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The influence of hydrogen peroxide initiator concentration on the structure of eucalyptus lignosulfonate

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ABSTRACT

In order to improve lignin-based materials' utilization, the grafting mechanism of lignin was studied by investigating hydrogen peroxide (H_2O_2) initiator's effect on the structure of eucalyptus lignosulfonate calcium (HLS). HLS was treated by low content of H_2O_2 (H_2O_2/HLS_{wt} = 1%, 2%, 4%) under various reaction temperature and time. Changes in HLS structure were investigated by difference UV, UV, FTIR, ^{1}H NMR, GPC and intrinsic viscosity. The results showed that though phenolic hydroxyl group (Ph-OH) of HLS was not oxidated to the quinoid structure, its content still decreased after treated by H_2O_2 initiator. Meanwhile, the new aryl–alkyl ether structures and increased average molecular weight were observed. A radical coupling mechanism for the decreasing Ph-OH group's content was proposed, which radicals may terminate between phenoxy and benzyl radicals. In addition, the cleavage of methoxyl-aryl ether made a decline in the content of syringyl units, while that of guaiacyl, *p*-hydroxyphenyl units and free aromatic C-5 hydrogen increased when HLS reacted with H_2O_2.

1. Introduction

Lignin is defined as an amorphous and three-dimensional phenolic bio-polymer which is composed of p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units [1]. These basic structural units are linked by several types of aryl–alkyl ether (α-O-4, β-O-4, etc.) and carbon–carbon linkages in an irregular formation [2]. The major functional groups of lignin include phenolic hydroxyl (Ph-OH) group, methoxyl group and aromatic ring in various amounts, depending on botanic origins and extraction processes [3]. The softwood lignin is primarily formed by G unit (95%), with a smaller number of methoxyl groups and larger proportion of free aromatic C-5 hydrogen; on the contrary, various ratios of S/G have been observed in hardwood, accompanied with a larger quantity of methoxyl groups [4].

With the exception of cellulose, lignin is the most abundant biomass on the earth. The worldwide production of industrial lignin has reached several hundreds of million tons annually. However, the majority of it was just fired and dumped into the landfill space as waste [5]. In order to fully utilize this low cost of resource, grafting method is considered as one of the effective techniques for altering the properties of lignin. Until now, a number of studies have been performed on the grafting of lignin with vinyl monomers to prepare high value of lignin-based polymer materials, such as thickening agents, wood-thermoplastic composites, compatilizers, sand stabilizers and flocculants [6–10].

It is widely acknowledged that the properties of the above lignin-based materials are highly associated with the length and percentage of the grafting chain which are the most two important parameters for graft polymers (grafting efficiency and grafting rate, respectively). Therefore, it is necessary to make great efforts on investigating the grafting mechanism in order to improve the industrial utilization of lignin-based materials. Current researches on the graft mechanism of lignin are mainly focused on the Ph-OH group which is widely viewed as the grafting site [6,11]. Obviously, its content is the most crucial aspect for tailoring the grafting efficiency and grafting ratio. However, it was reported that Ph-OH group's content in either kraft baggage lignin or lignosulfonic acid would decline under the treatment of low hydrogen peroxide (H_2O_2) content (H_2O_2/$lignin_{wt}$ = 1–8%), including dearomatization into quinones and even the destruction of the aromatic ring into carboxylic groups [12,13]. Similarly, large quantity of studies have been performed on the reaction of lignin with high content of H_2O_2 (H_2O_2/$lignin_{wt}$ = 1371.7%, 45.9%, 73.9%) which was widely used as a bleaching agent in paper industry [14–16]. Taking account of the above reports, it is assumed that H_2O_2 would result in the structural changes of lignin in the grafting reactions. However, little information has been reported on this aspect until now because it is traditionally assumed that low content of H_2O_2 (H_2O_2/$lignin_{wt}$ = 0.1–4%) only acts as an initiator in the graft copolymerization of lignin [17,18]. It has been reported that as for the

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H_2O_2	hydrogen peroxide
HLS	eucalyptus lignosulfonate calcium
Ph-OH	phenolic hydroxyl group
H	*p*-hydroxyphenyl
G	guaiacyl
S	syringyl
FTIR	Fourier transforms infrared
UV	ultraviolet spectrophotometery
DUV	difference Ultraviolet spectrophotometry
^{1}H NMR	hydrogen spectrum nuclear magnetic resonance
GPC	gel permeation chromatography
$[\eta]$	intrinsic viscosity
$\bar{M}_\eta$	viscosity-average molecular weight

lignin grafting reactions, almost all of the chemical initiator systems are based on H_2O_2 (e.g. the initiating systems of H_2O_2–$CaCl_2$, H_2O_2–$FeCl_2$ and H_2O_2) [17–19]. Hence, comprehensive researches about its influences (under low content) on the lignin structures, especially on the content of Ph-OH group and aromatic C-5 hydrogen, should be performed in view of the predominate role they play in the control of grating percentage [11,20]. Only in this way, high performance of lignin-based materials with desirable percentages of grafting ratio and grafting efficiency can be designed according to its utilization scopes.

In this paper, the eucalyptus lignosulfonate calcium (HLS) was selected because lignosulfonate has been extensively used in the industry [3]. HLS was analyzed for various weight concentrations of H_2O_2 (H_2O_2/HLS_{wt} = 1%, 2%, 4%) under different reaction temperature and time; other relative amounts of functional groups, such as the content of aryl–alkyl ether linkages and G/S/H units, were also studied by FTIR, UV and ^{1}H NMR spectroscopy under various reaction temperature and time. In addition, the average molecular weight of HLS was also evaluated before and after it reacted with H_2O_2.

2. Experimental

2.1. Materials

The eucalyptus lignosulfonate calcium (HLS, ~96% purity) was purchased from Aladdin Chemical Company. Analytical regent grade hydrogen peroxide (H_2O_2, 30%) was supplied from Kelong Chemicals Co. Ltd. (China).

2.2. HLS treated by H_2O_2 initiator

All reactions were carried out in a 100 ml three-necked flask equipped with a reflux condenser and magnetic stirrer. 8 g HLS was dissolved in distilled water (18.7 ml) at room temperature with constant stirring. The solution was immediately placed into the water bath and purged with nitrogen gas at least for 30 min. Subsequently, certain amount of H_2O_2 solution was added into the flask at predetermined temperature. The treated HLS was precipitated by dropping the reaction mixture into isopropanol and dried under vacuum (P < 0.1 MPa) at 80 °C until the weight did not change. The details of experimental conditions were recorded in Table 1.

2.3. Analytical methods

2.3.1. Difference ultraviolet spectrophotometry (DUV)

The content of phenolic hydroxyl (Ph-OH) groups was measured by DUV spectroscopy with the gross method as described by Arthur S. Wexler [21].

Table 1
The influence of reaction conditions on Ph-OH group content.

Samples[a]	H_2O_2 content (H_2O_2/HLS_{wt})	T (°C)	Time (h)	Ph-OH content (%)
HLS	–	–	–	1.94
HLS1	0.01	70	2	1.36
HLS2	0.02	70	2	1.32
HLS3	0.04	70	2	1.20
HLS4	0.02	40	2	1.33
HLS5	0.02	55	2	1.32
HLS6	0.02	85	2	1.22
HLS7	0.02	70	1	1.79
HLS8	0.02	70	3	1.34
HLS9	0.02	70	4	1.27

[a] Fixed conditions: HLS = 8 g; H_2O = 18.7 ml.

2.3.2. Ultraviolet spectrophotometery (UV)

UV spectra were recorded on a UV 2100 Spectrophotometer according to the method suggested by Dence [22]. The absorbance between 190 and 900 nm were measured in a double-beam spectrophotometer against the solvent.

2.3.3. Fourier transform infrared (FTIR)

FTIR spectra of samples were recorded on a Nicolet 560 FTIR spectrometer using KBr pellet technique. Each spectrum was recorded with 32 scans in the frequency range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1}. The absorption bands were assigned as suggested by Dence [23].

2.3.4. Hydrogen spectrum nuclear magnetic resonance (^{1}H NMR)

^{1}H NMR spectra of raw HLS and treated HLS solutions (15 mg sample contained in 0.5 ml DMSO-d_6) were recorded in a Bruker 400 spectrometer with a 90° pulse width and 48 scans respectively. A relaxation delay of 3 s was required to complete relaxation of all protons.

2.3.5. Average molecular weight determination

The average molecular weights of samples were analyzed by gel permeation chromatography (GPC). The Malvern GPC system consisting of a GPC Max auto-injector fitted to a TDA 305 triple detector array (differential RI, right angle light scattering, low angle static light scattering and four-capillary differential viscometer detectors). The column set was consisted of one A6000M.

The eluent was 0.05 M $NaNO_3$ solution. The experiments were run at a flow rate of 1.0 ml/min at 35 °C. The samples concentrations for HLS, HLS2, HLS6 and HLS9 were 9.6 mg/ml, 9.33 mg/ml, 6.58 mg/ml and 6.84 mg/ml, respectively. And the injection volume was 100 μl. The system was calibrated with seven polyethylene glycol standards (molecular weight at peak maximum, $\bar{M}_p$, 195, 630, 1090, 3450, 6100, 10 250, 20 800, respectively). The calculation of average molecular weight was according to the universal calibration method which was based on the relationship between retention volume and hydrodynamic volume.

Meanwhile, the intrinsic viscosity ($[\eta]$) of the solution was measured and the viscosity-average molecular weight ($\bar{M}_\eta$) was calculated by the Mark–Houwink equation: $[\eta] = K\bar{M}_\eta^\alpha$ (where K and α were obtained by online analysis of four-capillary differential viscometer detectors combined with GPC).

3. Results and discussion

3.1. DUV analysis of Ph-OH group

Ph-OH group is traditionally considered as an active center on lignin, due to the decreasing content of it observed after grafting reactions [20]. Here, after the grafting of acrylic acid onto HLS, the residual content of it was studied by DUV analysis. As illustrated in