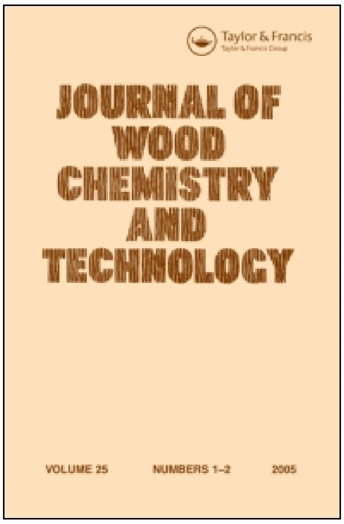


Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

PHOTOYELLOWING OF UNTREATED AND ACETYLATED ASPEN CHEMITHERMOMECHANICAL PULP UNDER ARGON, AMBIENT, AND OXYGEN ATMOSPHERES

Magnus Paulsson[a]; Lucian A. Lucia[b]; Arthur J. Ragauskas[b]; Cang Li[b]
[a] Department of Forest Products and Chemical Engineering, Chalmers University of Technology, Göteborg, Sweden [b] Institute of Paper Science and Technology, Atlanta, GA, U.S.A.

To cite this Article Paulsson, Magnus , Lucia, Lucian A. , Ragauskas, Arthur J. and Li, Cang(2001) 'PHOTOYELLOWING OF UNTREATED AND ACETYLATED ASPEN CHEMITHERMOMECHANICAL PULP UNDER ARGON, AMBIENT, AND OXYGEN ATMOSPHERES', Journal of Wood Chemistry and Technology, 21: 4, 343 — 360
To link to this Article: DOI: 10.1081/WCT-100108330
URL: http://dx.doi.org/10.1081/WCT-100108330

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 21(4), 343–360 (2001)

PHOTOYELLOWING OF UNTREATED AND ACETYLATED ASPEN CHEMITHERMOMECHANICAL PULP UNDER ARGON, AMBIENT, AND OXYGEN ATMOSPHERES

Magnus Paulsson,[1] Lucian A. Lucia,[2] Arthur J. Ragauskas,[2] and Cang Li[2]

[1]Chalmers University of Technology, Department of
Forest Products and Chemical Engineering,
SE-412 96 Göteborg, Sweden
[2]Institute of Paper Science and Technology,
500 10th Street NW, Atlanta, GA 30318-5794, USA

ABSTRACT

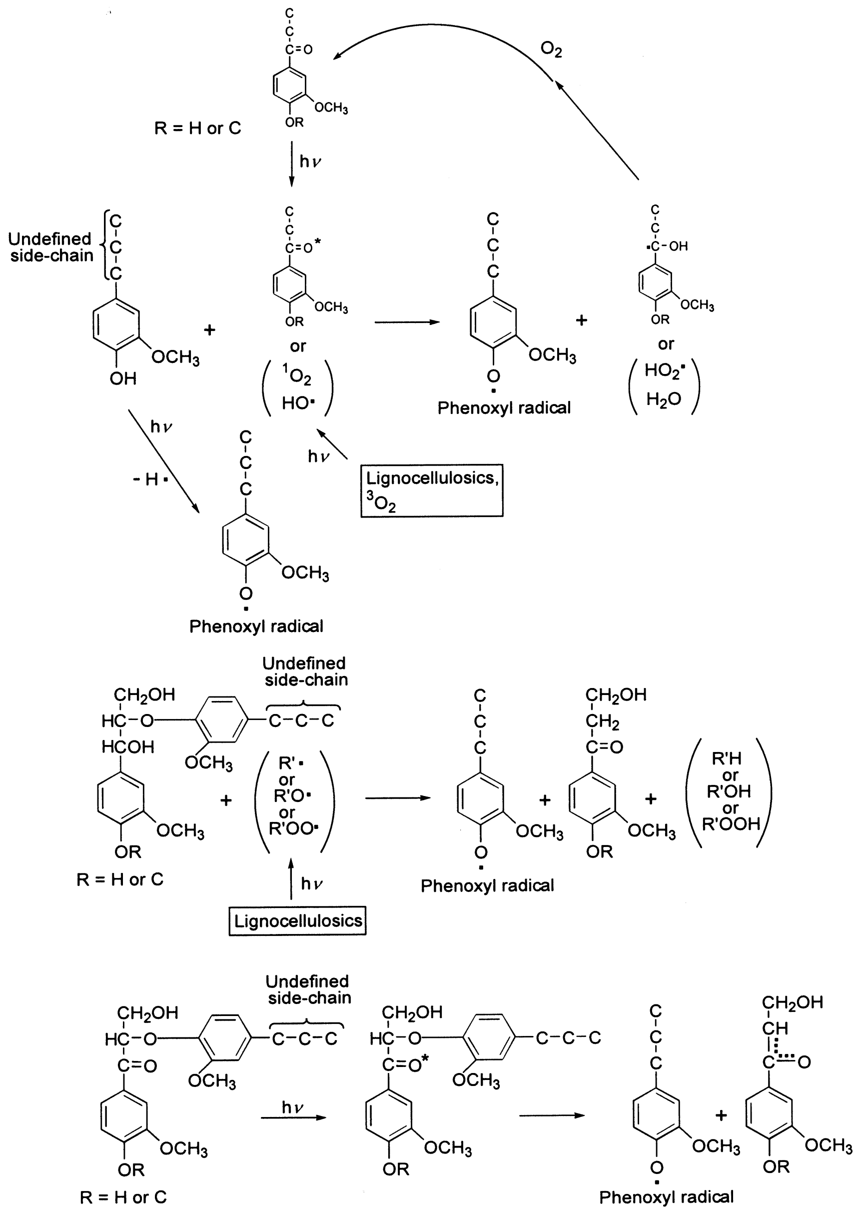
Untreated and acetylated hydrogen peroxide-bleached aspen chemithermomechanical pulp (CTMP) was subjected to accelerated light-induced aging in various atmospheres (argon, ambient, or oxygen). The photochemical changes that took place during irradiation were followed by solid-state UV/VIS diffuse reflectance spectroscopy. The degree of photoyellowing of the untreated CTMP decreased when the air in the surrounding atmosphere was replaced with oxygen-free argon. The decrease was only moderate, indicating that atmospheric oxygen is not of sole importance for the light-induced discoloration or that only a trace amount of oxygen (strongly adsorbed to the fiber material) is necessary to cause discoloration. Acetylation clearly diminished the kinetics of photoyellowing in all atmospheres resulting in substantially less absorption in the entire visible range ($\lambda > 400\,\text{nm}$). However, the development of chromophores was attenuated in an oxygen-enriched atmosphere, suggesting that oxygen is important for the color-retarding or photobleaching reactions of acetylated lignocellulosic materials. Independently of the degree of acetylation and the surrounding atmosphere, irradiation with UV/VIS fluorescent lamps generated an apparent absorption maximum around 360 nm with a shoulder at approximately 420 nm.

INTRODUCTION

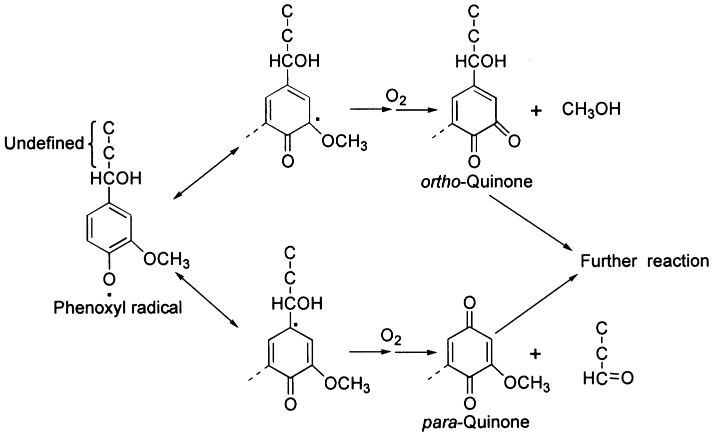
Enhanced production and efficient utilization of lignocellulosic products are issues of critical importance to both industry and society. Benefits from the manufacture of mechanical pulp include high yield and low cost. Although the production of mechanical pulp is environmentally benign and generates a low-cost product, the use of mechanical pulps is restricted severely by the tendency of mechanical pulps to undergo color reversion (yellowing) upon exposure to daylight and/or long-term storage at ambient temperatures. This discoloration is cited as the principal reason for limited commercial applications of mechanical pulps in high-quality printing papers.[1,2]

It is generally accepted that the photoyellowing initially is a surface phenomenon due mainly to photooxidation of lignin via a series of radical reactions.[3–6] Although significant progress has been made over the last decades in understanding and elucidating the mechanism of yellowing,[7,8] the course of the reactions is still not fully understood and requires further studies. Scheme 1 shows proposed reaction pathways for the formation of radicals (phenoxyl, ketyl, etc.) and Scheme 2 the proposed reaction pathways for the formation of chromophores (quinones). Insufficient knowledge of the precise reaction pathways leading to discoloration has, however, made it difficult to develop stabilizing treatments that meet all the needs of the paper industry.

The importance of atmosphere for the photoyellowing of lignocellulosic materials is currently an unresolved issue. Several studies indicate that oxygen is important for both the photodegradation of lignin and lignin model compounds as well as for the light-induced formation of chromophores in pulp and paper materials.[5,9–11] Other studies have, however, shown that oxygen is not necessary for degradation of lignin, lignin model



Scheme 1. Proposed reaction pathways for the formation of radicals during photoyellowing.



Scheme 2. Proposed reaction pathways for the formation of *ortho-* and *para-*quinones from phenoxyl radicals during photoyellowing.

compounds, or lignocellulosic materials.[4,12–20] For example, irradiation of lignin-rich papers in an atmosphere of inert gases or vacuum did not alter the general behavior; only a slight decrease in the extent of photoyellowing was observed.[4,12,13] This could be attributed either to incomplete removal of oxygen from the fiber material or to the formation of chromophores via reaction pathways not involving oxygen. It is also possible that only a trace amount of oxygen is necessary to produce photoyellowing. However, newsprint irradiated in nitrogen, carbon dioxide, or vacuum was reported to be almost completely stable to near UV radiation.[5] Furthermore, the discoloration of spruce milled wood lignin (MWL) required the presence of oxygen. Although no discoloration was observed without oxygen present, irradiation still caused chemical changes in the lignin structure. Lignin model compounds and hardwood and softwood MWL generated free radicals, both in an oxygen atmosphere and in an inert atmosphere when subjected to UV radiation.[21] Others have reported a change in molecular weight of spruce MWL (in dioxane solution) irradiated in an inert atmosphere.[18,19] However, lignin model compounds of the β-guaiacyl ether type, methoxylated stilbenes, and methoxy substituted polyacrylophenones were discolored upon exposure to UV radiation ($\lambda \geq 300\,\text{nm}$) under high-vacuum conditions.[14,16,17] Under these prerequisites, anaerobic reactions led to the formation of chromophores from the lignin-related models. To summarize, the need for oxygen for color formation during light-induced aging of lignin-containing materials is uncertain.

Several studies have shown that acetylation of wood constituents with acetic anhydride has the potential to inhibit photoyellowing and, in some cases, even to cause photobleaching of lignocellulosic materials.[22–29] The photostabilizing effect of acetylation is, at present, not fully understood. However, model compound studies[30,31] have shown that phenolic hydroxyl groups and γ-hydroxyl groups (in both β-0-4 and coniferyl alcohol structures) together with *ortho*-quinoid units are easily derivatized during the initial stage of acetylation. The benzylic hydroxyl groups in β-0-4 structures are acetylated more slowly and most of these groups are still present at a moderate extent of derivatization. This suggests that reactions involving cleavage of arylglycerol β-aryl ether structures are a less probable reaction pathway for chromophore formation during irradiation than reaction pathways involving photooxidation of free phenolic hydroxyl groups or cleavage of 2-aryloxy-1-arylpropanone structures, at least during the initial and most detrimental phase of photoyellowing. The importance of structures that can initiate discoloration of lignin-containing pulps and participate in a cyclic process must also be taken into consideration. The significance of the removal of *ortho*-quinoid units or some other still unknown structure for the brightness stability needs to be investigated further. The photobleaching of acetylated materials has been ascribed to the formation of acetyl peroxide or peroxides from the carbohydrate acetates formed during irradiation.[23,25] However, the effect of atmosphere on the aging properties of acetylated lignocellulosic materials has not been investigated.

In this paper, the effect of oxygen on the efficiency of photoyellowing of paper made from hydrogen peroxide-bleached aspen chemithermomechanical pulp (CTMP) is examined. The effect of atmosphere for the light-induced aging of acetylated aspen CTMP is also addressed.

EXPERIMENTAL

Materials

Commercially produced hydrogen peroxide-bleached aspen (*Populus tremuloides*) chemithermomechanical pulp (CTMP) was used as received for the studies described in this paper. The pulp was obtained as a dried sample. The high-brightness hardwood CTMP was manufactured using hydrogen peroxide both as a chemical pretreatment and in the bleaching stage. Table 1 summarizes selected pulp properties.

Handsheets (200 g/m^2) were prepared according to TAPPI Test Method T 205 om-88. Deionized water was used in the experiments. The paper sheets

Table 1. Description of the H_2O_2-Bleached Aspen CTMP Used in This Work

Pulp Property	Value
Freeness (ml CSF)	506
Bulk (cm^3/g)	2.0
Tear index ($mN\,m^2/g$)	3.8
Burst index ($kPa\,m^2/g$)	1.5
TAPPI brightness (%)	83.9
Opacity (%)	79.7
Fe (mg/kg)	3.4
Mn (mg/kg)	2.7
Mg (mg/kg)	65
Cu (mg/kg)	1.5
Ca (mg/kg)	370
Na (mg/kg)	4765

were conditioned at 23°C and 50% relative humidity according to TAPPI Test Method T 402 om-88 before further treatment.

Acetylation Procedure

The handsheets were acetylated at 100°C according to a previously described procedure.[32] The acetylated sheets were conditioned at 23°C and 50% relative humidity according to TAPPI Test Method T 402 om-88 before further studies.

Analysis

The acetyl content was calculated from the amount of acetate liberated after saponification of the untreated or acetylated samples with sodium hydroxide as previously described.[33] The acetyl content is given as a percentage of the dry weight of the sample.

Accelerated Light-Induced Yellowing

The paper samples were placed inside O-ring-sealed quartz vessels having a stopcock to a vacuum line. The quartz vessels were mounted in a merry-go-round apparatus that was placed inside a Rayonet photochemical reactor (Model RPR 100, The Southern New England Ultraviolet Company) outfitted with eight UV/VIS fluorescent lamps (RPR 5750 Å, The Southern New England Ultraviolet Company) displaying an emission maximum at 575 nm. The UV/VIS fluorescent lamps were rated at 8 W each. The spectral profile of the fluorescent lamp has been described elsewhere.[28]

The atmosphere during irradiation was either laboratory air, ultra-high purity research grade argon (99.999%), or ultra-high purity research grade oxygen (99.999%). All vessels were thoroughly vacuum-degassed ($<10^{-3}$ Torr) for 30 min and back-filled with a stream of the desired atmosphere. The cycle was repeated in triplicate and a positive head pressure of gas was maintained by attaching a thick-walled balloon (filled with argon, air, or oxygen) to the vessels. The temperature inside the vessels was $25 \pm 1^{\circ}C$. The samples were allowed to remain in the dark for 30–60 min after turning off the lamps prior to UV/VIS measurements.

Optical Measurements

TAPPI brightness and color changes, according to the CIELAB color scale (L^*-, a^*-, b^*-values), of non-irradiated and irradiated handsheets were measured using a Technidyne Brightmeter (Model S-5) according to TAPPI Test Method T 452 om-92 and TAPPI Test Method T 524 om-94, respectively. The post-color (PC) number, given at 457 nm, was determined as previously described;[34] $\text{PC number} = 100((k/s)_t - (k/s)_{t=0})$, $t =$ irradiation time, $k =$ light absorption coefficient, and $s =$ light scattering coefficient.

UV/VIS Diffuse Reflectance Spectroscopy

The UV/VIS spectra were recorded on a Perkin-Elmer Lambda 19 DM spectrophotometer equipped with a diffuse reflectance and transmittance accessory (Labsphere RSA-PE-90). The accessory is essentially an optical bench that includes double-beam transfer optics and six-inch diameter (154 mm) integrating sphere. Using an SRS-99-010-7890 standard, background corrections were collected. The absorbance (ABS) was calculated from the diffuse reflectance (R_∞) using the following expression derived from the Beer-Lambert law (cf. 35): $\text{ABS} = -\log R_\infty$. All spectra were averaged from a set of three to four measurements and are displayed as the difference spectra between an irradiated and a non-irradiated sample: $\Delta\text{ABS} = \text{ABS}_{\text{irradiated}} - \text{ABS}_{\text{non-irradiated}}$.

RESULTS AND DISCUSSION

Optical Properties After Aging in Various Atmospheres

Table 2 shows the optical properties of the untreated and acetylated hydrogen peroxide-bleached aspen CTMP as well as the post-color (PC) numbers after accelerated aging for 18 h in different atmospheres. The acetylation treatment resulted in a moderate brightness loss (about 5.7 brightness units for the high-acetylated samples) and shifted the color slightly towards yellow (higher *b**-value). This is in good agreement with results from earlier investigations.[32,36]

Lignin has been reported to be the most easily acetylated wood component followed by hemicelluloses, whereas cellulose (amorphous regions) is derivatized at a later stage.[37,38] The crystalline part of cellulose is considered to be unreactive towards acetylation.[39] If only phenolic hydroxyl groups were acetylated, the increase in acetyl content should be less than one percentage unit. It is therefore obvious that other hydroxyl groups are derivatized simultaneously even at short reaction times. Acetyl contents were also determined after prolonged irradiation (up to 144 h) and were found to change minimally (±0.2%) from their original non-irradiated values presented in Table 2.

The UV/VIS fluorescent lamps used for the accelerated tests emit light in the ultraviolet and visible range (from about 350–700 nm with a maximum output at 575 nm) and have a comparatively close match to conventional standard "cool white" fluorescent color used in many commercial lighting installations. Table 2 shows the photoyellowing (expressed as PC number) of untreated and acetylated paper samples aged under argon,

Table 2. Change in Optical Properties on Acetylation and Light-Induced Aging of H_2O_2 Bleached Aspen CTMP

		Unirradiated				Irradiated for 18 h		
						PC Number[1]		
	Acetyl Content, % by Mass	TAPPI Brightness (%)	*L**	*a**	*b**	Argon	Ambient	Oxygen
Control	0.6	83.9	96.0	−1.0	5.0	2.2	2.4	3.3
Acetylated	4.6	80.7	95.4	−0.9	6.7	1.8	1.8	1.6
	7.3	78.2	94.9	−0.7	7.6	1.5	1.3	0.5

[1] The post-color (PC) number at 457 nm (due to irradiation) was determined as previously described.[34]

ambient, or oxygen atmospheres. When the air in the surrounding atmosphere was replaced with oxygen-free argon (by repeated evacuation and flushing with argon), the degree of yellowing for the untreated control decreased only slightly. However, when the surrounding air was replaced with oxygen, the degree of yellowing increased by approximately 50% (cf. the PC values in Table 2). This is in general in agreement with the results obtained for hardwood and softwood hydrogen peroxide-bleached CTMPs, photoaged (UV lamps, 300–400 nm) in the absence or presence of UV-screens under various atmospheres (argon, ambient, or oxygen).[20] It is evident that the atmospheric oxygen plays some part in the light-induced discoloration of hydrogen peroxide-bleached hardwood CTMP, although the effect is not of sole importance.

Acetylation retards photoyellowing under ambient conditions as previously reported.[22–29] Replacing the air with argon had a moderate effect on the discoloration rate; the PC number for the high-acetylated handsheets (acetyl content of 7.3%) increased from 1.3 to 1.5, while for the low-acetylated handsheets (acetyl content of 4.6%), no noticeable difference was obtained in an inert atmosphere. However, when the oxygen concentration was increased, the photostability of the acetylated paper samples was improved, especially for the samples with high acetyl content (cf. Table 2).

It has previously been suggested that the photostability obtained by the acetylation treatment not only is an effect of retarding color-forming reactions, but also is a result of promoting photobleaching reactions.[28] The photobleaching of acetylated lignocellulosic materials has been ascribed to the formation of acetyl peroxide or peroxides from the carbohydrate acetates during irradiation.[23,25] It is also possible that the photostabilization effect of acetylation could be due, in part, to the photodegradation of peroxy radicals formed during photoyellowing. However, it is likely that oxygen also favors photobleaching reactions, at least for the handsheets with high acetyl content.

Solid-State UV/VIS Diffuse Absorption Difference Spectroscopy

Solid-state UV/VIS diffuse absorption difference spectroscopy is a powerful technique for the study of light-induced yellowing of lignin-containing materials.[35,40] The signal-to-noise ratio is low, however, in the region below 340 nm and care should therefore be taken to interpret the UV/VIS spectra in this region. Care should also be taken when evaluating the results after long UV exposure since the assumption of exponential distribution of chromophores in the thickness of the sheet may no longer be valid.[35]

Figures 1a–d show the UV/VIS absorption difference spectra (ΔABS vs. wavelength) for untreated hydrogen peroxide-bleached aspen CTMP recorded after aging for up to 18 h in argon, ambient, or oxygen atmospheres. The surrounding atmosphere had some influence on both the photochemistry and extent of discoloration, even if the effect was rather moderate (cf. 20). Irradiation in argon atmosphere generated an apparent absorption maximum at 360 nm that was slightly shifted to longer wavelengths (365 nm) when the concentration of oxygen in the surrounding atmosphere was increased. Chromophores absorbing around 420 nm were also formed during irradiation, especially in an oxygen-rich atmosphere (cf. Figure 1). The corresponding UV/VIS absorption difference spectra for the aspen CTMP acetylated to a high degree (acetyl content of 7.3%) is shown in Figures 2a–d. The photoaging properties for the low-acetylated CTMP (acetyl content of 4.6%) were, in general, the same, although shifted to a somewhat lower stability level as indicated by the lower derivatization degree; therefore, these properties will not be discussed further. The acetylated aspen CTMP generated an apparent absorption maximum in the same region (360 nm, cf. Figures 1a and 2a) as the unacetylated CTMP when irradiated in argon atmosphere. When the oxygen concentration was increased, the absorption maximum was shifted to slightly shorter wavelengths (355 nm). The shoulder at approximately 420 nm was, however,

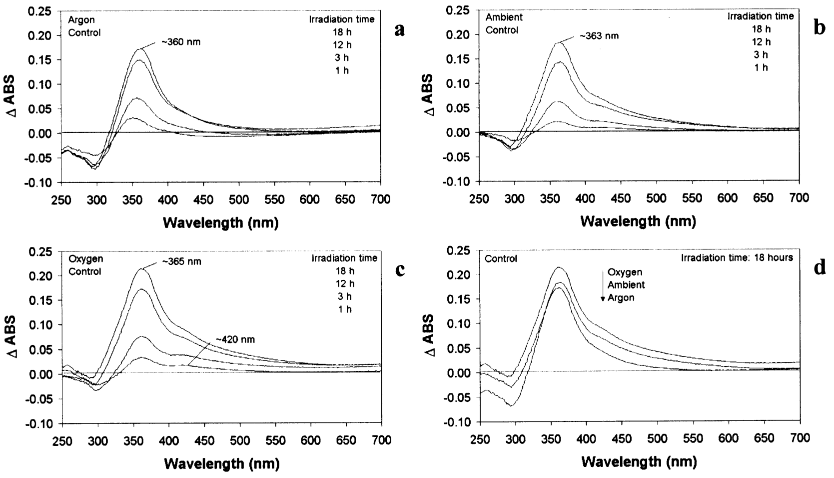


Figure 1. Absorption difference spectra of untreated hydrogen peroxide-bleached aspen CTMP after irradiation for various periods of time in different atmospheres ($\Delta ABS = ABS_{\text{irradiated}} - ABS_{\text{non-irradiated}}$).

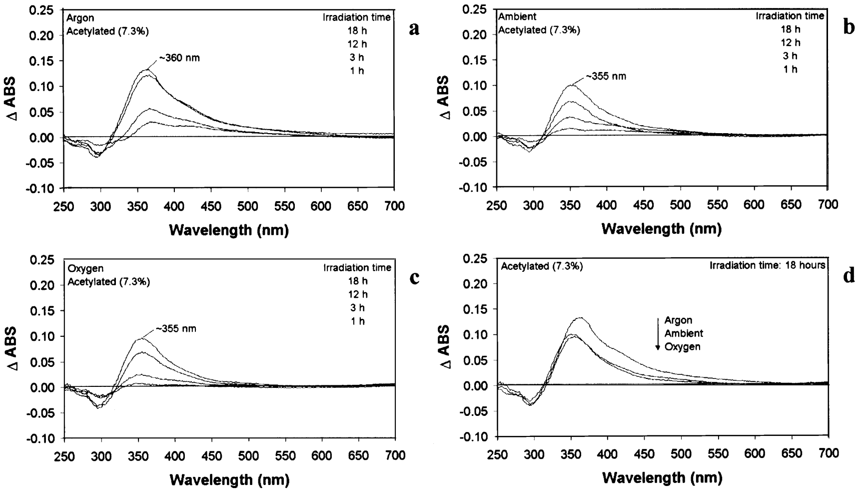


Figure 2. Absorption difference spectra of acetylated (acetyl content of 7.3%) hydrogen peroxide-bleached aspen CTMP after irradiation for various periods of time in different atmospheres ($\Delta ABS = ABS_{irradiated} - ABS_{non\text{-}irradiated}$).

somewhat less pronounced for the acetylated samples irradiated under the three different atmospheres. Furthermore, the chromophores formed during irradiation of the acetylated CTMP were substantially less in the whole UV–visible region.

Figure 3 shows the UV/VIS absorption difference spectra after prolonged irradiation for 114 h of both untreated and acetylated samples in argon or ambient atmospheres. Even after a severe irradiation, the effect of excluding oxygen from the atmosphere is the same as that observed after 18 h of irradiation, i.e., a somewhat higher stability level for the untreated CTMP and a lower stability level for the acetylated CTMP (see the discussion above). It is evident that oxygen plays an important role for decreasing the extent of discoloration of acetylated lignocellulosic materials.

Generally, UV/VIS diffuse reflectance spectroscopy of hydrogen peroxide-bleached softwood and hardwood pulps such as groundwood pulp (GWP), thermomechanical pulp (TMP), and CTMP, performed on both thin and thick sheets, shows an increased absorption in the UV region at 320–360 mm and in the visible region at 410–435 nm when exposed to UV radiation.[35,40–51] The increase in absorption in the UV region has been attributed to the formation of aromatic carbonyl groups ($\lambda_{max} \sim$ 330 nm) and to the formation of quinones, possibly methoxylated *para*- or

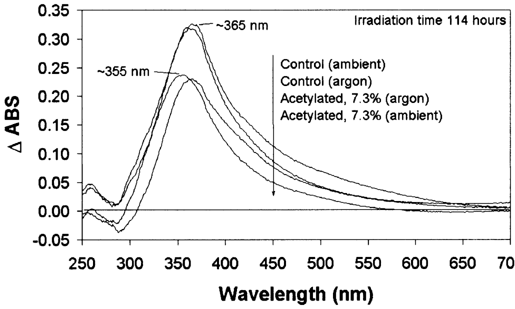


Figure 3. Absorption difference spectra of untreated and acetylated (acetyl content of 7.3%) hydrogen peroxide-bleached aspen CTMP after irradiation for 114 h in ambient and argon atmospheres ($\Delta\text{ABS} = \text{ABS}_{\text{irradiated}} - \text{ABS}_{\text{non-irradiated}}$).

ortho-quinones (monohydrate adduct (50, cf. 52), $\lambda_{\max} \sim 350$–370 nm). It is also possible that coniferaldehyde with an absorption maximum at ~350 nm, generated through photooxidation of coniferyl alcohol end-groups, contributes to the UV-absorption peak. The increase in the absorption in the visible region has been attributed to the formation of *ortho*-quinones, at least in an initial phase. Hydroxystilbenes, which can be introduced in the lignin moiety during high-yield pulping and alkaline bleaching conditions,[53–55] have been proposed as the leucochromophores that, to a large extent, are responsible for the initial discoloration of bleached high-yield pulps.[56,57] Simple stilbenes have an absorption maximum at about 330 nm in solution, but it is possible that this maximum can be shifted to higher wavelengths when incorporated in the lignin macromolecule due to steric and electronic effects of substituent groups. A red-shift of the UV/VIS absorption maxima of quinone and stilbene model compounds in the solid state (on filter paper or on bleached GWP or CTMP) compared with the absorption in solution has been reported.[49] The red-shift was 26 nm for a hydroxystilbene model and between 32 and 148 nm for quinoidic compounds; charge transfer complexes (quinone-phenol) might account for this effect.[49,58,59] It is difficult to access the changes seen in the UV/VIS spectra to the formation/destruction of chromophoric and leucochromophoric structures in the lignin since (i) most absorption data are given for simple model compounds in solution, and it is likely that the position of the absorption peaks may be different in the solid phase, and (ii) the position of absorption maxima of the chromophoric and leucochromophoric structures may be shifted when incorporated in the lignin macromolecule. Therefore, further studies are needed to determine the absorption characteristics of several classes of important structures when incorporated in different types of high-yield pulps.

The present investigation showed that regardless of the surrounding atmosphere, absorption peaks appeared in the above-mentioned UV and visible regions during light-induced aging of hydrogen peroxide-bleached aspen CTMP. The relationship between the peak areas and the position of the maxima was dependent to some extent on the surrounding atmosphere during irradiation. Untreated aspen CTMP was somewhat more prone to discoloration in an oxygen-rich atmosphere, while for acetylated aspen CTMP, the opposite was true. However, in both cases the formation of chromophores was not solely dependent on the presence of oxygen (under the prerequisite that oxygen was completely removed under the experimental conditions used).

CONCLUSIONS

This work demonstrates the usefulness of solid-state UV/VIS diffuse reflectance spectroscopy for the study of light-induced reversion of untreated and chemically modified high-yield pulps.

UV/VIS irradiation of untreated and acetylated aspen CTMP introduced chromophores with an absorption maximum near 360 nm and with a shoulder at approximately 420 nm independently of surrounding atmosphere. However, the relationship between the peak areas and the position of the maxima was dependent to some extent on the irradiation atmosphere. For untreated aspen CTMP, the development of chromophores was enhanced in an oxygen-rich atmosphere, while for acetylated aspen CTMP the opposite was true. However, in both cases the formation of chromophores was not solely dependent on the presence of oxygen.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the United States Department of Agriculture for support (Agreement Nos. 96-35103-3800 and 98-35501-6911).

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