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LIGHT-INDUCED YELLOWING OF MECHANICAL AND ULTRA-HIGH YIELD PULPS. PART 1. EFFECT OF METHYLATION, NaBH_4 REDUCTION AND ASCORBIC ACID ON CHROMOPHORE FORMATION¹

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ABSTRACT

Absorption difference spectra of bleached TMP irradiated with near-uv light exhibited two apparent absorption maxima at ≈ 410 nm and 330 nm. Experiments with borohydride-reduced pulp suggest that photochemical formation of aromatic carbonyls contributes to the $\lambda = 330$ nm peak. Chromophore formation followed an apparently first-order rate law, and the rate was unaffected by methylation of phenolic hydroxyl groups, or by exhaustive reduction of carbonyl groups with NaBH_4 . Methylation of phenolic hydroxyl, while having no effect on the kinetics of chromophore formation, did decrease the maximum change in absorption coefficient, ΔK^∞ . Treatment of bleached TMP with ascorbic acid slowed light-induced yellowing substantially; significant yellowing occurred only after 2 hours. Light-induced bleaching of a chromophore with $\lambda_{\text{max}} \approx 350$ nm, possibly a stilbene, occurred during the first 90 minutes of irradiation.

INTRODUCTION

Mechanical and ultra high-yield pulp can be produced commercially with ISO brightness above 80%. However, the rapid light-induced yellowing of this brightened pulp restricts its use to short-life, low-value paper products. If this high brightness could be stabilised, bleached mechanical pulp could replace some

of the bleached chemical pulp used in high-value grades of printing and writing papers, resulting in significant furnish-cost savings. To realise this stabilisation, an understanding of the underlying chemistry must be achieved.

Light-induced yellowing of wood pulps is commonly monitored by brightness measurements (reflectance at 457 nm) made before and after irradiation, and expressed as post-colour number (PC, equation 1)². $F(R_\infty)$ (equation 1a) is the familiar Kubelka-Munk remission function, where K and S are the absorption and scattering coefficients, respectively, and R_∞ is the reflectance of a homogeneous, optically thick sheet.

$$PC = 100 \left[F(R_\infty)_{after} - F(R_\infty)_{before} \right] \quad (1)$$

$$F(R_\infty) = \frac{K}{S} = \frac{(1 - R_\infty)^2}{2R_\infty} \quad (1a)$$

PC number offers little information regarding the chemical changes which occur during light-induced yellowing. The absorption maxima of the chromophores formed or destroyed in the yellowing reaction occur at $300 \text{ nm} < \lambda < 500 \text{ nm}$, wavelengths which are not probed by a simple brightness measurement. Further, since light-induced yellowing is a surface phenomenon, the distribution of chromophores after irradiation is not homogeneous, and equation 1a is no longer valid. Under such conditions, PC number depends not only on changes in the total number of chromophores, but is also a function of the distribution of chromophores within the sheet. Thus, PC number cannot measure the kinetics of chromophore formation.

These problems can be overcome by measuring the diffuse reflectance spectra of low-basis weight ($\approx 10 \text{ g/m}^2$) sheets. Under our irradiation conditions, these sheets maintain the homogeneous concentration of absorbers which is required for Kubelka-Munk analysis; thus, changes in the absorption coefficient caused by irradiation can be determined. Since the absorption coefficient is proportional to chromophore concentration, rates of chromophore formation can be determined.

Light-induced yellowing of mechanical pulp is attributed primarily to photo-oxidation of lignin³. Most mechanisms propose that aromatic ketones absorb near-uv light, and subsequently sensitise oxidation of the phenolic hydroxyl group^{4,5}. The presence of paramagnetic signals in irradiated milled-wood lignin or wood implicates the phenoxy radical in the mechanism^{6,7}. In this study, we used absorption difference spectroscopy to examine three aspects of this generalised mechanism. The role of phenolic hydroxyl groups was assessed by methylating these groups with dimethyl sulphate, and the importance of carbonyl groups was studied by reducing bleached pulp with sodium borohydride. The effect of ascorbic acid, an efficient radical scavenger, was also assessed.

EXPERIMENTAL

Washed and chelated black spruce TMP was bleached with 4% alkaline hydrogen peroxide at 60 °C for 2 hours at 20% consistency, giving pulp with an ISO brightness of 75%.

Phenolic hydroxyl groups were methylated by treating the pulp (10 g OD in 600 mL of equal volume water/ethanol/dimethoxyethane) with dimethyl sulphate, as previously described⁸. The reaction time was 7½ hours. The extent of methylation was controlled by the total amount of dimethyl sulphate added. Under these conditions, 90 mL dimethyl sulphate gave a methoxyl content of 7.23% and 125 mL gave a methoxyl content of 8.13%. Methoxyl contents were determined by Scharzwkopf Microanalytical Laboratories, Woodside, New York.

Bleached TMP was reduced by treatment with a 1% charge (on OD pulp) of NaBH₄ as a 10% aqueous solution. Oxygen was removed by continuously bubbling N₂ through the suspension. The reduction was monitored by periodically removing a sample and determining the absorption spectrum (below). The absorption band with $\lambda_{\text{max}} \approx 330$ nm decreased steadily up to 45 hours reaction time, then remained constant. These exhaustively reduced samples were used for photochemical experiments.

Phenolic hydroxyl contents were determined by aminolysis of phenolic acetates, as described by Gellerstedt and Lindfors⁹. Briefly, pulp samples were

acetylated using acetic anhydride, then deacetylated using pyrrolidine as the base. Under these conditions, phenolic acetates react much faster than aliphatic acetates. Thus, plots of N-acetyl pyrrolidine concentration vs time were linear, and the intercept of the plot gave the amount of N-acetyl pyrrolidine liberated from phenolic acetates.

Samples treated with ascorbic acid were prepared by soaking low-basis weight sheets in a solution of 5% ascorbic acid in 80/20 water/methanol overnight. Since ascorbic acid is easily oxidized in solution by dissolved oxygen, the solvent was deaerated by bubbling with nitrogen before preparing the solutions, and the samples were soaked under a nitrogen atmosphere. After soaking, the solution was carefully removed with a pipette, and residual solution was absorbed with a kraft blotter. The ascorbic-acid impregnated sheets were then dried under nitrogen.

Low basis-weight sheets were prepared by diluting ~ 0.6 g of pulp to ~ 0.4 percent consistency in a British sheet machine, then filtering the suspension onto a 74 μm Teflon mesh placed over the wire screen of the sheet machine. The mesh and the sheet were placed on a kraft blotter mesh side down, a Whatman filter paper (18.5 cm diameter) was placed on top, and the sheet was pressed manually with three or four passes of a couch roll. After peeling the Teflon mesh from the sheet, the sheet and filter paper were placed sheet-side down on a stainless steel plate, and were pressed for five minutes at 0.34 MPa. The sheets were dried under ambient conditions and cut into squares ~ 5 cm x 5 cm. The basis weight was determined by accurate measurement of area and mass.

The sheets were irradiated in a Rayonet RPR-100 merry-go-round photochemical reactor (Southern New England Ultraviolet Co., Branford, CT), with the carousel modified to hold a maximum of 18 sheets. The lamps contained a blacklight phosphor, which has a roughly Gaussian spectral distribution between 300 and 400 nm, and maximum output at \approx 350 nm. According to the

manufacturer, these lamps provide 24 W of energy, with an intensity at the centre of the reactor of 9.2 mW/cm².

The uv-visible absorption spectra were calculated from diffuse reflectance measurements using the following equations of Kubelka and Munk, as well as the remission function (equation 1a)¹⁰:

$$R_{\infty} + \frac{1}{R_{\infty}} = \frac{R_0 - R_w + w}{wR_0} + R_w \quad (2)$$

$$S = \frac{1}{b} \left[\frac{R_{\infty}}{1 - R_{\infty}^2} \right] \ln \left[R_{\infty} \left[\frac{1 - R_{\infty} R_0}{R_{\infty} - R_0} \right] \right] \quad (3)$$

K and S are, respectively, the absorption and scattering coefficients, R_{∞} is the reflectance of an optically thick sheet, R_w is the reflectance of an optically thin sheet over a white background of known reflectance w , R_0 is the reflectance of the optically thin sheet over a black, non-reflecting background, and b is the basis weight of the sheet. Reflectance measurements were made at 2 nm intervals using a Philips PU8800 uv-visible spectrophotometer equipped with an integrating sphere. An IBM XT-286 computer was used to collect data from the spectrophotometer, and to do the calculations to determine K. The black background was a Technidyne black body, while the white background was a 30 g disc of Halon, pressed at 28 MPa against a ground glass plate to give a matte surface. The matte surface minimises errors in R_w which occur because specular reflection from the backing is diffused by the sample, and therefore is not trapped by the gloss trap.

Averages of four to six samples were taken to account for any formation defects which occur in these sheets. The effect of each of the treatments was judged by comparison with a simultaneously irradiated, untreated bleached TMP sample.

Non-linear parametric fits to plots of change in absorption coefficient versus time were done using the Marquardt algorithm¹¹.

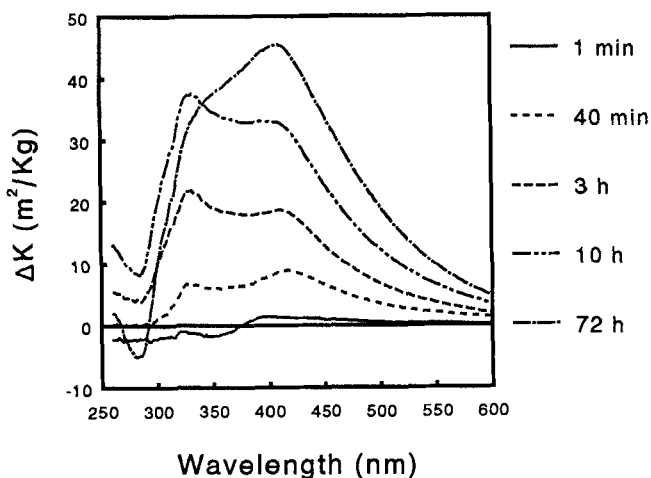


FIGURE 1: Absorption difference spectra of bleached TMP after various irradiation times.

RESULTS AND DISCUSSION

SPECTRA

Bleached TMP

Figure 1 shows the absorption difference spectra (ΔK vs wavelength) observed for bleached TMP at various irradiation times. A small loss of absorption (bleaching) occurred after one minute irradiation for wavelengths (λ) less than 370 nm, with an apparent minimum at ~ 350 nm. The absorption coefficient increased for $\lambda > 370$ nm. At longer times ΔK was positive and increasing, with two apparent maxima (λ_{\max}) at ~ 330 nm and 410 nm.

The absorption coefficient at any wavelength is given by equation 4¹², where ϵ and C are, respectively, the extinction coefficient and the concentration of species i .

$$K(\lambda) = \sum_i 2\epsilon_i(\lambda)C_i \quad (4)$$

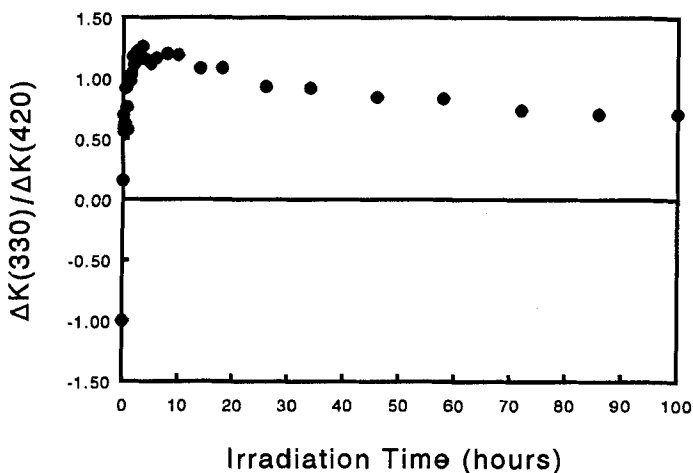


FIGURE 2: Ratio of the change in absorption coefficient at 330 nm to the change in absorption coefficient at 420 nm, as a function of irradiation time.

For the simplest case where a single precursor P gives one chromophore C , the change in absorption coefficient at time t is given by equation 5; application of the mass balance condition of equation 6 gives equation 7.

If the spectral changes in figure 1 were due to the formation of only one chromophore, then $\Delta K(\lambda_i)/\Delta K(\lambda_j)$, the ratio of the changes in absorption coefficient at any two wavelengths i and j , would be equivalent to $\Delta\epsilon(i)/\Delta\epsilon(j)$, the

$$\Delta K(t, \lambda) = 2(\epsilon_C(\lambda) C(t) + \epsilon_P(\lambda) P(t) - \epsilon_P(\lambda) P_0) \quad (5)$$

$$P_0 = P(t) + C(t) \quad (6)$$

$$\Delta K(t, \lambda) = (\epsilon_C(\lambda) - \epsilon_P(\lambda)) C(t) = \Delta\epsilon(\lambda) C(t) \quad (7)$$

ratio of the change in extinction coefficients, a constant independent of irradiation time. The ratio $\Delta K(330)/\Delta K(420)$ (figure 2) increased rapidly during the first three hours of irradiation to a value slightly greater than one, remained fairly

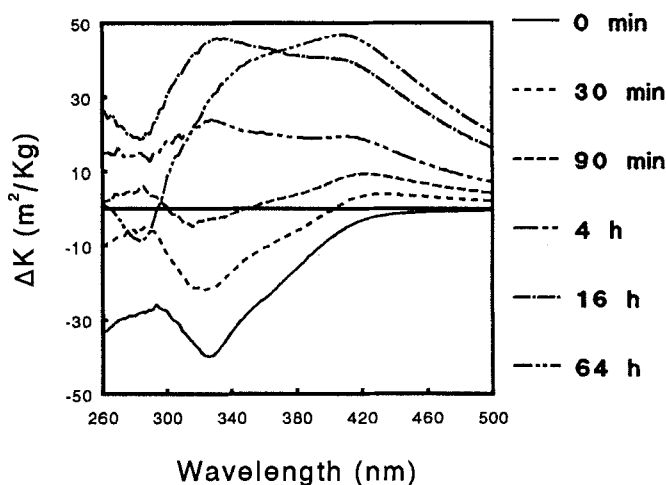


FIGURE 3: Absorption difference spectra for bleached TMP which was exhaustively reduced with sodium borohydride before irradiation.

constant until about 10 hours irradiation, then declined slowly. Thus, the changes observed here reflect the independent¹³ formation of at least two different chromophores.

Effect of Borohydride Reduction

Figure 3 shows the difference spectra (relative to unirradiated bleached TMP) from bleached TMP reduced with NaBH_4 . Exhaustive borohydride reduction caused a loss in absorption with $\lambda_{\text{max}} \approx 330$ nm. We attribute this change to the loss of aromatic carbonyl groups, since the absorption maxima of aliphatic carbonyls occur at wavelengths well below 300 nm. The tail of the absorption band for the aromatic ketones extended to wavelengths greater than 400 nm, *i.e.*, into the visible region. Thus, the characteristic yellow cast of bleached TMP, relative to bleached kraft pulp of similar brightness, is caused at least partly by the aromatic carbonyls in lignin.

When borohydride-reduced pulp was irradiated, the absorption at $300 \text{ nm} < \lambda < 400 \text{ nm}$ increased rapidly. Borohydride reduction of the irradiated sample reversed these absorptions, giving difference spectra identical to that observed for reduction of unirradiated bleached TMP. For irradiation times of four hours and longer, the difference spectra of reduced pulp were identical to those of simultaneously irradiated, unreduced pulp. We interpret these spectral changes as evidence that benzyl alcohol groups in lignin can be photooxidized to aromatic ketone groups. This is exactly opposite to the behaviour of spruce milled-wood lignin in solution; Lin and Kringstad reported that the absorptions due to aromatic ketones are bleached, both in the presence and the absence of oxygen⁴.

In a recent ³¹P NMR study, Lebo *et al.*¹⁴ found the first direct evidence supporting the proposition that quinones are formed in light-induced yellowing. In our experiments, the absorption at $\lambda > 400 \text{ nm}$ was completely eliminated after treatment with sodium borohydride, for pulps irradiated for less than four hours. This is consistent with identification of the chromophores responsible for this absorption as quinones. For pulps irradiated about four hours or longer, these reagents removed most, but not all, of the absorption at $\lambda > 400 \text{ nm}$. This indicates that other chromophores, not reducible by sodium borohydride, are formed at longer irradiation times.

Effect of Ascorbic Acid

Figure 4 shows the difference spectra for irradiated bleached TMP samples which were soaked in solutions of 5% ascorbic acid in an 80/20 volume mixture of water and methanol. A striking aspect of these spectra is the photochemical bleaching which occurred for $300 < \lambda < 400 \text{ nm}$ during the first two hours of irradiation. The most prominent feature which was bleached had $\lambda_{\text{max}} = 350 \text{ nm}$, but a smaller peak with $\lambda_{\text{max}} = 315 \text{ nm}$ was also bleached. This photobleaching was also observed for bleached, borohydride-reduced pulps treated with ascorbic acid.

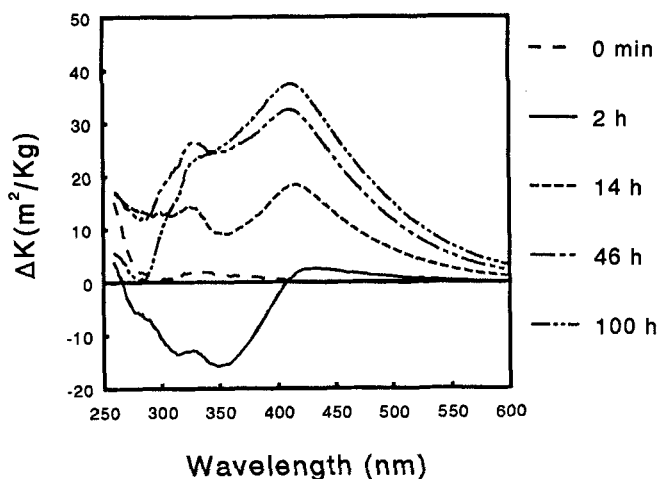
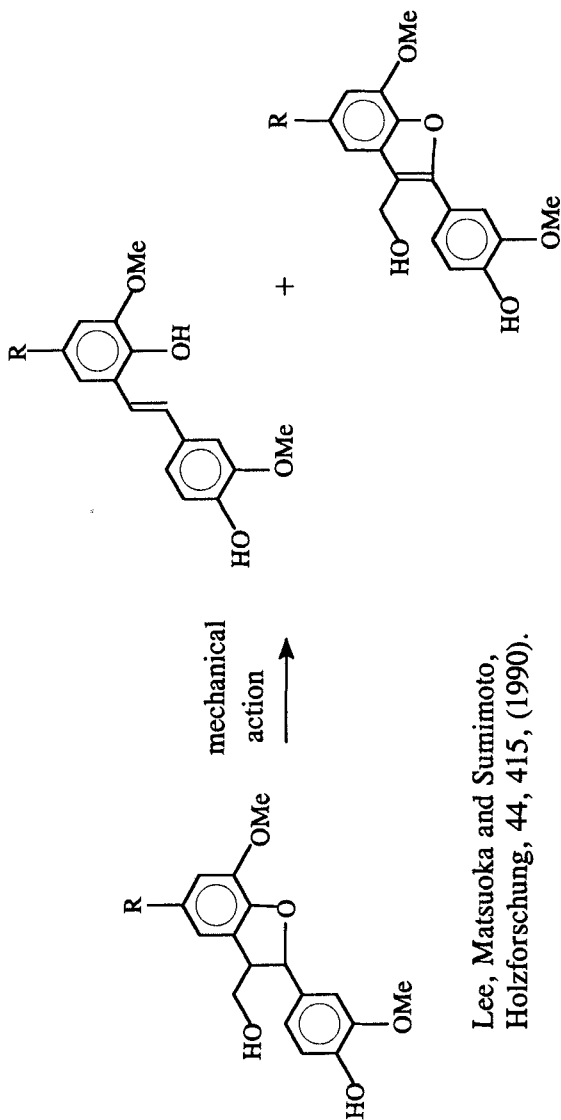


FIGURE 4: Absorption difference spectra of bleached TMP treated with ascorbic acid, after various irradiation times.

Light absorption at $300 \text{ nm} < \lambda < 400 \text{ nm}$ in bleached TMP is usually attributed to aromatic ketones; this photochemical bleaching suggests that at least one other chromophore, inert to borohydride but destroyed photochemically in the presence of ascorbic acid, also absorbs in this region. The identity of this chromophore is not known - we suggest stilbene as a good candidate. Phenylcoumaran lignin model compounds, when milled or refined, give small yields of stilbene chromophores (figure 5)¹⁵. Stilbene models bearing a phenolic group have a solution uv-absorption maximum at $\approx 330 \text{ nm}$ ¹⁶; the well-known red-shifting of electronic absorption in the solid state could easily shift the absorption maxima of such stilbene chromophores to 350 nm in solid lignin. Finally, this proposition would also explain why borohydride reduction of milled-wood lignin solutions gives only partial stability to photochemical yellowing, while catalytic hydrogenation gives complete stability¹⁷. In further work, we plan to explore the role such a chromophore might have in light-induced yellowing.



Lee, Matsuoka and Sumimoto,
 Holzforschung, 44, 415, (1990).

FIGURE 5: Ball-milling or refining phenylcoumaran model compounds gives small yields of stilbenes and phenylcoumarones¹⁵.

	Bleached TMP	Bleached TMP treated to different methoxyl contents with dimethyl sulphate	
Methoxyl Content (% by mass)	4.44 %	7.23 %	8.13 %
PhOH/C ₉	0.128 ± 0.002	0.039 ± 0.004	0.0091 ± 0.0008

Ascorbic acid inhibited the rapid increase in absorption at 330 nm. For pulps not treated with ascorbic acid, this absorption eventually became larger than that at 410 nm, and then smaller again at long irradiation (figures 1 and 3). This did not occur in pulp treated with ascorbic acid; the peak at 410 nm was always the largest peak in the spectrum (figure 4). This suggests that the chromophore with $\lambda_{\max} \approx 350$ nm is removed permanently by photobleaching.

KINETICS

Effect of Methylation

Phenolic hydroxyl contents were determined using the technique of Gellerstedt and Lindfors⁹, and are listed in Table 1 along with methoxyl contents. Our value of 0.128 phenolic hydroxyl groups per C₉ unit for bleached black spruce TMP is about 30% higher than the value of 0.10 reported by Goring and Yang for black spruce wood¹⁸. We attribute this difference to the formation of phenolic hydroxyl groups by the mechanical action of refining, and by peroxide bleaching.

If only phenolic hydroxyl groups are methylated, the methoxyl content of bleached TMP should increase from 4.44% to about 4.9%. The data in Table 1

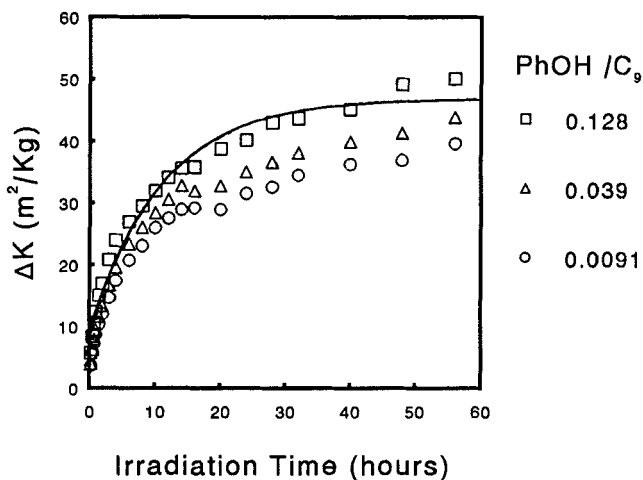


FIGURE 6: Change in absorption coefficient at 420 nm for bleached TMP and bleached, methylated TMP. Solid line is the best fit to equation 8 obtained for bleached TMP, PhOH content = 0.128/ C_9 . Fits to the other two data sets are omitted for clarity.

indicate that phenolic hydroxyl groups are still present at methoxyl contents far above 4.9%. Clearly, treatment of mechanical pulps with dimethyl sulphate methylates other hydroxyl groups simultaneously with phenolic hydroxyl groups; thus, methoxyl content is a poor indicator of the extent of methylation of phenolic hydroxyl groups.

The spectral changes observed for bleached TMP treated with dimethyl sulphate were the same as those observed for bleached TMP, except that the absorption band with $\lambda_{\max} \approx 330$ nm formed more slowly during the early stages of the reaction. This may indicate that phenolic hydroxyl groups are implicated in the formation of this band.

The time dependence of ΔK at 420 nm for methylated and unmethylated bleached TMP (figure 6) is representative of behaviour observed at all wavelengths. The rate curves could be fit by an exponential function (equation 8) with three non-linear parameters B_1 , B_2 , and B_3 .

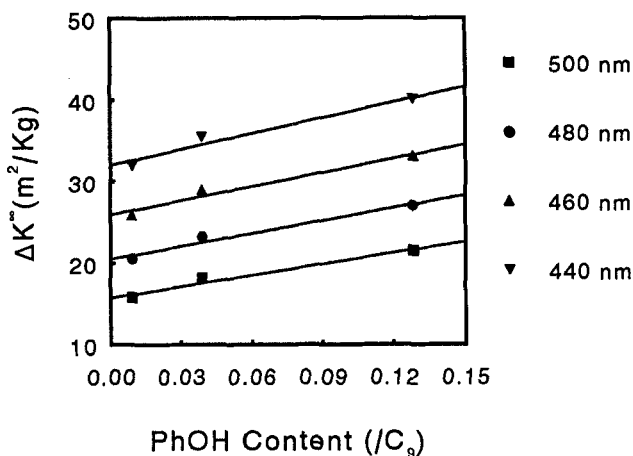


FIGURE 7: ΔK^∞ vs phenolic hydroxyl content at some representative wavelengths.

$$\Delta K(t) = B_1 + B_2(1 - e^{B_3 t}) \quad (8)$$

$$\Delta K(t = \infty) = \Delta K^\infty = B_1 + B_2 \quad (8a)$$

Kinetic aspects of these curves will be discussed later; here we point out that the limiting value of ΔK , ΔK^∞ , decreased modestly with decreasing phenolic hydroxyl content, in agreement with earlier studies^{19,20}. From fits to equation 8, we were able to estimate ΔK^∞ (equation 8a). Plots of ΔK^∞ versus phenolic hydroxyl content were linear at all wavelengths, and the intercepts on the ΔK^∞ axis were non-zero (figure 7). We interpret the intercept as the increase in absorption coefficient which would occur if all phenolic hydroxyl groups were blocked. As the data in Table 2 show, at least 75% of the total change in absorption coefficient arises from groups other than the phenolic hydroxyl group. Thus, if the phenoxy radical is an the important intermediate in the yellowing reaction, then it must be formed from non-phenolic structures in lignin, as well as from phenolic hydroxyl.

λ/nm	ΔK^∞ * (bleached TMP)	ΔK_0^∞ **	$\Delta K_0^\infty/\Delta K^\infty$
500	21.5	15.8	0.73
490	24.3	18.1	0.75
480	27.0	20.5	0.76
470	30.0	23.2	0.77
460	33.1	26.0	0.78
450	36.5	28.9	0.79
440	40.1	32.0	0.80
430	43.6	35.1	0.80
420	46.8	37.9	0.81
410	49.0	39.9	0.81
400	49.8	40.7	0.82
390	50.1	41.1	0.82
380	50.1	41.2	0.82
370	50.5	41.6	0.82
360	50.2	41.6	0.82
350	49.8	40.8	0.82
340	49.9	41.5	0.83
330	47.2	39.4	0.83
320	40.5	33.3	0.82
310	31.2	24.4	0.78
300	22.8	16.8	0.74

* Taken from fits of $\Delta K(t)$ vs time for bleached TMP to equation 5.
 ** Intercept of linear fits to plots of ΔK^∞ versus PhOH content (figure 7).

A likely non-phenolic source of the phenoxy radical is the light-induced cleavage of the aryl-ether bond in phenacyl-aryl ether groups (figure 8)^{21,22}. The upper limit for phenacyl-aryl ethers in lignin is 0.07/C₉ (aromatic ketone content of lignin is estimated at 0.07/C₉ unit²³), and we have measured 0.13 phenolic hydroxyl groups /C₉ for bleached, black spruce TMP. If phenolic hydroxyls and phenacyl-aryl ethers were the only precursors to chromophores, blocking the

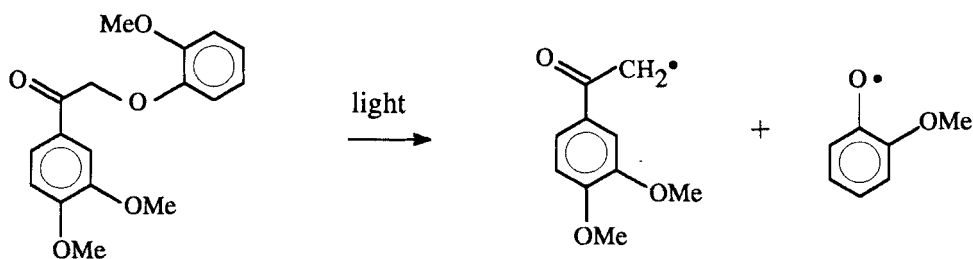


FIGURE 8: Light-induced cleavage of the aryl-ether bond in a phenacyl aryl-ether lignin model compound.

phenolic hydroxyls should reduce ΔK^∞ of $0.13/(0.13 + 0.07) \times 100 \sim 65\%$, rather than the approximately 25% observed (Table 2).

We offer four suggestions that might account for this discrepancy: 1) Benzyl aryl-ether groups might provide an additional source of phenoxy radicals. Models for the benzyl aryl-ether linkage in lignin give photoproducts consistent with phenoxy radical intermediates²⁴. These model compounds absorb light of shorter wavelength ($\lambda < 295$ nm) than is present in daylight, but the complex structure of lignin may extend the tail of the absorption of such groups sufficiently to allow light of wavelengths > 300 nm to initiate formation of phenoxy radicals. 2) The benzyl alcohol function of α -OH, β -O-4 structures is photooxidised to carbonyl, generating new phenacyl aryl-ether groups. 3) Ketone excited states may also sensitise degradation and colour formation from the polysaccharides in the pulp. 4) The oxidation of the phenoxy radical to a chromophore is a propagation step of a radical chain reaction; hence, each phenoxy radical can effect the formation of more than one chromophore group.

Kinetics of Chromophore Formation

Chromophore formation in bleached TMP, or in methylated bleached TMP, followed an apparently first-order rate law (figure 6, equation 8). Values of B_3 obtained from fits to equation 8, which might be regarded as a rate

TABLE 3

Parameter B_3^* Obtained from Fits of ΔK vs time to Equation 8 for Methylated Bleached TMP

PhOH Content /C ₀	0.128 (Bleached TMP)	0.039	0.0091
λ /nm	B_3 /hr ⁻¹	B_3 /hr ⁻¹	B_3 /hr ⁻¹
500	0.064	0.066	0.068
490	0.060	0.064	0.063
480	0.063	0.067	0.066
470	0.066	0.070	0.069
460	0.070	0.074	0.073
450	0.074	0.078	0.077
440	0.079	0.084	0.082
430	0.086	0.091	0.088
420	0.092	0.098	0.095
410	0.10	0.11	0.10
400	0.11	0.12	0.12
390	0.12	0.13	0.13
380	0.13	0.15	0.14
370	0.14	0.17	0.16
360	0.15	0.19	0.18
350	0.18	0.21	0.20
340	0.20	0.23	0.21
330	0.24	0.27	0.24
320	0.27	0.31	0.28
310	0.32	0.35	0.32
300	0.33	0.39	0.37

* Uncertainty in the rate constants is $\approx 10\%$

parameter, were wavelength dependent. This wavelength dependence is probably a manifestation of the complexity of the reactions leading to chromophore formation, and it precludes interpretation of B_3 as the rate constant for a specific reaction. Nonetheless, some inferences regarding the effect of alkylation can be made. At any wavelength, the values of B_3 were unaffected by phenolic hydroxyl content (Table 3). The main effect of alkylation appears to be removal of latent chromophores; there is no fundamental alteration of the reaction mechanism.

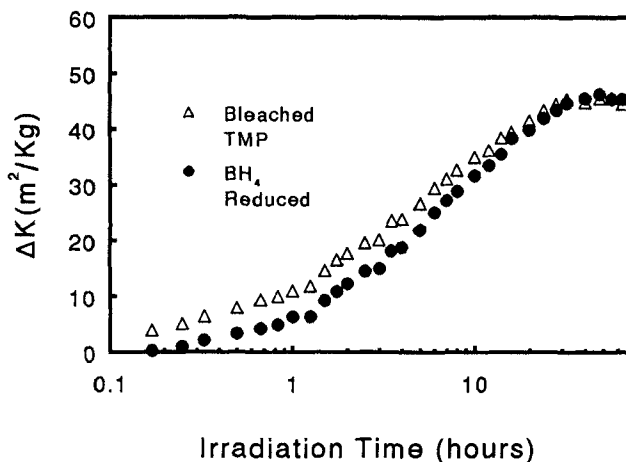


FIGURE 9: Change in absorption coefficient at 420 nm versus log time for bleached TMP, and bleached TMP reduced with sodium borohydride.

As other authors^{19,20,25,26} have also noted, reduction with borohydride had no significant effect on the rate of chromophore formation (figure 9). Thus, Ek *et al.*²⁶ suggest that aromatic ketones may not be important in the mechanism. We feel that this conclusion is premature, since difference spectra of borohydride reduced pulp (figure 3) suggest that aromatic ketones are rapidly formed by irradiation. Moreover, Tschirmer and Dence²⁰ report that reduction of unbleached Norway spruce TMP, followed by alkylation of phenolic groups with propylene oxide, gives pulp with brightness stability comparable to fully-bleached hardwood-kraft pulp. This suggests that phenolic groups are involved in the photochemical formation of aromatic carbonyls.

In agreement with earlier reports²⁷⁻²⁹, ascorbic acid significantly slowed light-induced yellowing. Plots of ΔK (420 nm) against log time (figure 10) showed that, for about the first two hours of irradiation, almost no chromophore formation occurred in bleached TMP treated with ascorbic acid. After this induction period, chromophore formation increased, and appeared to occur at

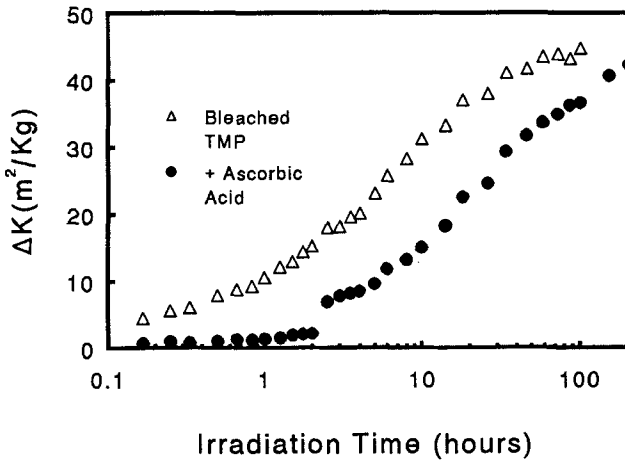


FIGURE 10: Change in absorption coefficient at 420 nm versus log time for bleached TMP, and bleached TMP treated with ascorbic acid.

about the same rate as in untreated pulps. The value of ΔK^∞ was about the same as for untreated bleached TMP, but about twice as much irradiation time was required to reach this value.

This behaviour is consistent with a predominately radical mechanism for photochemical yellowing, and an anti-oxidant role for ascorbic acid. In biological systems, ascorbic acid inhibits lipid peroxidation both by scavenging hydroperoxyl radicals, and by regenerating α -tocopherol (vitamin E, an alkyl-substituted phenol) from the α -tocopheryl radical³⁰. By analogy, it is reasonable that ascorbic acid scavenges phenoxyl radicals generated in irradiated pulp and becomes oxidised. When the ascorbic acid has been consumed, the radical yellowing reactions resume.

CONCLUDING REMARKS

Our study of the light-induced changes in the uv-visible spectra of bleached TMP has revealed the complexity of the photochemistry of mechanical

pulp, and perhaps poses more questions that it answers. If aromatic carbonyls are formed photochemically, then borohydride reduction experiments alone cannot resolve their role in light-induced yellowing. Our analysis suggests that homolytic cleavage of the β -O-4 aryl ether bond is an important reaction, since only 25% of the increase in absorption coefficient can be linked directly to phenolic hydroxyl. Finally, photochemical bleaching caused by ascorbic acid indicates the presence of another chromophore, possibly stilbene, which absorbs in the near-uv region, and raises the question of how its photochemistry contributes to light-induced yellowing.

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