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Preparation and performance of lignin–phenol–formaldehyde adhesives

Mingzhu Zhao [a,b], Junling Jing [a,b], Yanchao Zhu [a], Xiaomin Yang [a], Xiaofeng Wang [a,*], Zichen Wang [a]

[a] State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, China
[b] Foxconn China measurement Center, Kunshan 215301, China

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ABSTRACT

Steam explosion lignin phenol formaldehyde (SEL–PF) adhesives were prepared by ternary gradual copolymerization. The parameters for the phenolate of steam explosion lignin (SEL) and preparation of SEL–PF adhesives were optimized. Under the optimum phenolate conditions, the phenolic hydroxyl content of lignin increased by 130%, whilst the methoxyl content was reduced by 68%. The SEL–PF adhesives were used to prepare plywoods by hot-pressing. The pH value, viscosity, solid content, free phenol content and free formaldehyde content of SEL–PF adhesives were investigated. The bonding strengths of the plywoods glued with SEL–PF adhesives were determined. The maximum SEL replacement percentage of phenol reached 70 wt%, and the properties of adhesives and plywoods met the Chinese National Standard (GB/T 14732-2006) for first grade plywood.

1. Introduction

Phenol formaldehyde (PF) adhesives have excellent performance including high bonding strength, excellent water resistance, heat resistance and chemical stability [1]. They are used in many wood processing industries such as particleboard, wood panels, fiber boards and plywood etc [2–8]. PF adhesives are generally synthesized using petro-chemicals such as phenol and formaldehyde with alkaline catalysts. However, the consumption of petroleum and petro-chemicals has increased sharply recently, which has intensified the energy crisis. Research on the substitution of petro-chemicals by natural products are of environmental and economic benefit [9].

Lignin has been used as a phenol substitute in the synthesis of PF adhesives due to its similar structure to phenol [10,11]. Due to the chemical activity of lignin being lower than phenol, it is essential to modify lignin to enhance its reactivity. It contains both the phenolic and hydroxyl groups, which can be used as reactive sites for chemical modification [12,13]. There are three major modification methods: methylolation [14–17], demethylation [18], and phenolate [19–21]. Methylation does not increase the number of reactive sites on the lignin structure, thus leading to minimal increase in activity. Demethylation can increase the number of reactive sites, but the application is limited because of the complex processes involved and high cost. Although the phenolate approach is a simple process, it can, in theory, increase the number of reactive sites so the phenolate has been considered the most promising modification method.

Whilst the synthesis reactions of PF adhesives are generally catalyzed by alkalies, the phenolate approach to lignin modification usually relies on acid catalysis [20,21]. Thus the excess acid needs to be neutralized after the lignin has been phenolated. This results in the production of waste material which can lead to pollution related issues. In this article, steam explosion lignin (SEL) was used to substitute part of the phenol component in the preparation of phenolic-based adhesives. The phenolate modification of lignin and the preparation of SEL–PF adhesives were both catalyzed by alkali. Formaldehyde was gradually added to the ligninphenol solution. SEL–PF adhesives were prepared by ternary gradual copolymerization. The parameters for phenolate of SEL and preparation of SEL–PF adhesives have been investigated.

2. Materials and methods

2.1. Materials

Steam explosion lignin (SEL) was purchased from GY Energy in Anhui province of China. SEL was extracted from industrial steam

* Corresponding author. Tel.: +86 431 85155358; fax: +86 431 85155358.
E-mail address: wangxf103@jlu.edu.cn (X. Wang).

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exploded wheat straw hood by spray drying and spherical foam preparation. The molecular weight is about 17,000. Phenol, formaldehyde solution (37–40%) and sodium hydroxide (NaOH) were of analytical grade and were used without further purification.

2.2. Phenolate of lignin

NaOH, lignin, phenol and water were mixed in the various mass ratios indicated in Table 1 and stirred, resulting in the formation of a ligninphenol solution. In order to investigate lignin, the pH value of the reaction mixture was adjusted to 2 by adding 12 wt% hydrochloric acid. After separation by centrifugation, the precipitated lignin was washed with ether until a neutral pH was obtained, followed by drying in a vacuum oven at room temperature.

2.3. Preparation of adhesives

2.3.1. Preparation of PF adhesives

Phenol and formaldehyde were reacted in the molar ratio of 1:1.5, and formaldehyde was divided into two parts to add into the reaction system. NaOH, phenol and water were mixed and stirred at 50 °C for 20 min. Then the first part of formaldehyde (80% of the total amount of formaldehyde ultimately used) was added into the flask and reacted at 60 °C for 1 h. When the temperature was increased to 80 °C, the rest of the formaldehyde was added and the reaction was conducted at 80 °C for 2 h. The product was dehydrated at reduced pressure until its viscosity reached 300–700 mPa s. Thermosetting phenolic resin adhesive was obtained.

2.3.2. Preparation of SEL–PF adhesives

SEL–PF adhesives were prepared by gradual polymerization: preparation of ligninphenol solution and preparation of SEL–PF adhesives. Sufficient SEL to substitute 10–70 wt% of the phenol, phenol and formaldehyde in a molar ratio of 1:1.5, NaOH and water were mixed in a four-neck flask. In addition, 10% additional formaldehyde to SEL weight ratio was added. At first, SEL, phenol, NaOH and water were mixed and stirred at 90 °C for 1.5 h to obtain the ligninphenol solution. Then the formaldehyde was gradually added to the flask in two batches with the precise steps employed being similar to the preparation of the PF adhesives.

Table 1
Effect of the experimental parameters on the phenolic hydroxyl group content of ligninphenol.

Sample	Lignin: phenol (mass ratio)	NaOH concentration (wt% of the mass of lignin and phenol)	Temperature (°C)	Time (h)	Phenolic hydroxyl (mmol/g)
1	7:3	4	80	2	2.76
2	7:3	4	85	2	3.38
3	7:3	4	90	2	3.57
4	7:3	4	95	2	3.12
5	7:3	4	100	2	2.87
6	7:3	4	90	0.5	3.27
7	7:3	4	90	1	3.63
8	7:3	4	90	1.5	3.86
9	7:3	4	90	2.5	3.39
10	2:8	4	90	2	3.50
11	3:7	4	90	2	4.08
12	4:6	4	90	2	4.16
13	5:5	4	90	2	3.87
14	6:4	4	90	2	3.70
15	8:2	4	90	2	3.26
16	4:6	2	90	1.5	3.84
17	4:6	4	90	1.5	3.89
18	4:6	6	90	1.5	3.96
19	4:6	8	90	1.5	4.20
20	4:6	10	90	1.5	3.83

2.4. Preparation of plywoods

Adhesives (PF and SEL–PF) obtained above were used to prepare plywoods. Standard single-layer sheets (poplar) of dimensions $400 \times 400 \times 2.0\ mm^3$ were dried to 5 wt% moisture content, coated with $310\ g/m^2$ adhesive to prepare three-layer plywoods, then hot-pressed at 150 °C and 1.5 MPa for 7 min. The plywood samples were kept indoors for 24 h, and then machined to produce lap-shear specimens of the type and dimensions indicated in Fig 1. 10 samples of each adhesive were selected randomly and tested for wet tensile strength. The wood failure percentage for each specimen was assessed visually after testing and assessed in accordance with Chinese National Standard (GB/T 14732-2006).

2.5. Characterization

The phenolic hydroxyl content of SEL and ligninphenol was measured by means of Folin–Ciocalteu (F–C) reagent [22]. The principle is based on the iso-phosphotungstic acid salt, molybdate and phenolic hydroxyl reaction which results in a blue-colored product. With the phenol employed the phenolic hydroxyl group content was 10.6 mmol/g. The methoxyl content of SEL and ligninphenol was measured according to the modified procedure of Viebock and Schwappach [23]. The principle of the method is that the lignin reacts with concentrated hydriodic acid and the methoxy of lignin will fracture and generate methyl iodide. The methoxy content was determined by using methyl iodide absorption. Infrared spectra were recorded on a Perkin Elmer SPECTRUM 2000 Fourier transform infrared (FT-IR) spectrometer and KBr pellets. The properties of the adhesives (viscosity, solid content, free phenol content, free formaldehyde content, bonding strength) were determined in accordance with the corresponding Chinese National Standards (GB/T 14732-2006). The specimens were tested for shear stress by tension loading until failure with an AG-120KN benchtop universal testing machine at a loading rate of 10 mm/min. Before testing bonded plywood joints were all pre-treated by the following four steps: (1) immersing in boiling water for 4 h; (2) drying at 63 ± 3 °C for 20 h; (3) immersing in boiling water for 4 h; (4) cooling for 10 min. The values proposed in the National Standard (GB/T 14732-2006) are listed in the first rows of Table 2.

3. Results and discussion

3.1. Characterization of lignin

To investigate the effect of the experimental parameters on the phenolic hydroxyl content of ligninphenol, samples were prepared

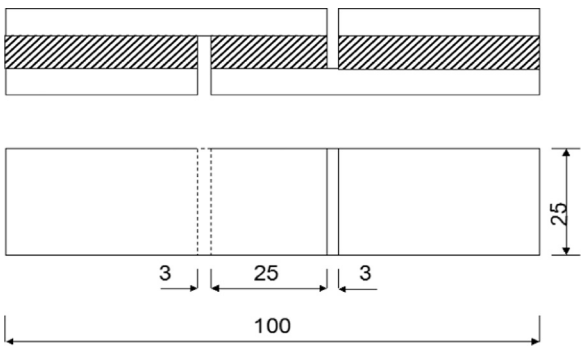

Fig.1. Shape and dimension of test piece.