

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 phenoxy

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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

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