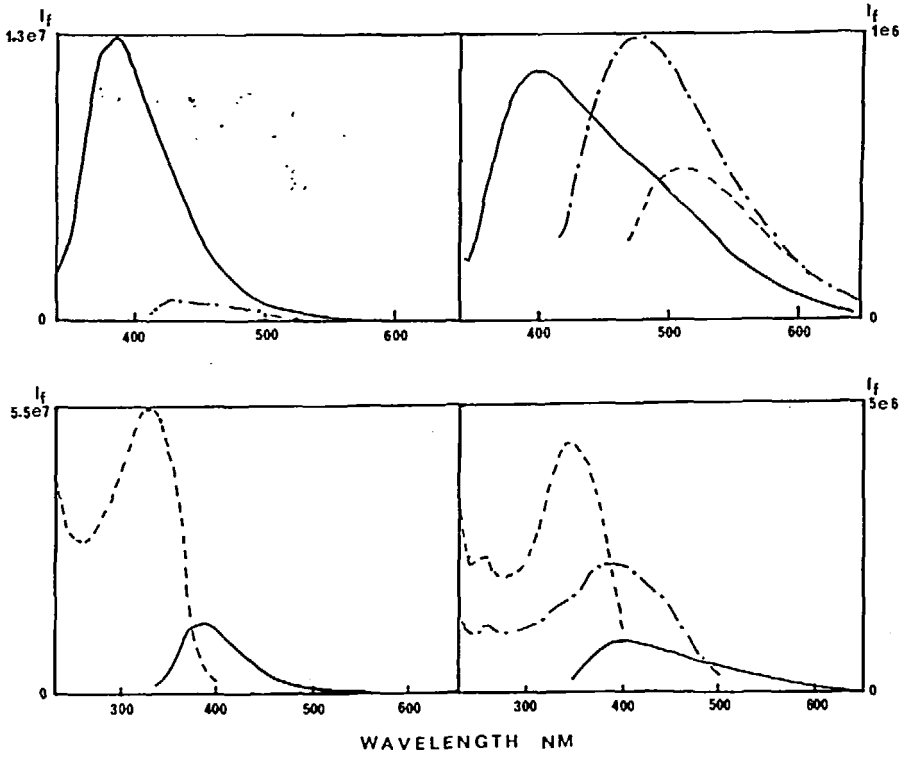

Figure 6: Fluorescence spectra of HOPBL in HPC films. The emission are corrected for the contribution of HPC. (a), (b), (c) and (d) have the same legends as in Figure 1.

oxygen, fluorescence emission is observed[6]. The residual emission observed in MWL is probably partly ascribable to this type of chromophore.

Compared to MWL, peroxide-bleached lignin (LHO) is characterized by a one order of magnitude increase in the emission quantum yield when the excitation is fixed at 330 nm (Table 1). Moreover, the emission is situated near the blue part of the visible region (Fig. 2 and Table 1) (emission maximum: 415 nm). When the excitation wavelengths are set at 400 and 450 nm, the emission maxima (470 and 520 nm respectively) are shifted to shorter wavelengths compared to those for MWL. The excitation spectra are also affected by peroxide-bleaching. The spectrum recorded for an observation wavelength situated at 420 nm presents a maximum at 340 nm, and

Table 1: Fluorescence quantum yields (Φ_F) and relative fluorescence intensities (Q_F) of the various lignins incorporated in HPC films

sample	λexcit. nm	non-irradiated		irradiated	
		Q_F rel.	Φ_F	Q_F rel.	Φ_F
MWL	330	1	0.12 10^{-3}	1	0.11 10^{-3}
	400	4		1.6	
	450	6.6		3.4	
LHO	330	1	2.5 10^{-3}	1	4 10^{-3}
	400	0.4		1.1	
	450	0.18		0.7	
BL	330	1	9.2 10^{-3}	1	5.1 10^{-3}
	400	0		1	
	450	0		0.6	
HOBL	330	1	120 10^{-3}	1	19 10^{-3}
	400	0.02		0.6	
	450	0		0.3	
PBL	330	1	24 10^{-3}	1	11 10^{-3}
	400	0		0.7	
	450	0		0.35	
HOPBL	330	1	150 10^{-3}	1	30 10^{-3}
	400	0.05		1	
	450	0.00		0.4	

the one observed at 520 nm, a maximum at 380 and a shoulder at 440 nm (Fig. 2). These observations are in accordance with a decrease in carbonyl groups in LHO compared to MWL (*vide infra*). According to Lundquist's results[4], the emission at 415 nm is attributable essentially to biphenyl groups and to non-carbonylated conjugated double bond (stilbenes and ferulic acid structures) whereas the long wavelength emission is probably partly due to residual phenolic coniferaldehyde, the presence of which we have shown[2] by ionization difference UV spectroscopy. The differences noted in the emission spectra for the three excitation wavelengths and in the excitation spectra for the two observation wavelengths indicate that lignin in the solid state does not behave as a single chromophore. This is in contrast to Lundquist's results[4] for the fluorescence of spruce MWL in a dioxane-water mixture.

- BL and HOBL

The effect of sodium borohydride reduction of MWL and LHO on fluorescence emission is a complete disappearance of the long-wavelength contribution and an increase in the quantum yield of almost two orders of magnitude (Figures 3 and 4 and Table 1). A maximum is observed at 400 nm for BL (excitation maximum: 340 nm) and at 390 for HOBL (excitation maximum: 310 nm). A slight emission for HOBL is also seen when the film is excited at 400 nm. These results are in accordance with the assignment of the long wavelength fluorescence emission to coniferaldehyde structures and quinones which were reduced by the sodium borohydride. The effect of $NaBH_4$ reduction on lignin fluorescence in solution observed by Lundquist[4] is different from what we have observed for reduced lignin in the solid state. He found the same emission maximum with and without reduction and noted that the emission intensity increased by only one order of magnitude. These differences noted between Lundquist's and our results might be due the lignin material and/or to the solid nature of the matrix. The emission at 390-400 nm is mainly ascribable to biphenyl structures and partly to stilbenoid chromophores[7]. The difference in the wavelength maxima of the emission and excitation spectra of NBHL and HONBHL is probably caused by conformational effects in the biphenyl structures in the solid carbohydrate matrix.

- PBL and HOPBL

The hydrogenation treatment over Pd/C does not greatly modify the shape of the fluorescence spectra compared to those of BL and HOBL, and only slightly increases the fluorescence quantum yields (Figs 6, 7 and Table 1). The emission maxima are situated at 390 in each case and the excitation maxima, at 340 nm for PBL and at 330 nm for HOPBL. These observations are in accordance with the role played by biphenyl structures in the fluorescence emission, the contribution of conjugated double bond chromophores being eliminated in this case.

b) Irradiated films

- MWL and LHO

Irradiation does not affect appreciably the shape and the quantum yields of the fluorescence spectra of MWL (Fig. 1 and Table 1) even though photobleaching and aromatic structure loss have been observed by UV/Vis absorption spectroscopy[2]. This poor sensitivity is probably due to the yellow-colored substances initially present in the material which quench the fluorescence and thus mask the photodegradation process.

The brightness reversion of LHO is revealed in the fluorescence spectra by an intensity increase and a bathochromic shift of the long wavelength emissions, the maxima now being situated at 455, 500, and 525 nm respectively (Fig. 2 and Table 1). The excitation spectra present a maximum at 310 nm, a shoulder at 350 nm (observation: 420 nm) and a broad band centered at 400 nm (observation: 520 nm).

- BL and HOBL

The fluorescence spectra of BL and HOBL display a similar behavior under irradiation (Figures 3-4 and Table 1). A strong contribution is seen in the long wavelength region of the irradiated sample which is absent in the non-irradiated sample. The BL emission spectra display maxima at 400 nm (shoulder: 510 nm), 485 nm and 530 nm. The excitation spectra show maxima at 355 nm (observation: 420 nm) and 400 nm (observation: 520 nm). The values for HOBL are as follows: emission maxima 400, 465 and 520 nm; excitation maxima: 340 nm (observation: 420 nm) and 380 (observation: 520 nm). A decrease of the quantum yields (excitation: 330 nm) is observed after irradiation.

-PBL and HOPBL

The emission and excitation spectra of PBL and HOPBL irradiated films are very similar (Figures 5-6 and Table 1). The maxima are situated i) for emission at 397, 480 (shoulder: 510 nm) and 520 nm for PBL and at 400, 480 (shoulder: 500 nm) and 510 nm for HOPBL ii) for the excitation at 340 nm (observation: 420 nm), 385 nm (shoulder: 440 nm) (observation: 520 nm) for PBL and at 350 nm (observation: 420 nm), 385 nm (shoulder: 440 nm) (observation: 520 nm) for HOPBL. In addition, a decrease in the quantum yields were observed for both samples after irradiation of the films.

One common feature produced by the irradiation of films incorporating lignin, whether it is reduced or non-reduced, hydrogenated or non-hydrogenated, is the formation of species emitting around 500 nm with an excitation maximum centered near 400 nm. These emissions have to be compared to those of non-irradiated LHO films which show fluorescence in this area and which has been partly attributed to coniferaldehyde structure types. Even though UV irradiation of bleached and/or reduced lignin can create aldehydic groups from coniferyl alcohol structures, some other chromophores have to be invoked to explain the emission of the hydrogenated films. Becker[8] has shown that 2,2'-phenolic biphenyls derivatives are oxidized by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to benzofuranyliden-2-ones and then to fluorescent isoxindigo and dibenzonaphthyrone structures absorbing in the 400 nm

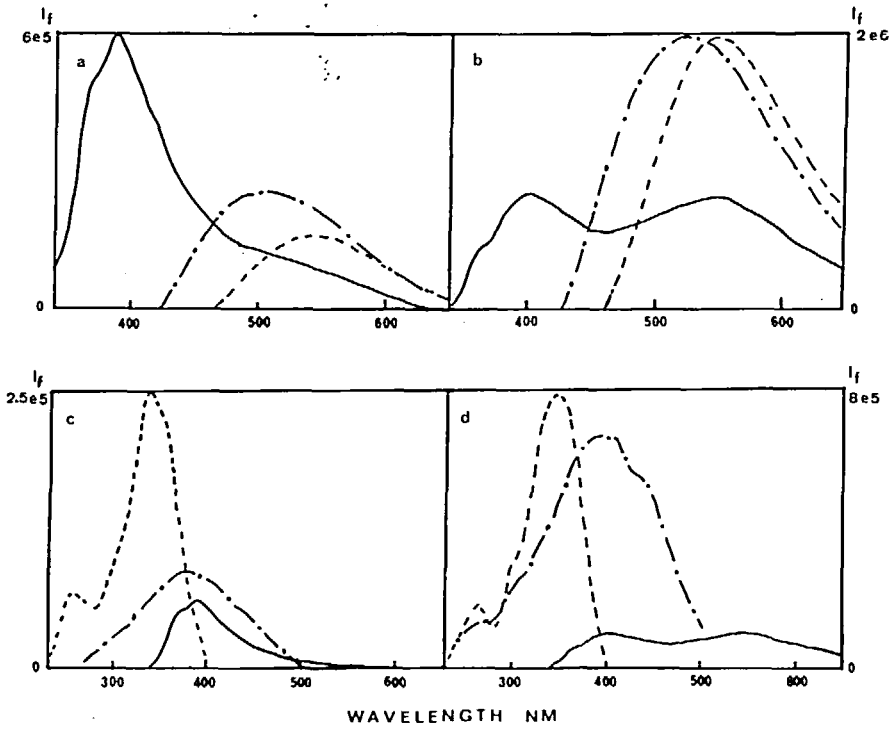

Figure 7: Fluorescence spectra of MWL treated with sodium bisulfite ((a) and (c)) and sodium dithionite ((b) and (d)) in solution and incorporated into HPC films. The emission are corrected for the contribution of HPC; (non-irradiated films).
(a) and (b): emission spectra (——): excitation wavelength 330 nm; (—•—): excitation wavelength 400 nm; (- - -): excitation wavelength 450 nm
(c) and (d): excitation spectra (—•—): emission wavelength 520 nm; (- - -): emission wavelength 420 nm; emission spectra (——): excitation wavelength 330 nm

region and emitting fluorescence at 500 nm. It is possible that some related structures are formed during the photooxidation of 5,5'-phenolic biphenyl groups.

To check the relative importance of coniferaldehyde groups and quinones, which might be formed during irradiation, for the quenching of the emission at 400 nm and to the fluorescence at 500 nm, MWL was treated with sodium dithionite (which is known to reduce quinone in hydroquinones very efficiently) and with sodium bisulfite (which readily reacts with α-carbonyl groups and coniferaldehyde chromophores). The treated lignins were incorporated into HPC films and the fluorescence spectra were recorded. The curves are presented in Figure 7. A stronger effect of bisulfite compare to dithionite is observed, underlining the important role of α-carbonyl groups and coniferaldehyde structures in the quenching of fluorescence at 400 nm. Nevertheless, the emission at 500 nm still remains (excitation maximum near 400 nm) and may perhaps originate from structures of the same type as those involved after oxidation of the phenolic biphenyl entities by DDQ. The fluorecence experiments indicate a parallel between the colored structures formed by light and those existing in softwood native lignin which is formed by oxidation of coniferyl alcohol in biochemical processes.

CONCLUSION

The use of HPC films incorporating milled wood lignin before and after various chemical treatments in homogeneous solution has been shown to be very useful for studying the brightness reversion of high-yield pulps, particularly by fluorescence. The contribution of the carbohydrate matrix was eliminated and the quality of the films allowed the measurement of emission quantum yields, as previously was possible only for solutions. It was observed that fluorescence emission of lignin at 400 nm, mainly caused by biphenyl groups, is efficiently quenched by chromophores containing keto entities (α-carbonyl groups, coniferaldehyde structures and quinones). Irradiation of the various films induces a decrease of emission in the blue part of the spectra (400 nm) and an increase in the long-wavelength region (500 nm). In addition to the photochemical generation of coniferaldehyde groups emitting around 500 nm, the involvement of other chromophores formed by photooxidation of phenolic biphenyls appears to be a possible explanation for the emission of hydrogenated films (PBL and HOPBL) at 500 nm after UV irradiation. Further work is underway in this laboratory to verify this hypothesis.

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