

OPTICAL PROPERTY ANALYSIS OF THERMALLY AND PHOTOLYTICALLY AGED *EUCALYPTUS CAMALDULENSIS* CHEMITHERMOMECHANICAL PULP (CTMP)

Yao Chen,^a Yongming Fan,^{a,*} Mandla A. Tshabalala,^b Nicole M. Stark,^b Jianmin Gao,^a and Ruijie Liu^a

To investigate the optical properties of chemithermomechanical pulp (CTMP) from *Eucalyptus camaldulensis*, one group of samples of CTMP was aged by heating, and another group was first subjected to bleaching with different bleaching agents, and then aging by exposure to sunlight. Chromophores were analyzed using diffuse reflectance UV-Vis spectra (DRUV), and the brightness and color parameters (L^* , a^* , b^*) were analyzed using colorimetry. Results showed that the color reactions of the pulp, upon heating, were enhanced in the presence of moisture. There was a linear relationship between the pulp initial moisture content (MC) and the intensity of UV-Vis absorption. The contribution of different chromophores to pulp color was analyzed with the help of bleaching agents: hydrogen peroxide, sodium dithionite, and sodium borohydride. Sodium borohydride and hydrogen peroxide treatments resulted in a decrease in the absorption band at 280 nm along with the shoulder near 320 nm, which could be attributed to conjugated C=O and C=C systems. Similarly, sodium dithionite treatment also led to a decrease in absorption of the carbonyls and double bonds conjugated with aromatic double bonds. The chromaticity parameters of bleached pulp increased after exposure to sunlight. A correspondingly higher concentration of quinoid structures was found.

Keywords: CTMP; Pulp; Optical properties; Yellowing; Light irradiation; Heat treatment

Contact information: a: College of Material Science and Technology, Beijing Forestry University, Beijing 100083, China; b: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, One Gifford Pinchot Drive, Madison, WI 53726-2398, United States;

* Corresponding author: fanym@bjfu.edu.cn

INTRODUCTION

A major problem with paper manufactured from pulps produced by mechanical and chemithermomechanical methods is the potential to undergo yellowing (brightness reversion) upon exposure to sunlight (Heitner 1993) and heat. The low brightness stability, caused by high concentrations of chromophores, limits its utilization. Although neither the precise nature of the chromophores responsible for yellowing nor the exact mechanism for their formation are fully understood, it is generally accepted that residual lignin in the pulp after bleaching plays a very important role in brightness reversion (Hon 1991). There is also a general agreement that the initial color reversion processes are associated with photochemical processes. In this regard, a number of researchers have attempted to elucidate the mechanism of photodegradation of wood (Müller et al. 2003), pulp (Bonini

et al. 1998a; Zhu et al. 1995), extracted lignin (Bonini et al. 1998b, 2002), and lignin model compounds (Crestini and D'Auria 1996, 1997). Although many questions still remain, it is generally accepted that the photo-oxidation of lignin in the presence of oxygen is the main cause of yellowing (Forman 1940). Lignin contains numerous chromophores and is a very efficient absorber of ultraviolet radiation. The lignin photo-degradation process is initiated by the absorption of ultraviolet radiation between 290 and 400 nm (Van den Akker et al. 1949). Agarwal and Atalla (1993) reported the existence of ring-conjugated double bonds such as those in aromatic ketones (α -carbonyl groups), α,β -C=C bond of coniferyl alcohol, and the γ -C=O bond of coniferaldehyde structural units in yellowed pulps. Hirashima (1994) hypothesized that coniferyl alcohol structures, such as the p-hydroquinone/p-quinone redox couple by virtue of being precursors of yellowed products, could be implicated in the photo-yellowing of pulps. However, no conclusive evidence has yet been provided that coniferaldehyde or alcohol causes photo-yellowing. The published research, carried out on bleached TMP by Agarwal (1998), suggested that Raman data did not provide any support to the possibility that o-quinone groups were generated upon photo-yellowing.

Important intermediates in the photo-yellowing process are phenoxy free-radicals, which are oxidized in the presence of singlet oxygen into chromophoric structures of carbonyl compounds as well as ortho- and para-quinonoids (Müller et al. 2003). Quinone-methide groups can also be formed from corresponding hydroquinone structures that are present in pulps. Chromophores such as alkylated phenols and quinone in lignin, which are abundant in non-bleached mechanical and CTMP pulps (Agarwal and Landucci 2004), can absorb sunlight in the UV-Vis region and undergo photochemical reactions that result in the formation of color substances through excited species and free radical pathways (Gellerstedt and Zhang 1992; Leigh et al. 1996). These free radicals may then cause photo-oxidation and degradation of lignin, which results in formation of colored unsaturated carbonyl compounds, leading to color changes (Pandey 2005; Mitsui 2004a; Mitsui et al. 2004b). Stilbenes, quinoid structures, as well as coniferaldehyde, have been confirmed to be the most important chromophores, and it has been suggested that these compounds are formed through photochemical reactions, which may produce phenolic radicals and form the o-quinones (Paulsson and Ragauskas 2000; Jääskeläinen et al. 2006). Formation of new phenolic hydroxyl groups and aromatic carbonyl groups upon irradiation with near ultraviolet light was explained in terms of the light-induced breakdown of etherified aryl glycerol- β -aryl ether structures in lignin (Schmidt and Heitner 1992). Singlet oxygen plays a significant role in photodegradation of wood surfaces (Hon and Chang 1982) and lignin (Bonini et al. 2002), and induces degradation of the lignin model compounds of hardwood and softwood lignin. The degradation rate of lignin increases in the presence of singlet oxygen sensitizer in pulps. The photo-induced yellowing has also been attributed to the photo-reactivity of phenolic chromophores absorbing UV-Vis radiation above 300 nm and giving phenoxyl radicals by direct photolysis mechanism without any need for photo-sensitizers (Fornier et al. 1990).

Chemical modification of potential chromophoric groups has been examined (Schmidt and Heitner 1991; Castallan et al. 1992). The removal of photosensitive carbonyl groups by reduction was shown to have a limited effect in protecting lignin against photo-degradation. Derivatization of hydroxyl groups by alkylation or acylation

was more successful. Acetylation of groundwood pulps improved the resistance towards light and, in some cases, also resulted in photo-bleaching of the pulp (Ek et al. 1992). Acetylation can also inactivate or remove some chromophores initially present in non-bleached or dithionite-bleached pulps (Paulsson and Simonson 2002). Methylation in the presence of a cationic phase transfer catalyst was reported to reduce the yellowing rate significantly in the case of hydrogen peroxide bleached CTMP (Castallan et al. 1992; Pan et al. 1992).

The color of pulp is modified, acquiring a yellowish tonality, upon heating. This is often explained as being due to the formation of colored degradation products from lignin. The formation of oxidation products such as quinones has also been given as the reason for color change (Bekhta and Niemz 2003). In lignin, there is a cleavage of β -O-4 linkages and a reduction of methoxyl content leading to a more condensed structure (Wikberg and Maunu 2004).

The current work is aimed at providing new insights into the optical properties of chromophores in CTMP formed during heating or natural aging processes. Both of these processes are encountered in the pulp and paper refining process. Different bleaching agents were employed to elucidate the formation of different classes of chromophores. The primary action of sodium borohydride is the reduction of conjugated and non-conjugated carbonyls to the corresponding alcohols (Carey and Sundberg 1983). Hydrogen peroxide reacts more readily with quinones on the fiber surface than with coniferaldehyde groups associated with lignin in the fiber wall (Keating et al. 2006). However, few reports have addressed the effects of sodium dithionite on chromophores. Taking advantage of the differences in reactions of pulp chromophores with the different bleaching agents, hydrogen peroxide, sodium dithionite, and sodium borohydride, were used to determine the contribution of the different chromophores to the pulp color. Chemical structure of chromophores in pulp was analyzed by DRUV spectroscopy, which was found to be sensitive enough to observe the changes in those chromophores, especially those occurring in the aromatic units. Changes in pulp brightness and color parameters (L^* , a^* , b^*) with different moisture contents and exposure time were determined. Results from this study provide a better understanding of the changes in the chromophore structures as a result of heating or sunlight irradiation, and a suggestion for selecting suitable bleaching conditions for producing high-quality CTMP pulps with high brightness.

EXPERIMENTAL

Materials

Eucalyptus camaldulensis CTMP was obtained from a pilot plant in Beijing, China. The pulp was prepared by chemical pre-treatment of *Eucalyptus* wood chips with NaOH (3%) and Na₂SO₃ (3%) based on wood chips dry weight.

Heat Aging Process

For the heat aging process, non-bleached pulp sheets with different initial MC were heated in a sealed stainless steel autoclave for 48 hours at 80°C and 120°C,

respectively. For the preparation of the paper sheet, the pulp slurry was filtered on a Buchner funnel lined with a 40 mesh copper wire. Each filter cake was pressed under the same pressure and duration with the help of a hydraulic press to get rid of free water. The basis weight of the handsheet was controlled to around 200 g/m². To obtain different MC, wet paper sheets were put into the chamber of a vacuum freeze-drier and were taken from it after 0, 3, 5, 7, or 9 hours of drying. The MC values were measured according to the standard method GB/T 741-1989. Before performing color measurements and spectroscopic analyses, they were vacuum-dried for 7 days at room temperature over phosphorus pentoxide.

Bleaching Process

Chelation of the pulp was conducted before the bleaching process to get rid of metal ions present in the non-bleached pulp (Lapierre 1995). The chelation stage was performed at 80°C for 40 min at 10% consistency with 0.4% EDTA (5g/l) followed by washing prior to bleaching.

CTMP was bleached using sodium dithionite, sodium borohydride, or hydrogen peroxide. Sodium dithionite bleaching was conducted at room temperature for 24 hours with the chelated pulp sample mixed with 60 mL Na₂S₂O₄ (70 g/L, based on pulp dry weight). The pH was adjusted to 8.0 with NaOH (1 mol/L).

Sodium borohydride bleaching was performed for 48 hours at room temperature with the chelated pulp sample (2g, dry weight) mixed with the NaBH₄ (25%) at 2.5% consistency.

Hydrogen peroxide bleaching was performed at 80°C for 2.5 hours at 10% consistency using 6% H₂O₂, 5.4% NaOH, 0.05% MgSO₄ and 2% Na₂SiO₃ (on pulp).

After bleaching, the pulp was rinsed with 1L aliquots of distilled water until a neutral pH was attained.

Light Aging Process

The pulp bleached with hydrogen peroxide was selected for irradiation tests under natural sunlight. Pulp sheets were prepared with the same methods as used for the heat ageing process. To obtain the different MC values, the sheets were first vacuum dried to obtain 0% MC. Then the dried sheets were adjusted to 20% MC by adding distilled water based on the dry weight of the sheets. After stabilization for 24 hours, the sheets with initial moisture content of 0% and 20% were sealed in polyethylene (PE) bags and exposed to sunlight (250 to 300 lx) for 1 h, 2 h, 4.5 h, and 16 h, respectively.

Brightness and Chromaticity Determination

The brightness and color parameters were determined using a ZB-A colorimeter (Hangzhou Zhibang Co. Ltd, Zhejiang, China). Four overlapped pulp sheets were used for the measurement. The brightness was obtained using the reflectance at 457 nm based on the International Organization of Standard (ISO). The color parameters L^* , a^* , and b^* for the pulps bleached with the different agents were determined by the CIELAB system, in which L^* denotes lightness from 0% (black) to 100% (white), a^* denotes from green (- a) to red (+ a), and b^* denotes from blue (- b) to yellow (+ b). The parameters were analyzed with a D65 standard illuminant and 10° standard observer. The values of the

color parameters were measured on at least five replicate samples. In the CIELAB color system, the L^* value can be thought as a lightness factor. L^* represents reflectance of a sample. An L^* value of 0 means the sample does not reflect light; an L^* of 100 means the sample reflects 100% of incident light; an increase in L^* means the sample has faded or lightened.

Diffuse Reflectance UV-Vis (DRUV) Spectra

The diffuse reflectance spectra of control and treated pulp samples were recorded at room temperature on a UV-3100 UV-Vis near-IR spectrophotometer (Shimadzu, Japan) equipped with an integrating sphere. The reflectance spectra were recorded against BaSO₄ as a white (R_∞) optical standard. This study was carried out in the wavelength range 240 to 800 nm. The reflectance spectra of four overlapped pulp sheets were observed and were converted to absorbance spectra (K/S) using the Kubelka-Munk equation (Kubelka and Munk 1931; Kubelka 1948),

$$K/S = \frac{(1-R)^2}{2R} \quad (1)$$

where R is the measured reflectance with values between 0 to 1 and K and S are the absorption and scattering coefficients, respectively. Difference spectra were calculated by subtracting the reflectance spectrum of the control non-bleached sample from the treated samples (Eq. 2), and plotted as a function of wavelength. Therefore, the difference spectrum represents a net change in brightness reversion. Based on the Kubelka–Munk theory, we can assume that $\Delta(K/S)$ signifies appearance or formation of chromophores in the pulp after treatment.

$$\Delta(K/S) = (K/S)_{after} - (K/S)_{before} \quad (2)$$

The final spectrum is the mean value of three measurements at different locations on the pulp sheet surface.

RESULTS AND DISCUSSION

Effect of Heat Treatment on Yellowing

Brightness and color parameters of the non-bleached CTMP pulp with different MC heat treated for 48 h at 80°C and 120°C are shown in Tables 1 and 2, respectively.

It can be seen that the brightness and L^* value decreased after heat treatment, and the changes were more obvious for samples heat treated at higher temperatures. L^* value also decreased with increasing initial MC. The chromaticity parameters a^* and b^* increased with an increase in MC. This suggests that the color reactions of the CTMP upon heating were enhanced at the presence of moisture.

Table 1. Brightness and Color Parameters of Non-bleached CTMP Pulp Heat Treated for 48 h at 80°C

Initial MC (%)	Brightness	L^*	a^*	b^*
11.13 ^b	43.39 (± 0.11) ^a	80.53 (± 0.24)	4.55 (± 0.04)	13.42 (± 0.08)
13.17	42.52 (± 0.16)	79.68 (± 0.19)	4.72 (± 0.03)	13.64 (± 0.13)
21.59	40.89 (± 0.19)	79.08 (± 0.22)	4.92 (± 0.06)	13.99 (± 0.13)
38.24	38.25 (± 0.21)	77.16 (± 0.14)	5.84 (± 0.05)	15.01 (± 0.09)
52.92	36.23 (± 0.13)	75.26 (± 0.17)	6.78 (± 0.07)	15.76 (± 0.11)

^a Values in parentheses represent the standard deviation of five replicates.
^b CTMP before heat treatment

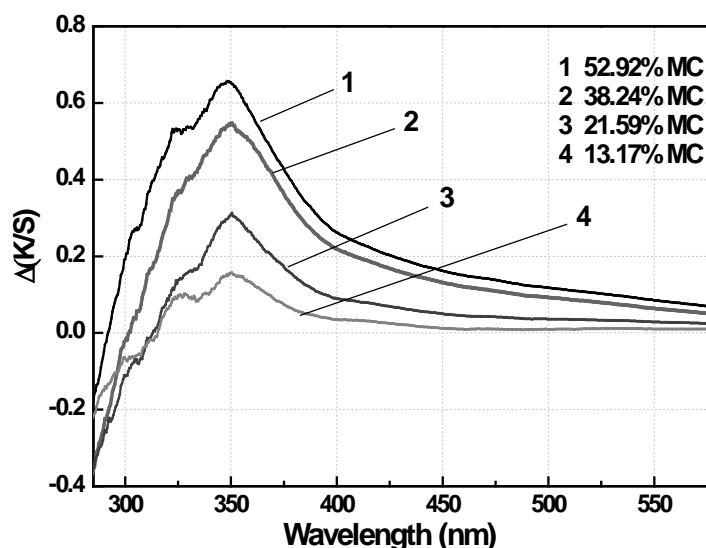
Table 2. Brightness and Color Parameters of Non-bleached CTMP Pulp Heat Treated for 48 h at 120°C

Initial MC (%)	Brightness	L^*	a^*	b^*
11.13 ^b	43.39 (± 0.11) ^a	80.53 (± 0.24)	4.55 (± 0.04)	13.42 (± 0.08)
17.30	19.15 (± 0.04)	64.43 (± 0.13)	8.89 (± 0.11)	21.27 (± 0.18)
28.80	18.48 (± 0.09)	62.38 (± 0.21)	9.10 (± 0.07)	22.06 (± 0.22)
35.16	17.90 (± 0.07)	60.35 (± 0.16)	9.68 (± 0.03)	23.11 (± 0.15)

^a Values in parentheses represent the standard deviation of five replicates.
^b CTMP before heat treatment

Figures 1 and 3 show the K/S difference spectra $\Delta(K/S)$ for the pulp samples with various initial MC heated at 80°C and 120°C.

It can be observed that light absorption across the visible region intensified with MC increase. An absorption peak at 350 nm and a shoulder at 330 nm emerged after heat treatment. Both of the peaks increased with MC increase. No shoulder at 330 nm can be found when samples were heat-treated at 120°C. A practically linear relationship can be observed between the pulp initial MC and the intensity of absorption at 330 and 350 nm when CTMP pulps were subjected to heat treatment at 80°C and 120°C (Figs. 2 and 4, respectively).

**Fig. 1.** $\Delta(K/S)$ spectra of CTMP pulp with different MC heat treated at 80°C

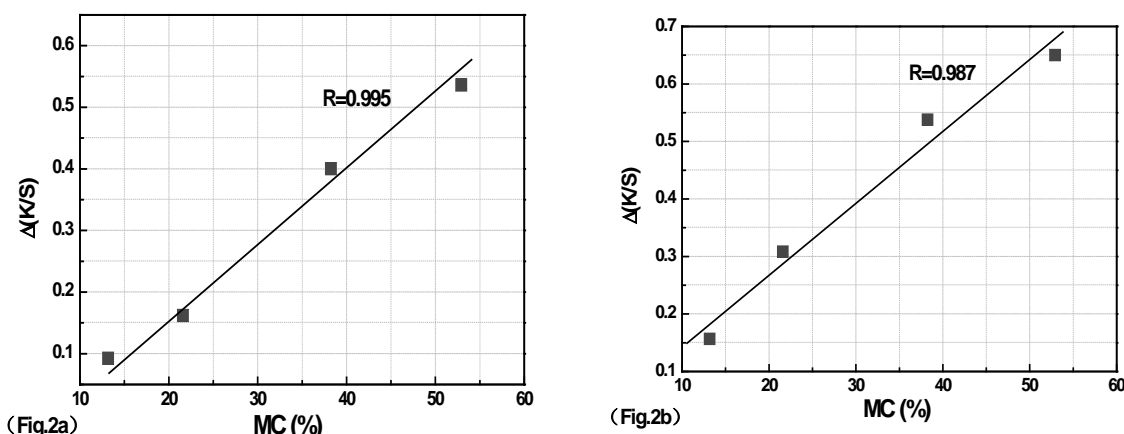


Fig. 2. The values of $\Delta(K/S)$ at (a) 330nm and (b) 350 nm of CTMP pulp heat treated at 80°C

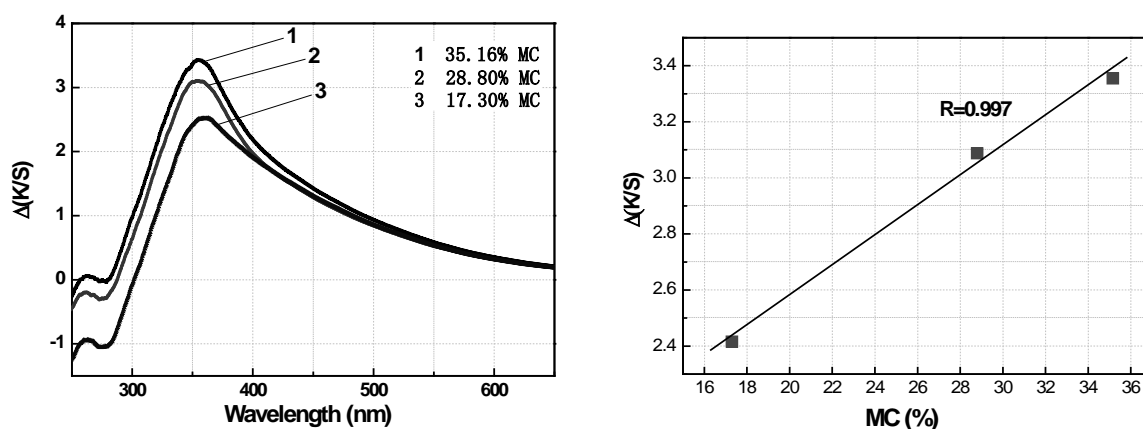


Fig. 3. $\Delta(K/S)$ spectra of CTMP pulp with different MC heat treated at 120°C

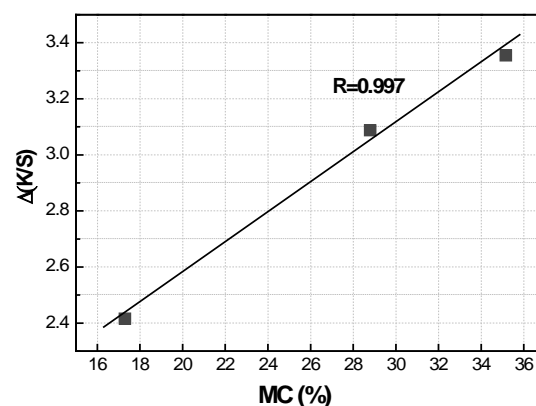


Fig. 4. The values of $\Delta(K/S)$ at 350 nm of CTMP pulp heat treated at 120°C

The absorption features near 350 and 330 nm are believed to be due to an n- π electron transition of the C=O groups in lignin (Holthius et al. 1985; Scott 1964). The maximum absorption at 352 nm corresponds to the coniferaldehyde chromophore known to exist in CTMP (Polcin and Rapson 1971; Castallan 1992). It can be inferred that conjugated carbonyl groups were formed in the heat treatment process by way of depolymerization or oxidation. It can be seen that the shoulder at 330 nm vanished and the band at 350 nm broadened after heat treatment at 120°C. It is well known that increasing conjugation increases the absorptivity and also shifts the band to longer wavelengths (Williams and Fleming 1995). Therefore, it can be concluded that higher temperature treatment may result in more conjugated chromophores, which may influence the absorbance spectral range. 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 matrix. A red-shift of the UV/VIS absorption maxima of quinone and stilbene model compounds in the solid state compared with the absorption in solution has been reported (Zhang and Gellerstedt 1998). 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 also account for this effect (Furman and Lonsky 1986, 1988).

Effect of Bleaching on Optical Behavior

Brightness and color parameters

Results from Table 3 indicate that the pulp brightness was affected to different extents by the various bleaching agents. A similar trend was observed with L^* , which indicated that the structures of chromophores were changed or destroyed during the bleaching. The chromaticity a^* and b^* decreased remarkably after bleaching. The decrease in b^* can be attributed to partial destruction of conjugated carbonyl groups (Kishino and Nakano 2004), and the decrease in a^* , to a destruction of quinoid structures.

Table 3. Brightness and Color Parameters of CTMP pulps before and after Bleaching

Bleaching agent	Brightness	L^*	a^*	b^*
CTMP(non-bleached)	43.39 (± 0.11) ^a	80.53 (± 0.24)	4.55 (± 0.04)	13.42 (± 0.08)
Na ₂ S ₂ O ₄	55.26 (± 0.17)	85.89 (± 0.23)	2.67 (± 0.06)	11.50 (± 0.08)
NaBH ₄	62.94 (± 0.29)	88.84 (± 0.15)	1.94 (± 0.02)	9.10 (± 0.07)
H ₂ O ₂	82.70 (± 0.23)	96.00 (± 0.31)	-1.09 (± 0.01)	4.71 (± 0.08)

^a Values in parentheses represent the standard deviation of five replicates.

Diffuse reflectance UV-Vis spectra

The DRUV spectra (in Kubelka-Munk units) of the CTMP before and after bleaching are shown in Fig. 5, and the net change in absorbance, $\Delta(K/S)$, after bleaching is shown in Fig. 6. It was observed that sodium borohydride treatment removed absorption bands in the range 280 to 320 nm. The absorption in this region is attributed to conjugated C=C groups such as hydroxy substituted aromatic acetophenone type moieties in the pulp lignin (Archard and Michell 1989), and structures similar to those found in the carbonyl moiety of compounds like coniferaldehyde, sinapic acid methyl ether, and o-hydroxyacetophenone. The band found near 320 nm in o-hydroxyacetophenone has also been attributed to either a carbonyl $n-\pi^*$ transition or to an electron transfer band (Scott 1964). The absorbance maximum at 280 nm in the UV spectrum could be attributed to lignin (Keating et al. 2006). It can be seen from the $\Delta(K/S)$ spectra that hydrogen peroxide treatment resulted in decreased absorptions at 280, 320, and 340-360 nm. The most probable assignment of the absorption at 340-360 nm is to o-quinonoid and p-quinones structures (Paulsson and Ragauskas 2000). Imsgard et al. (1971) found that a polymeric quinone made by oxidizing isoeugenol absorbed at 380 nm. This band has a broad tail into the visible region and would certainly be a major contributor to the pulp color. The weakening of this band by the hydrogen peroxide treatment is a major factor in the improved paper brightness. Some of the carbonyls and double bonds conjugated with aromatic ring were also decreased by sodium dithionite bleaching, as indicated by the decrease of absorption bands at 300 nm. The substantial decrease of the absorption at 350 nm can be attributed to the degradation of coniferaldehyde (Jääskeläinen et al. 2006).

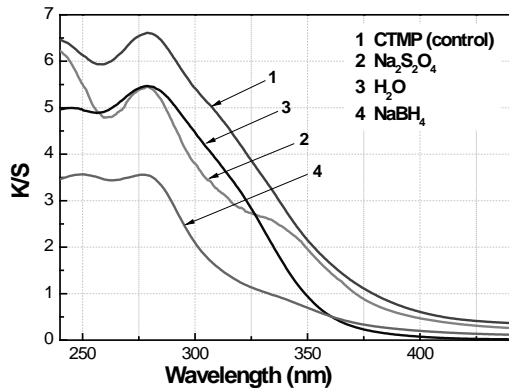


Fig. 5. Diffuse reflectance UV-Vis spectra of bleached CTMP

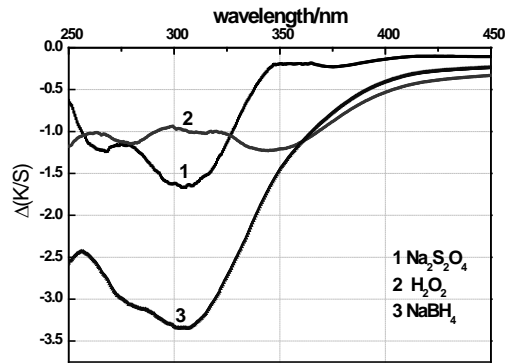


Fig. 6. Difference diffuse reflectance UV-Vis spectra of reduction in absorption

Effect of Irradiation on Hydrogen Peroxide Bleached CTMP (BCTMP)

The ISO brightness and chromatic parameters (L^* , a^* , b^*) of the hydrogen peroxide bleached pulp sheets after being exposed to sunlight for 1, 2, 4.5, and 16 hours, when the initial MC was 0% or 20%, are shown in Fig. 7.

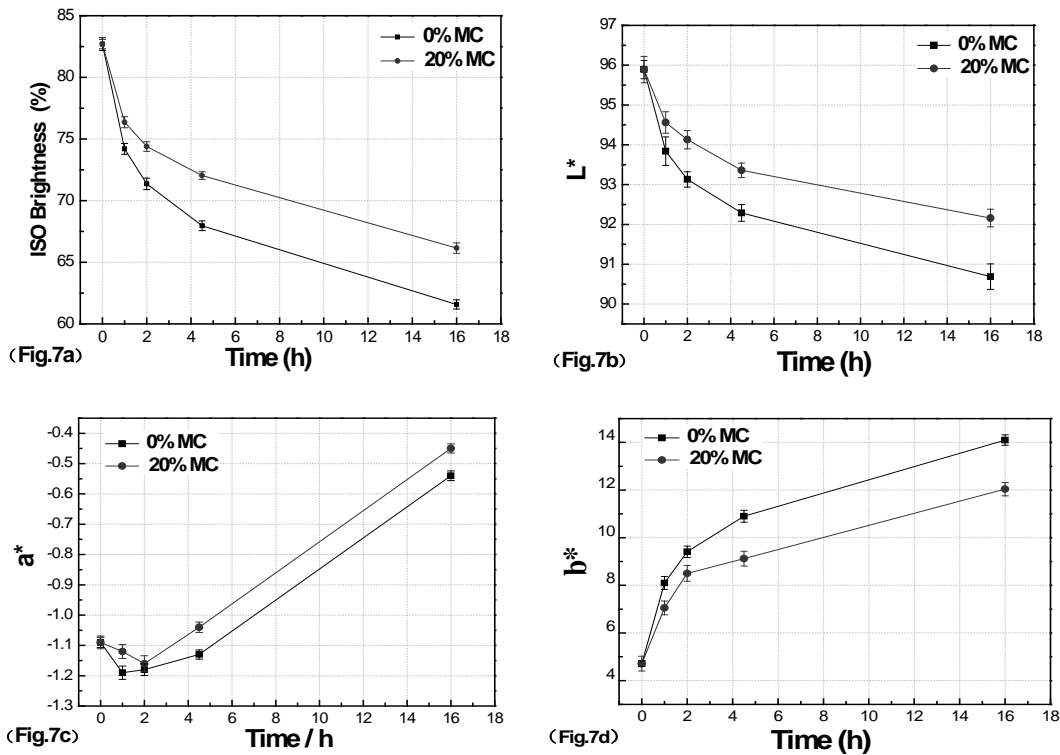


Fig. 7. Brightness and color parameters of BCTMP exposed to sunlight for different times. (a) ISO Brightness; (b) L^* ; (c) a^* ; (d) b^*

A rapid decrease in brightness and L^* was observed when the irradiation time increased. Lower brightness of the pulp with 0% initial MC was observed compared with 20% MC. The a^* values decreased after the first 1 to 2 hours of irradiation when the MC

was 0% or 20%, and then increased with the increase in exposure time. It is worth noting that the a^* values decreased in the first 2 hours of irradiation. The cause of this initial decrease in a^* values is presently unknown. It is possible that during the initial 2 hours, the rate of diffusion of the chromophores to the surface of the pulp is lower than their rate of migration or conversion into other colorless surface compounds. Longer irradiation time and higher initial MC resulted in an increase in a^* .

Although both a^* and b^* values increased with irradiation time, initial moisture content affected the a^* and b^* values differently. At 0% MC, the a^* values were lower compared with a^* values at 20% MC. However, the opposite was true for the b^* values, which were higher at 0% MC compared with 20% MC. The increase in b^* suggested that irradiation resulted in the formation of new products that absorbed in the violet-green region of visible light (i.e., an increase in visible yellowing).

A comparison of the DRUV spectra of the pulp samples exposed to sunlight is shown in Figs. 8a and 8b.

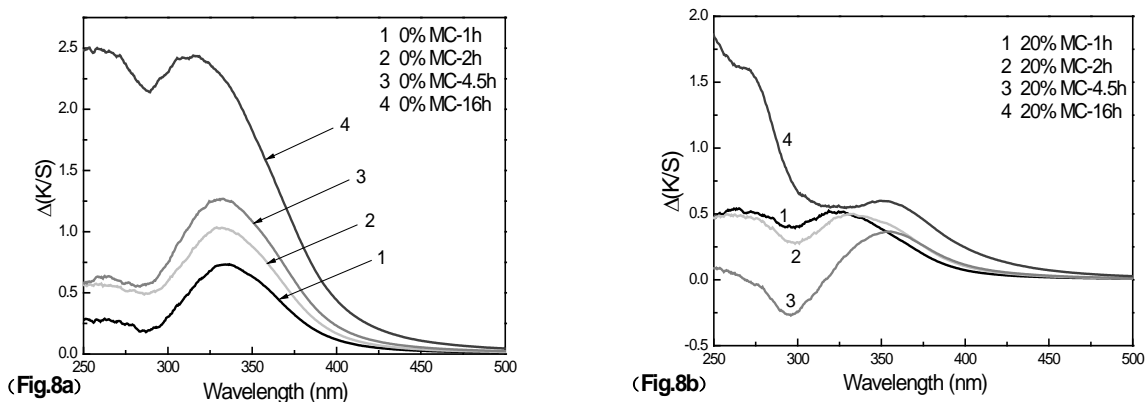


Fig. 8. DRUV spectra of BCTMP irradiated for different time at (a) 0% MC, and (b) 20% MC

A clear increase in absorption can be observed at 330 nm after the pulp had been exposed to the sunlight for a period of time when the initial MC was 0%. This is believed to be due to the formation of conjugated carbonyl groups (Imsgard 1971). By comparison, the absorption bands at 330 nm were much smaller when the initial MC was 20%, while a new absorption band at 350 nm appeared after longer irradiation time. The increase in absorption in the UV region at 320 to 360 nm has been attributed to the formation of aromatic carbonyl groups and to the formation of quinones, possibly methoxylated para- or ortho-quinones. It is also possible that coniferaldehyde with an absorption maximum at 350 nm, generated through photo-oxidation of coniferyl alcohol end-groups, contributes to the UV-absorption peak.

CONCLUSIONS

The evolution of optical properties of CTMP from *Eucalyptus camaldulensis* caused by aging was investigated. The brightness and L^* decreased, and the chromaticity a^* and b^* increased after heat treatment. Increase in chromophores upon heating was

enhanced with an increase in initial MC. There is a linear correlation between the pulp initial MC and the intensity of absorption at 330 nm and 350 nm in DRUV spectra. Conjugated carbonyl groups were formed in the heating process by depolymerization or oxidation pathways.

The different types of chromophores in CTMP from *Eucalyptus camaldulensis*, which contribute to the color conversion, were evaluated with the help of different bleaching and aging processes. The brightness and L^* values of the pulp increased after bleaching, while both the chromaticity a^* and b^* decreased. The absorption bands near 280 and 320 nm can be decreased by sodium borohydride or hydrogen peroxide treatment. The bands near 360 nm were considerably decreased by treatments with hydrogen peroxide. Sodium dithionite bleaching also diminished some of the carbonyls and double bonds conjugated with aromatics. Coniferaldehyde degraded after bleaching. The results based on the variation of the maximum intensity of the $\Delta(K/S)$ spectra with the bleaching process are in good agreement with the results obtained by the CIELab system. Color substances that absorbed in the violet-green region of the visible spectrum to produce a yellowish color were formed after irradiation. An increased concentration of quinoid structures was found when the pulp was exposed to sunlight due to photo-induced oxidation. From an applications point of view, this result indicates that for *Eucalyptus* CTMP, sodium borohydride treatment is consistently better than sodium dithionite in decreasing absorption across the entire UV/visible region, with the most significant decrease at 320 nm. Similar to sodium borohydride treatment, the main mode of reaction of hydrogen peroxide treatment is destruction of conjugated carbonyls, such as coniferaldehyde and quinones substances. Longer irradiation time and higher initial MC resulted in a more reddish and yellowish color. The oxidation and polymerization reactions of pyrocatechols are responsible for the formation of these dark color substances.

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REFERENCES CITED

- Agarwal, U. P., and Atalla, R. (1993). "Chapter 2 Raman spectroscopic evidence for coniferyl alcohol structures in bleached and sulfonated mechanical pulps," In: Heitner, C., and Scaiano, J. C. (eds.), *Photochemistry of Lignocellulosic Materials*, ACS Symposium Series 531, Proceedings of 203rd national meeting of the American Chemical Society, 1992 April 5-10, San Francisco. Washington, DC: American Chemical Society, 26-44.

- Agarwal, U. P. (1998). "Assignment of the photo yellowing-related 1675 cm⁻¹ Raman/IR band to p-quinones and its implications to the mechanism of color reversion in mechanical pulps," *J. wood Chem.Technol.* 18(4), 381-402.
- Agarwal, U. P., and Landucci, L. L. (2004). "FT-Raman investigation of bleaching of spruce thermomechanical pulp," *J. Pulp Paper Sci.* 30, 269-274.
- Archard, M., and Michell, A. J. (1989). "Diffuse reflectance ultraviolet spectroscopic studies of paper," *UV Instruments at Work* 49, 1-4.
- Bekhta, P., and Niemz, P. (2003). "Effect of high temperature on the change in color, dimensional stability and mechanical properties of spruce wood," *Holzforschung* 57, 539-546.
- Bonini, C., D'Auria, M., D'Alessio, L., Mauriello, G., Viggiano, D., and Zimbardi, F. (1998a). "Singlet oxygen degradation of lignin in the pulp," *J. Photochem. Photobiol. A: Chem.* 118, 107-110.
- Bonini, C., D'Auria, M., D'Alessio, L., Mauriello, G., Tofani, D., and Viggiano, D. (1998b). "Singlet oxygen degradation of lignin," *J. Photochem. Photobiol. A: Chem.* 113, 119-124.
- Bonini, C., Carbone, A., and D'Auria, M. (2002). "Singlet oxygen mediated degradation of lignin. A kinetic study," *Photochem. Photobiol. Sci.* 1(6), 407-411.
- Carey, F. A., and Sundberg, R. J. (1983). *Advanced Organic Chemistry. Part B: Reactions and Synthesis*, Plenum Press, New York.
- Castallan, A., Nourmamode, A., Fournier de Violet, P., Colombo, N., and Jaeger, C. (1992). "Photoyellowing of milled wood lignin and peroxide-bleached milled wood lignin in solid 2-hydroxypropyle cellulose after borohydride reduction catalytic hydrogenation in solution: An UV-visible absorption study," *J. Wood Chem. Technol.*, 12, 1-7.
- Crestini, C., and D'Auria, M. (1996). "Photodegradation of lignin: The role of singlet oxygen," *J. Photochem. Photobiol. A: Chem.* 101, 69-73.
- Crestini, C., and D'Auria, M. (1997). "Singlet oxygen in the photodegradation of lignin models," *Tetrahedron* 53, 7877-7888.
- Ek, M., Lennholm, H. G., and Iversen, T. (1992). "A study on the mechanism of the photo-yellowing of partially acetylated groundwood pulps," *Nord. Pulp Pap. Res. J.* 7, 108-112.
- Fournier de Violet, P., Nourmamode, A., Colombo, N., Zhu, J. H., and Castellan, A. (1990). "Photochemical brightness reversion of peroxide bleached mechanical pulps in the presence of various additives," *Cellulose Chem. Technol.* 24(2), 225-235.
- Forman, L. V. (1940). "Action of ultraviolet light on lignin," *Paper Trade J.* 111, 34-39.
- Furman, G. S., and Lonsky, W. F. W. (1986). "Charge-transfer complexes in kraft lignin. Part 3: Implications on the possible occurrence of charge-transfer complexes in residual lignin and in lignin of light-induced yellowed high-yield pulps," IPC Technical Paper Series Number 198, The Institute of Paper Chemistry, Appleton, WI, USA.
- Furman, G. S., and Lonsky, W. F. W. (1988). "Charge-transfer complexes in kraft lignin part 1: Occurrence," *J. Wood Chem. Technol.* 8(2), 165-189.
- Gellerstedt, G., and Zhang, L. (1992). "Formation and reactions of leucochromophoric structures in high-yield pulping," *J. Wood Chem. Technol.* 12(4), 387-412.

- Heitner, C. (1993). "Light induced yellowing of wood containing papers," In: Heitner, C., and Scaiano, J. C. (eds.), *Photochemistry of Lignocellulosic Materials*, ACS Symposium Series, 531, New York, USA: American Chemical Society, pp. 3-25.
- Hirashima, A., Tarui, H., and Eto, M. (1994). "Synthesis and octopaminergic agonist activity of 2-(arylimino)thiazolidines, 2-(aralkylamino)-2-thiazolines and related compounds," *Biosci Biochem Biotech.* 58, 1206-1209.
- Holthuis, J. J. M., van Oort, W. J., Römken, F. M. G. M., Renema, J., and Zuman, P. (1985). "Electrochemistry of podophyllotoxin derivatives. Part 1. Oxidization mechanism of etoposide (VP-16-213)," *J. Electroanal. Chem.* 184, 317-329.
- Hon, D. N. S. (1991). *Photochemistry of Wood*. In: Hon, D. N. S., Shiraishi, N. (eds.), *Wood and Cellulosic Chemistry*, Marcel Decker Inc., New York, Basel, pp. 525-555.
- Hon, D. N. S., and Chang, S. T. (1982). "Participation of singlet oxygen in the photodegradation of wood surfaces," *Wood Sci. Technol.* 16, 193-201.
- Imsgard, F., Falkehag, S. I., and Kringstad, K. P. (1971). "On possible chromophoric structures in spruce wood," *Tappi* 54(10), 1680-1684.
- Jääskeläinen, A. S., Saariaho, A. M., Vyörykkä, J., Vuorinen, T., Matousek, P., and Parker, A. W. (2006). "Application of UV-Vis and resonance Raman spectroscopy to study bleaching and photoyellowing of thermomechanical pulps," *Holzforschung* 60(3), 231-238.
- Keating, J., Johansson, C. I., Saddler, J. N. and Beatson, R. P. (2006). "The nature of chromophores in high-extractives mechanical pulps: Western red cedar (*Thuja plicata* Donn) chemithermomechanical pulp (CTMP)," *Holzforschung* 60, 365-371.
- Kishino, M., and Nakano, T. (2004). "Artificial weathering of tropical woods. Part 2: Color change," *Holzforschung* 58 (5), 558-565.
- Kubelka, P., and Munk, F. (1931). "Ein Beitrag zur Optik der Farbanstriche," *Zeitschrift für technische Physik* (12), 593-601.
- Kubelka, P. (1948.) "New contributions to the optics of intensely light-scattering materials. Part I," *Journal of the Optical Society of America* 38(5), 448-457.
- Lapierre, L., Bouchard, J., Berry, R. M., and Van Lierop, B. (1995). "Chelation prior to hydrogen peroxide bleaching of kraft pulps: An overview," *Journal of Pulp and Paper Science* 21(8), J268-273.
- Mitsui, K. (2004a). "Changes in the properties of light-irradiated wood with heat treatment. Part 2. Effect of light irradiation time and wavelength," *Holz Roh Werkst* 62, 23-30.
- Mitsui, K., Murata, A., and Tolvaj, L. (2004b). "Changes in the properties of light-irradiated wood with heat treatment. Part 3. Monitoring by DRIFT spectroscopy," *Holz Roh Werkst* 62, 164-168.
- Müller, U., Rätzsch, M., Schwanninger, M., Steiner, M., and Zöbl, H. (2003). "Yellowing and IR-changes of spruce wood as result of UV-irradiation," *J. Photochem. Photobiol. B: Biol.* 69(2), 97-105.
- Pan, X., Lachenal, D., Lapierre, C., Monties B. (1992). "Structure and reactivity of spruce mechanical pulp lignins part1: Bleaching and photobleaching of in situ lignins," *J. Wood Chem. Technol.* 12, 135-147.
- Pandey, K. K. (2005). "A note on the influence of extractives on the photodiscolouration and photo-degradation of wood," *Polym. Degrad. Stab.* 87, 375-379.

- Paulsson, M., and Ragauskas, A. J. (2000). "Chemical modification of lignin-rich paper. Light-induced changes of softwood and hardwood chemithermomechanical pulps: The effect of irradiation source." In: *Lignin: Historical, Biological, and Materials Perspectives*, Glasser, W. G., and Northey, R. A., and Schultz, T. P. (eds.), ACS Symposium Series, American Chemical Society, Washington, 742, 490-504.
- Paulsson, M., and Simonson, R. (2002) "Acetylation of lignin and photostabilization of lignin-rich mechanical wood pulp and paper," In: *Chemical Modification Properties and Usage of Lignin*, Hu, T. Q. (ed.), Kluwer Academic/ Plenum, New York, USA, 221-245.
- Polcin, J., and Rapson, W. H. (1971). "Effects of bleaching agents on the absorption spectra of lignin in groundwood pulps: Part 1. Reductive bleaching," *Pulp Pap. Mag. Can.* 72(3), 69-80 (T103-T125).
- Schmidt, J. A., and Heitner, C. (1992). "Light induced yellowing of mechanical and ultra high yield pulps. Part 2: The role of etherified guaiacylglycerol- β aryether groups," in Proceeding 2nd Eur. Work. Lignocel and Pulp, Grenoble, France, 49-55.
- Schmidt, J. and Heitner, C. (1999). "Use of diffuse reflectance UV-visible spectroscopy to characterize chromophores in wood fibers," In: *Advances in Lignocellulosics Characterization*, Argyropoulos, D. S. (ed.), TAPPI Press, Atlanta, GA, pp. 179-199.
- Scott, A. I. (1964). *Interpretation of the Ultraviolet Spectra of Natural Products*, Pergamon, London, pp. 102.
- Van den Akker, J. A., Lewis, H. F., Jones, G. W., and Buchanan, M. A. (1949). "The nature of the color changes in groundwood," *Tappi* 32, 4, 187-192.
- Wikberg, H., and Maunu, S. (2004). "Characterisation of thermally modified hard- and softwoods by ¹³C-CPMAS NMR," *Carbohydr. Polym.* 58, 461-466
- Leigh, W. J., Lewis, J., Lin, V., and Postigo, J. A. (1996). "The photochemistry of 3, 3', 4, 4'-tetramethoxyand 4-hydroxy-3, 3', 4'-trimethoxystilbene-models for stilbene chromophores in peroxide-bleached, high-yield wood pulps," *Can. J. Chem.* 74, 263-275.
- Williams, D. H., and Fleming, I. (1995). *Spectroscopic Methods in Organic Chemistry*, 5th Ed., McGraw-Hill International, Bath, UK.
- Zhu, J. H., Olmstead, J. A., and Grey, D. G. (1995). "Fluorescent detection of o-quinones formed in lignin-containing pulps during irradiation," *J. Wood Chem. Technol.* 15(1), 43-64.
- Zhang, L., and Gellerstedt, G. (1998). "Quinonoid lignin chromophores and their contribution to photoyellowing," 3rd European Workshop on Lignocellulosics and Pulp, Stockholm, Sweden, August 28-31, pp. 293-295.

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