Studies on photostability of butyrylated, milled wood lignin using spectroscopic analyses

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Abstract

Photo-stabilisation of butyrylated milled wood lignin (MWL) was investigated in this study. Chemical changes were confirmed by NMR and FT-IR spectra after butyrylation. Improvements in the photostability of MWL by butyrylation were evaluated by spectral analyses including ESR, FT-IR and UV–VIS spectra. From ESR analyses, butyrylation reduces the amount of phenoxyl free radicals of MWL after UV irradiation, which results in inhibiting the photo-oxidation of lignin followed by a significant decrease in the formation of colored chromophores. The carbonyl, carboxyl and quinonoid structures were less detected in the butyrylated MWL after UV irradiation than those of untreated MWL, and the content of degraded water-soluble materials from the photo-degradation of MWL was also reduced upon butyrylation.

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1. Introduction

Lignin is not only one of the major components of lignocellulosic materials but also an abundant natural polymeric material on earth [1]. Lignin is an amorphous, polyphenolic material arising from an enzyme-mediated dehydrogenative polymerization of three phenylpropanoid monomers, coniferyl, sinapyl and *p*-coumaryl alcohols. The functional groups attached to the phenylpropanoid skeleton include phenolic hydroxyl, benzylic hydroxyl, and carbonyl groups. As a consequence of light absorption by lignin chromophores, lignin is destroyed by UV light. Initially, the discoloration of lignocellulosic material is readily observed [2–5]. It is found that the main chemical species causing the photo-discoloration of wood or high-yield pulps is lignin [6–11].

Four possible routes have been proposed for the photo-oxidation of lignin. Route 1: direct absorption of UV light by conjugated phenolic groups to form the phenoxyl radicals; route 2: abstraction of phenolic hydroxyl hydrogen as a result of aromatic carbonyl triplet excitation to produce ketyl and phenoxyl radicals; route 3: cleavage of non-phenolic phenacyl- α -O-arylethers to phenacyl–phenoxyl radical pairs; and route 4: abstraction of the benzylic hydrogen of the guaiacylglycerol- β -arylether group to form the phenoxyl radicals [7]. The phenoxyl radicals would readily be oxidized to form the quinonoid colored chromophores [6,7]. Resolving the problem of photo-discoloration of wood or lignin-rich pulps remains a challenging area of wood chemistry and pulp and papermaking research.

There are two modes of inhibiting photo-yellowing of lignin-containing materials. The first mode involves the use of chemical additives applied to the wood or high lignin-containing paper to block UV light using UV absorbing compounds or quenching the phenoxyl

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free-radical with hydrogen donating compounds [7,11–13]. The second mode involves chemical modification of lignin by substitution of the phenolic hydroxyl group so as to stop the initiation and subsequent radical reactions of reactive functional groups leading to the formation of chromophoric derivatives [14–16]. Paulsson et al. reported that the chromophores formed during UV irradiation of acetylated chemithermomechanical pulp (CTMP) were substantially less in the whole UV–VIS region [17]. In our previous study, the efficiency of butyrylation in preventing the photo-discoloration of wood was more remarkable than that of acetylation [18,19]. The detailed mechanisms of photo-yellowing inhibition of butyrylated wood need further investigations.

The MWL has been used as a representative source of native lignin. Therefore, the photochemistry of lignin has been frequently studied with MWL [6,11,20]. In this paper we report the chemical changes of MWL during photo-oxidation by FT-IR and ESR spectroscopies, the chemical characteristics of MWL after butyrylation, and the photo-stabilising effect on milled wood lignin of butyrylation.

2. Material and methods

2.1. Preparation of milled wood lignin

China fir (*Cunninghamia lanceolata* var. *lanceolata*) sawdust (60 mesh) was extracted in a Soxhlet apparatus with alcohol–toluene (1:2, v/v) for 24 h, followed by another extraction with water for 24 h and then oven-dried at 105 °C. The milled wood lignin (MWL) was isolated using a planetary ball mill (Retsch PM400) according to methods reported elsewhere [21,22].

2.2. Butyrylation of milled wood lignin

Milled wood lignin was immersed in neat liquid butyric anhydride and heated at 125 °C for 3 h. After the treatment, the butyrylated MWL specimens were purified to remove unreacted anhydride, and then oven-dried. The weight gain (W_G) of MWL after butyrylation was 36%.

2.3. ^1H NMR spectra

^1H NMR (^1H nuclei magnetic resonance) spectra were obtained by the Bruker DMX-300 FT-NMR spectrometer using DMSO- d_6 as the solvent. Chemical shifts were calculated relative to TMS (tetramethylsilane) for spectrometer control.

2.4. FT-IR spectra

The FT-IR spectra were obtained using a Bio-Rad FTS-40 spectrometer incorporating a Spectra Tech diffuse reflectance accessory unit. The spectral resolution was 4 cm^{-1} and the scanning range was from 400 to 4000 cm^{-1} .

2.5. Ultraviolet light irradiation

The accelerated light-fastness test of specimens was conducted in a QUV light-fastness tester (Q-Panel Company) equipped with UVA-351 fluorescent lamps. It operates over a 315-nm to 400-nm range with a peak emission at 351 nm. The temperature of the black panel was $60 \pm 2\text{ }^\circ\text{C}$.

2.6. ESR analyses

The electron spin resonance (ESR) spectra were obtained by Bruker EMX-10 spectrometer. The frequency of microwave is 9 GHz. The temperature of sample was set at $-196\text{ }^\circ\text{C}$. The power of the mercury lamp was 200 W. To evaluate the tested specimens in the same C_9 units, formations of phenoxyl radicals of both MWL specimen (5 mg) and butyrylated MWL specimen (6.8 mg) under UV irradiation were measured, respectively, at different irradiation durations.

2.7. UV–VIS absorption spectral analyses

The UV–VIS spectra were measured using a UV–VIS spectrophotometer (Jasco V-550) using 1 cm cells. The scanning range was from 200 to 800 nm. The weight of MWL and butyrylated MWL were 5 and 6.8 mg, respectively. The water-soluble extracts of MWL and butyrylated MWL after irradiation were measured by UV–VIS absorption spectroscopy.

3. Result and discussions

3.1. Chemical characteristics of butyrylated MWL

Fig. 1b shows the ^1H NMR spectrum of butyrylated MWL (W_G 36%). The appearance of absorption peak at 0.77 ppm of treated specimen is due to the methyl group (CH_3). The 1.43 ppm and 2.17 ppm bands of the treated specimen are due to the methylene group (CH_2) and the methylene group adjacent to the carbonyl group ($\text{CH}_2\text{C}=\text{O}$), respectively. Data from the NMR analyses clearly revealed that the reaction occurred in the MWL and the butyryl groups were formed after treatment.

The FT-IR spectrum of MWL treated with butyric anhydride is shown in Fig. 2b. Obviously, the O–H absorption band (3430 cm^{-1}) of butyrylated MWL

Fig. 1. ^1H NMR spectra of China fir MWL after butyrylation. (a) MWL; (b) butyrylated MWL.

Fig. 2. FT-IR spectra of China fir MWL after butyrylation. (a) MWL; (b) butyrylated MWL.

disappeared, which was consistent with the previous results [18]. A significant reduction in the hydroxyl group content of MWL revealed that the butyryl groups substituted nearly the hydrogen atoms of the entire

hydroxyl groups of MWL after modification. The carbonyl absorption peak appearing at 1740 cm^{-1} and the enhanced C–O absorption band (1180 cm^{-1}) confirmed the formation of ester bond after butyrylation.

Fig. 3. ESR spectra of butyrylated MWL during UV light irradiation. (a) MWL; (b) butyrylated MWL.

Fig. 4. FT-IR spectra of MWL after irradiation. (a) Unirradiated; (b) 4-day irradiation; (c) 12-day irradiation.

3.2. Photo-stabilising effect of MWL after butyrylation treatment

Fig. 3a shows ESR spectra of untreated China fir MWL before and after exposing to UV irradiation. The ESR signal of phenoxyl radicals (g value ≈ 2.003 , line width = 16 G [23]) from the photolysis of wood continuously increased over time (0–60 min). These phenoxyl radicals would cause further photo-degradation of MWL. The ESR spectra of sample modified with butyric anhydride are shown in Fig. 3b. Before the irradiation, modified specimen generated much less phenoxyl radicals than the untreated sample. Similarly, the intensity of phenoxyl radical of treated specimen slightly increased during the irradiation, whereas that of phenoxyl radicals was approximately 3 fold less than that of untreated sample. The ESR data reveal clearly that the butyrylation inhibits the generation of phenoxyl radicals in wood during irradiation.

The chemical structures of MWL changed significantly after irradiation, as shown in Fig. 4. An increase in the intensity of absorption band at 1740 cm^{-1} ($\text{C}=\text{O}$) suggested that the content of carbonyl groups of MWL increased after exposure to UV light (Fig. 4b and c). The relative peak height ratio of non-conjugated carboxylic

acid and ester to total carbohydrates is 0.61 (I_{1740}/I_{860} , in Table 1) for MWL specimen before irradiation. The I_{1740}/I_{860} ratio increased to 5.61 after 12 days of irradiation. The relative ratio of conjugated carbonyl group (1667 cm^{-1}) for unexposed MWL was 1.93, which increased to 5.23 after 12 days of irradiation. This obvious increase in the intensity of absorption band at 1667 cm^{-1} (conjugated carbonyl group) indicated the generation of derivatives containing the conjugated carbonyl group after irradiation. The broad O–H absorption band occurring at 3460 cm^{-1} in relation to the increase in the carbonyl group revealed the formation of the carboxylic acid. As for the relative peak height ratio of the lignin aromatic ring characteristic band (I_{1510}/I_{860} , in Table 1), it decreased upon extending the irradiation time, from 7.89 to 5.64; and its retention ratio was 71.5%. The decrease in the intensity of absorption band at 1510 cm^{-1} (aromatic skeletal vibration) indicated that the aromatic ring of lignin was deteriorated after 12-day UV irradiation.

Fig. 5 shows the changes of butyrylated MWL after irradiation. Broadening of the absorption peak at 1740 cm^{-1} ($\text{C}=\text{O}$) indicated a slight increase in the content of carbonyl groups of butyrylated wood. The relative peak height ratio of I_{1740}/I_{860} , as shown in

Table 1

Changes in the relative intensities of infrared absorption bands of MWL and butyrylated MWL after irradiation

Specimens	Irradiation time (day)	I_{1510}/I_{860}	I_{1594}/I_{860}	I_{1667}/I_{860}	I_{1740}/I_{860}	I_{3450}/I_{860}
Control	0	7.89	3.40	1.93	0.61	2.85
	4	6.68	4.43	3.06	2.58	3.30
	12	5.64	5.83	5.23	5.61	4.78
Butyrylation	0	6.95	3.46	2.11	11.67	0.17
	4	6.53	4.23	2.45	11.92	0.79
	12	6.41	4.40	2.96	12.15	1.33

Fig. 5. FT-IR spectra of butyrylated MWL after irradiation. (a) Unirradiated; (b) 4-day irradiation; (c) 12-day irradiation.

Table 1, increased slightly from 11.67 to 12.15 as the irradiation time was prolonged. The ratio I_{1510}/I_{860} decreased from 6.95 to 6.41 after 12-day irradiation. The decrease in the intensity at 1510 cm^{-1} (lignin aromatic ring) of butyrylated MWL was less than that of MWL. These results demonstrated that the butyrylated MWL was more resistant to the UV light.

Fig. 6 shows the UV absorption spectra of water-soluble extracts of both MWL and butyrylated MWL after 12 days of irradiation. The UV absorption bands at 203.5, 232, and 282 nm observed in the spectrum of the water-soluble extracts of MWL were due to small amounts of low molecular weight (MW) and water-soluble lignin (Fig. 6b). After irradiation, the UV absorption of water-soluble extracts of MWL increased dramatically (Fig. 6d). The striking UV absorption bands appearing at 241 and 260 nm were attributable to the unsaturated bond and carbonyl groups. The UV

absorption above 300 nm of the water-soluble extracts from irradiated MWL also increased, indicating the formation of conjugated chromophores, such as quinonoid compounds [7,17].

The UV absorption bands of the water-soluble extracts of butyrylated MWL (Fig. 6a) were less than those of MWL. The water-soluble derivatives of butyrylated MWL increased after irradiation (Fig. 6c). The absorption intensity in the UV and visible light regions of butyrylated MWL was less than that of MWL after irradiation. It showed that butyrylation could reduce the amount of chromophores induced by UV light.

Results obtained from the aforementioned spectral analyses revealed that hydroxyl groups of MWL were replaced by butyryl groups after the butyric anhydride treatment. Since the formation of phenoxyl radicals was inhibited effectively. After UV irradiation, the butyrylated MWL was more resistive to UV light. Accordingly, butyrylation reduced the generation of colored chromophoric derivatives such as quinonoid compounds and consequently inhibited the photo-degradation of MWL, which is one of the possible reasons endowing the butyrylated wood with remarkable light-fastness [18,19].

4. Conclusion

The generation of phenoxyl radicals of butyrylated MWL was less compared with the untreated MWL during UV irradiation. Meanwhile, the carbonyl and conjugated carbonyl groups for forming chromophores, such as quinones, and water-soluble derivatives generated in the irradiated MWL were significantly reduced by butyrylation. These results demonstrated that the lignin bonded with butyryl group was more stable and resistant against UV light.

Fig. 6. UV absorption spectra of water-soluble extracts of MWL and butyrylated MWL after irradiation.

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