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Photoyellowing of chemically modified chemithermomechanical pulps (CTMP) from *Eucalyptus globulus* under various atmospheres

Abstract: Chemithermomechanical pulps (CTMP) were prepared from *Eucalyptus globulus* and photoirradiated, and the responses have been examined by means of ultraviolet (UV) microspectrophotometer. The absorbance in the UV spectra of fiber walls increased in the range of 300 to 350 nm as a result of photoirradiation, indicating the formation of conjugated double-bond systems in the fiber walls. These spectral changes occurred only on the irradiated surface of sheets. CTMP photoirradiation under various atmospheres indicated that the presence of oxygen in the irradiation atmosphere is not necessary for CTMP yellowing. In nitrogen or vacuum, photoyellowing was at the same level as observed under oxygen. This observation was interpreted as a result of direct elimination of proton radicals from free phenolic groups and/or cleavage of β -aryl ether linkages. This induced probably the excited triplet state of α -carbonyl structures in CTMP, which leads to chromophore formation in the absence of oxygen. Reduction of CTMP with sodium borohydride impeded effectively the effects of photoirradiation only in the absence of oxygen. On the contrary, acetylation of CTMP had no effect in the absence of oxygen but led to photobleaching in the presence of oxygen.

Keywords: chemical modification of CTMP, CTMP, *Eucalyptus*, oxygen, photoyellowing, UV microspectrophotometer (UMSP)

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Introduction

Mechanical and chemomechanical pulps contain a large amount of lignin and extractives and these lead to the problematic photoinduced yellowing via oxidative mechanisms of high-quality printing papers (Spinner 1962; Leary 1968; Kringstadt 1969; Heitner 1993). It was established that lignin-based reactions are more relevant with this regard than those of extractives. Several reaction mechanisms have been proposed:

- The key pathway is initiated by photoinduced radical reactions (Schmidt and Heitner 1997).
- The phenoxyl pathway is promoted by direct excitation or free radical scavenging by phenolic groups (Castellan et al. 1990; Jaeger et al. 1993; Li and Ragauskas 1999).
- The phenacyl pathway is initiated by direct excitation of carbonyl groups (Gratzl 1985; Vanucci et al. 1988; Castellan et al. 1989; Hon 1992).
- The phenoxyl quinone redox cycle is also possible (Castellan et al. 1993; Ragauskas 1993; Lennholm et al. 1994).
- Stilbene photodegradation also may contribute to the process (Gellerstedt and Zhang 1992; Leigh et al. 1996).

Carbonyl and phenolic hydroxyl groups play an important role in the photoyellowing of papers, which is mediated by quinone formation from lignin structures. Agarwal (1999) pointed out that pathways that lead to the formation of stilbenes and/or *o*-quinones are not important and other authors also found that stilbene does not play a key role in photoyellowing (Ruffin et al. 1998; Ruffin and Castellan 2000). Strong experimental support was presented for the direct photo-oxidation of hydroquinones to *p*-quinones, whereas hydroquinones could be identified in pulps before photoirradiation by Raman methods (Agarwal 1998). On the contrary, the role of *o*-quinones in chemithermomechanical pulps (CTMP) of western red cedar was emphasized by Keating et al. (2006).

The mechanisms of photoyellowing are very complex. In the present article, the influence of the atmosphere on the photoyellowing is in focus, as literature data with this regard are not transparent in view of the many parameters influencing the results. Therefore, acetylated and/or reduced *Eucalyptus* CTMP were photoirradiated under various atmospheres to provide a better understanding of the contributions of oxygen, carbonyl groups, and phenolic hydroxyl groups in the lignin structure of CTMP to photoyellowing of CTMP.

Materials and methods

Materials

Two *Eucalyptus globulus* trees (T39 and M17, age 9.5 years) were selected from two plantation sites in Western Australia. Wood chips were prepared in a laboratory chipper, and the average chip size was 25–30 mm in length, 15–20 mm in width, and 2–3 mm in thickness.

CTMP preparation

The chips were impregnated with a 5% sodium sulfite solution at 70°C for 1 h before refining. The first refining was conducted at 135°C (preheating, 5 min; refining, 3 min) in a D-type defibrator. A PFI mill was used for the second refining (pulp consistency, 20%; clearance, 5 mm). Refined pulps were screened by a laboratory flat screen with an 8 cut plate. Refined CTMP were produced from the samples T39 and M17.

Photoirradiation and ultraviolet (UV) spectra

Hand sheets from unmodified CTMP (samples T39 and M17) were irradiated with UV light at 360 nm for 60 min. The brightness of the sheets was measured before and after photoirradiation. Subsequently, the irradiated CTMP sheets were cut into sections (1×3 mm) and embedded in epon resin. Cross-sections (thickness, 1 μm) from the embedded sheets were cut with a glass knife on an ultra-microtome. Measured spots in several fiber walls in the sections were selected from the irradiated surface, center area, and back side (opposite to irradiated side) of the paper sheets (Figure 1). UV spectra of the spots with 1 μm diameter in the fiber walls were measured with a Carl-Zeiss UV microspectrophotometer (UMSP).

Chemical modification

A part of CTMP T39 was air-dried and acetylated with acetic acid anhydride in a pyridine solution and then reduced with sodium borohydride. Hand sheets (180 g m⁻² basis weight) were prepared from unmodified and modified CTMP by a hand sheet machine.

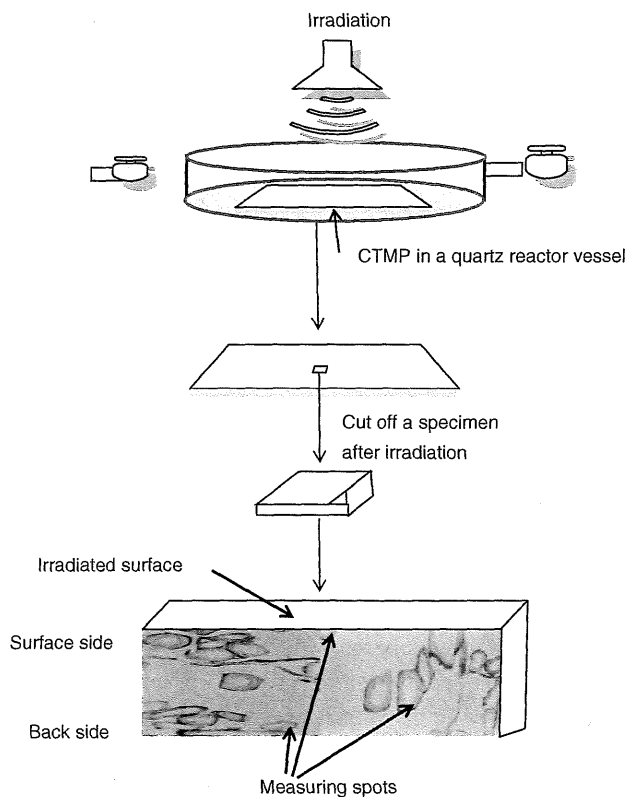


Figure 1 Preparation of ultrathin sections from irradiated pulp sheets.

Photoirradiation under variable atmospheric conditions

Hand sheets from unmodified and modified CTMP T39 were placed in a quartz vessel, which was evacuated, and oxygen or nitrogen was introduced by means of a vacuum-purge procedure (repeated three times). Then, the test sheets were photoirradiated with a UV lamp for 30, 60, and 120 min. The quartz vessel was 15 mm in height and 65 mm in diameter, and paper sheet size was 50×50 mm². The brightness of CTMP sheets was measured before and after photoirradiation according to Kojima et al. (2008). ΔB was calculated as an index of the color reversion: $\Delta B = 100 (B_0 - B_i) / (B_0)$, where B_0 is the brightness of CTMP sheets before UV photoirradiation and B_i is the brightness of CTMP sheets after irradiation for 30, 60, and 120 min.

Results and discussion

UV spectra of fiber walls in paper sheets

Two paper sheets were prepared; sample T39 was selected from a high photosensitive CTMP and sample M17 from a less photosensitive CTMP. Their chemical and optical properties are shown in Table 1.

Table 1 Chemical and physical properties of the samples derived from the *E. globulus* trees M17 and T39

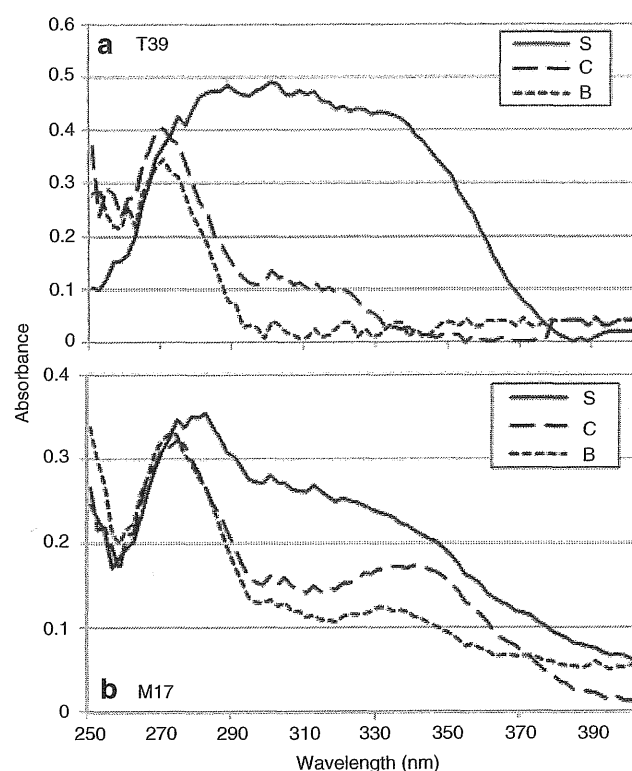
	M17	T39
Holocellulose	86.4	86.9
α -Cellulose	44.9	46.7
Klason lignin	17.0	15.9
Extractives	3.7	2.8
Brightness, ISO%	64.9	66.5
Pc No.	1.95	2.15
ΔB	18.5	22.4
SO ₃ ⁻ , mmol/100 g	10.1	15.3
COO ⁻ , mmol/100 g	82.4	79.6

$$*Pc\ No.=\frac{[(1-R_{24})^2/2R_{24}-(1-R_0)^2/2R_0]}{R_0}\times 100.$$

R_0 is brightness of CTMP and R_{24} is brightness after 24 h heating.

Changes in the UV spectra of fiber walls of the photoirradiated paper are presented in Figure 2. In each sample, the UV spectrum of the fiber wall on the irradiated surface of the sheets indicated strong absorbance in the region of 270–350 nm, and a significant increase in absorbance was observed for sample T39 because of its high photosensitivity.

Obviously, a conjugated double-bond system was induced only in the surface layers in the lignin structures

**Figure 2** UV spectral changes of irradiated fiber wall of the samples: (a) T39 and (b) M17. B, sample from the back-side; C, sample from the center; S, surface sample.

upon irradiation, as the center and backside of the irradiated sheets were not affected significantly. Paulsson et al. (2001) described similar results while measuring the UV-visible absorbance of paper sheets by diffuse reflectance spectroscopy and found that absorbance in the range of 300–400 nm increases after photoirradiating under oxygen or nitrogen atmosphere.

Effect of temperature upon irradiation on ΔB of CTMP

Radical reactions, such as abstraction of proton radicals from phenolic hydroxyl groups, are accelerated at higher temperatures (Albaladejo et al. 2003). To estimate this effect, the pulp sheets were subjected to photoirradiation at -2°C , 25°C , and 70°C in air. As shown in Figure 3a, increasing the irradiation temperature from 25°C to 70°C enhanced the brightness loss (ΔB) and this result confirms corresponding literature data. It was found nearly seven decades before (Nolan et al. 1945) that photoyellowing is higher at 100°C compared with that at room temperature, when ground wood pulp (GP) is irradiated in a quartz vessel with a mercury arc lamp. The influence of temperature on the formation of quinone structures in wood was clearly elaborated by Ganne-Chédeville et al. (2012) by means of Fourier transform infrared-attenuated total reflection and ultraviolet (UV) resonance Raman techniques.

Effect of atmospheric gas on photoyellowing

The rates of ΔB of the CTMP sheets initiated by UV photoirradiation under variable atmospheres are listed in Table 2. For unmodified CTMP, replacing air with nitrogen or vacuum had no noticeable effect on ΔB , whereas the ΔB under oxygen atmosphere was somewhat lower than that in air and nitrogen (Figure 3b). Accordingly, oxygen seems to suppress photoyellowing to some extent.

This finding specifies literature data as one of the most important intermediates for chromophore formation – the phenoxy radical – supposed to be oxidized to quinone chromophores by oxygen, peroxy, and alkoxy radicals (Schmidt and Heitner 1995). According to Beyer et al. (1995), oxygen plays a key role in chromophore formation. A frequent proposal is that carbon-centered radicals, generated by photodegraded lignin, combine with oxygen and give rise to peroxy and alkoxy radicals. These reactive intermediates have been suggested to be involved in the formation of ketyl structures (Leary 1994).

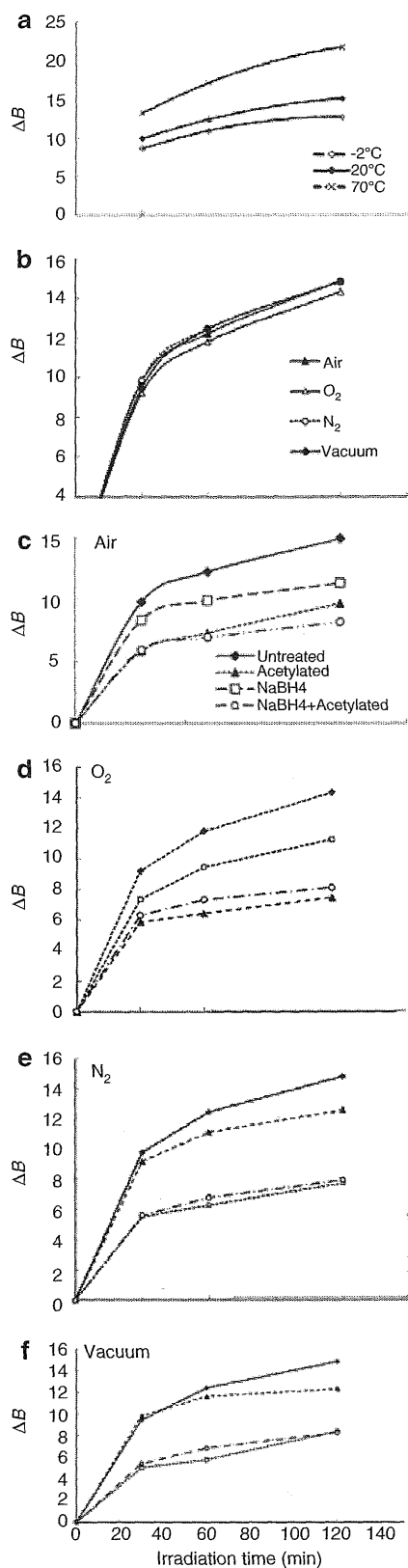


Figure 3 Changes of color (ΔB) of various CTMPs as a function of irradiation time and other parameters. (a) Irradiation temperature, (b) irradiation atmosphere, (c) treatment type in air, (d) treatment type in O_2 , (e) treatment type in N_2 , and (f) treatment type in vacuum.

Photoyellowing of mechanical pulps in oxygen and in unreactive atmospheres of nitrogen or carbon dioxide was compared a long time ago. For example, Leary (1968) reported that photoyellowing of newsprint papers did not occur when irradiated under nitrogen or carbon dioxide atmosphere. Distine et al. (1996) demonstrated that photolysis of MWL in a dioxane solution is different in oxygen and in nitrogen atmosphere. In the latter, MWL underwent both photofragmentation and polymerization reactions, whereas, in oxygen, only photofragmentation occurred. It was also observed that lignin-rich papers in inert atmosphere or in vacuum did not alter essentially their general behavior, and only a slight decrease in the extent of photoyellowing was observed (Andtback et al. 1989).

The deviating results to literature data may be partly explained by the different wood species under study. Li and Ragauskas (2000) pointed out that the photoyellowing behavior of hardwood and softwood CTMPs are different. However, the influence of the atmosphere on the photoyellowing is not yet clear in view of the great number of the yellowing parameters, such as the light source, the wavelength, irradiation time, wood species, and the content and properties of different components of the pulp sheets (amount and structure of lignin and extractives; trace elements; water content). The observation that photoyellowing occurs in the absence of oxygen can be interpreted that the elimination of proton radicals from free phenolic groups and/or cleavage of β -aryl ether linkages is induced by the excited triplet state of α -carbonyl structures in CTMP. Both reactions introduce phenoxy radicals followed by formation of colored quinones within the lignin molecules.

The role of oxygen in photoyellowing of mechanical pulps cannot be ignored or neglected. Oxygen may stimulate quinone formation, but also photobleaching may be promoted by oxygen. Leary (1967) showed that yellowing is induced at 360–410 nm but also in the range of the visible light 410 to least 520 nm. Andray et al. (1991) reported that the transition from photoyellowing to photobleaching occurs between 340 and 400 nm, and this effect is well pronounced in the range of 500–600 nm. Dugal and Aziz (1993) observed that, below 340 nm, photoyellowing takes place and, between 340 and 400 nm, photobleaching is prevailing. Accordingly, in the case of photoirradiation at 360 nm, photoyellowing and photobleaching of TMPs go parallel. This is the reason why changes in ΔB of in oxygen or air are influenced by these competing reactions. In this context, it is remarkable that the modern UV resonance Raman spectroscopy method may contribute a lot for elucidating the mechanisms of photoyellowing and bleaching of TMPs (Jääskeläinen et al. 2006).

Table 2 Yellowing (ΔB data) of modified pulps after photoirradiation under various atmospheres

Modification	Atmospheres	ΔB data after the irradiation times of			
		0 min	30 min	60 min	120 min
Untreated	Air	0	9.79	12.22	14.88
	O ₂	0	9.20	11.80	14.32
	N ₂	0	9.80	12.46	14.83
	Vacuum	0	9.46	12.43	14.86
Acetylated	Air	0	5.82	7.28	9.66
	O ₂	0	5.85	6.43	7.47
	N ₂	0	9.21	11.13	12.61
	Vacuum	0	9.83	11.64	12.32
Reduced	Air	0	8.34	9.89	11.29
	O ₂	0	7.34	9.46	11.26
	N ₂	0	5.53	6.31	7.75
	Vacuum	0	5.05	5.78	8.39
Acetylated+reduced	Air	0	5.93	6.93	8.16
	O ₂	0	6.31	7.33	8.12
	N ₂	0	5.53	6.70	7.83
	Vacuum	0	5.42	6.86	8.28

Effect of chemical modification on photoyellowing

The effects of chemical modification of pulps on photoyellowing are presented in Figures 3c to f. In all samples, the initial ΔB rates were fast, and the extent of yellowing rate became gradually slow for the irradiation period from 60 to 120 min. Figure 3c shows the effects of acetylation and reduction with sodium borohydride.

The reduction converts the carbonyl groups to hydroxyl groups, and by this, mean photosensitive moieties such as α -carbonyl, conjugated aldehyde, coniferyl aldehyde, and *p*-hydroquinone groups are eliminated. Surprisingly, the effect of the removal of the photosensitive carbonyl groups turned out to be very limited. In contrast, derivatization of hydroxyl groups by acetylation resulted in strong suppression of photoyellowing in air. This effect was also observed with reduced and acetylated CTMPs, and this effect was stable even after 120 min irradiation. According to the literature, reduction with sodium borohydride does not photostabilize GP against light reversion in air (Manchester et al. 1960; Leary 1968; Lorås and Rengard 1969; Tschirner and Dence 1988). In this context, the finding of Agarwal (1999) is remarkable that α -carbonyl groups, stilbenes, and *o*-quinones are not important for photoyellowing of mechanical pulps.

The effects of chemical modification on photostability under oxygen are shown in Figure 3d. Whereas the acetylated CTMP was slightly protective against photoirradiation rather than the reduced and acetylated CTMP, the

responses of the modified CTMP sheets to irradiation were similar to those in air. The positive effect of acetylation of mechanical pulps was also observed by others (Manchester et al. 1960; Ek et al. 1992; Paulsson et al. 1995). Lorås (1968) proposed the formation of acetyl peroxide or peroxides derived from carbohydrate acetates during irradiation. Also here, the competing effects of photoyellowing and photobleaching should be considered. For example, the apparently suppressed photoyellowing by acetylation may also be the result of the contribution of photobleaching effects.

Opposite effects of reduction and acetylation were observed on irradiation under nitrogen (as shown in Figure 3e). Reduction of CTMP resulted in effective resistance to photoirradiation, whereas acetylation of CTMP had no effect on photoyellowing. Probably, radical cleavage of β -aryl ether linkages initiated by the excited triplet state of α -carbonyl groups occurred and led to the formation of new phenoxy radicals in lignin. In this case, acetylation was not helpful and only reductive treatment suppressed photoyellowing in nitrogen atmosphere. The same results were obtained under irradiation in vacuum as shown in Figure 3f. Irradiation under nitrogen or vacuum should induce the same photoyellowing reactions. The absence of oxygen may inhibit chromophore formation by reduction of carbonyl groups in CTMP. On the contrary, acetylation of CTMP had essentially no effect on resistance to photoirradiation under nitrogen or vacuum, and in the presence of oxygen, photobleaching occurred.

Conclusion

Hand sheets from *Eucalyptus* CTMP were photoirradiated; then, the fiber walls in the hand sheets were analyzed with UMSP. The absorbance of fiber walls increased in the range of 300–350 nm by photoirradiation because conjugated double-bound systems were created in the cell walls. These spectral changes occurred only on the irradiated side of the hand sheets, and no substantial changes were observable in the central and backside.

The results of CTMP photoirradiation under various atmospheres indicated that the presence of oxygen was not necessary for photoyellowing. Apparently, chromophore

formation is also possible in nitrogen or vacuum via direct elimination of proton radicals from free phenolic groups and/or cleavage of β -aryl ether linkages. Probably, oxygen accelerates the chromophore formation, such as quinone structures, but it also contributes to their photodecomposition. Reduction of CTMP with sodium borohydride provided effective resistance to photoirradiation only in the absence of oxygen. On the contrary, acetylation of CTMP had no effect in the absence of oxygen but promoted oxygen-mediated photobleaching.

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