Lignin-based Grinding Wheels with Aluminum Oxide: Synthesis and Characterization

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By using renewable inexpensive plant-derived materials such as lignin and furfuryl alcohol, a new bio-based, easily-prepared, and industrially suitable thermosetting grinding wheel named lignin-furanic grinding wheel (LFG) was prepared and characterized. Cross-linking between lignin and furfuryl alcohol under acidic conditions was established by carbon-13 nuclear magnetic resonance (13C-NMR) and electrospray ionization mass spectrometry (ESI-MS). In addition, as the results of thermomechanical analysis (TMA) and thermogravimetric analysis (TGA) suggested, the lignin-furanic resin exhibited high resistance to heat, and the glass transition temperature (T_9) as high as 170 °C. The new lignin-based grinding wheel presented no pores or cracks in the surface and it had a high hardness and compression resistance compared to the commercial phenolic grinding wheel (PG). Moreover, it exhibited high abrasiveness, and the cutting time for a metal tube was shorter than that of PG.

Keywords: Lignin-based resin; Furfuryl alcohol; Grinding wheel; Abrasiveness; Renewable materials

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INTRODUCTION

In recent decades, the abrasive grinding wheels based on phenol formaldehyde (PF) resin have been widely used in the abrasive industry (Krenkel *et al.* 2002; Haug and Rebstock 2003). However, the problem of formaldehyde release largely limits continuous industrial developments. As a consequence, with the increasing needs for environmentally friendly materials in the grinding wheel industry, considerable research has been conducted to develop natural biobased materials obtained from forests and the agricultural fields to replace PF resin for the preparation of grinding wheels.

In recent years, natural lignin extracted from plants (Chakar and Ragauskas 2004; Borges da Silva *et al.* 2009) has been widely used as biobased material in replacement of petrochemical products because of their similar structures of phenolic compounds (Vazquez *et al.* 1995; Turnnen *et al.* 2003) and their unique thermal stability (Xue *et al.* 2014). Meanwhile, lignin-based materials, such as lignin-phenolic grinding wheels (Zhang *et al.* 2017b), lignin-epoxy polymer materials (Nonaka *et al.* 1997), and ligninpolyurethane foam (Saraf *et al.* 1985; Rials and Glasser 1986), also have been developed. About 55 million tons of lignin each year has been generated as a by-product of the pulp and paper industry (Thring *et al.* 1997; Calvo-Flores and Dobado 2010). Most of this lignin is burned or discarded as waste, and only a small amount of lignin has been utilized to prepare some industrial products, usually having low value.

Furfuryl alcohol originating from the hydrolysis of high-yield biomass, such as

wheat, corn, and sugarcane, has successfully been used to prepare many renewable materials without formaldehyde such as tannin-furanic based adhesive (Zhang *et al.* 2017a), foam (Tondi *et al.* 2008; Lacoste *et al.* 2013), rigid plastic (Li *et al.* 2013), grinding wheels (Lagel *et al.* 2015; Zhang *et al.* 2015), and polylignin-furfuryl alcohol thermosets (Guigo *et al.* 2010). These biobased materials presented excellent mechanical properties compared with PF-based materials. Generally, lignin is mainly composed of three different types of units, which are *p*-hydroxyphenyl propane (Fig. 1a), guaiacyl (Fig. 1b), and syringyl (Fig. 1c). The cross-linking of the chains between the phenol ring of lignin and the furan ring of furfuryl alcohol is facilitated under acidic conditions (Guigo *et al.* 2010). Lignin-furanic (LF) resin is considered to be a potential component for grinding wheel preparation due to its low cost and non-toxic properties.

In this research, the biobased resins made with lignin and furfuryl alcohol were successfully synthesized and characterized. The LF resin explored is based on the coreactions of lignin and furfuryl alcohol under acid conditions. Then, the grinding wheels based on the lignin-furanic resin matrix and aluminum oxide abrasive particles were prepared and examined. This study is important for the development of a grinding wheel based on a renewable resin to replace industrial PF resin-based grinding wheels.



Fig. 1. Main units of lignin: a) p-hydroxyphenyl propane; b) guaiacyl; and c) syringyl

EXPERIMENTAL

Materials

Alkali lignin was obtained as a brown powder, extracted with a mild alkaline solution from wheat residue, supplied by the Long Live Biological Technology Company (Shangdong, China). The particle size of lignin averaged 50 µm, and the lignin had been dried before it was used. Furfuryl alcohol (with a purity of 98%), para-toluene-4-sulphonic acid (p-TSA, with a purity of 97.5%), and lactic acid were purchased from Acros Organics (Geel, Belgium). The aluminum oxide particles (with a size of 0.4 mm) and a steel tube (diameter of 7 mm, inner diameter of 6 mm, and length of 0.8 m) were supplied by Run Xin Materials Company (Kunming, China).

Preparation of grinding wheels

PF resins were mechanically stirred in a flask for 20 s. Afterwards, the mixtures were put in a mold (100 mm of diameter) with three layers of fiber glass. The molds were placed in a press for 1.5 h at 150 °C under a pressure of 8 MPa for curing. After curing, the grinding wheels were cooled and 22 mm diameter holes were drilled at their centers, named PEG. Also, furfuryl alcohol and lignin were mixed in a flask and stirred for 20 s with a mechanical stirrer. Lactic acid was then added, the main purpose of which was to increase the toughness of grinding wheel. After stirring for 20 s, the p-TSA as a catalyst

was added and stirring continued for another 20 s. Then, the aluminum oxide particles (Alu) were mixed with the lignin-based resins. The mass ratio of Alu/resin was 1.5 and 2. The proportions referenced the work of Lagel *et al.* (2015). Next, the mixtures were placed in a mold (100 mm of diameter) with three layers of fiber glass, which was added in order to improve the cutting performance and structural stability of the grinding wheel sheet. This system was placed in a press at 150 °C under a pressure of 8 MPa for 1.5 h. After curing, these grinding wheels were cooled and drilled in their centers at 22 mm. The composition and processes for the preparation of the grinding wheels are shown in Table 1.

Sample	Lignin (g)	Furfuryl Alcohol (mL)	Alu (g)	Lactic Acid (mL)	p-TSA (mL)	Mass ratio of Alu : resin	Mass ratio of resin : LA
S1	28	28	84	8	8.0	1.3:1	8:1
S2	28	42	105	10	8.0	1.3:1	8:1
S3	28	56	126	0	1.2	1.5:1	-
S4	28	56	126	12	1.2	1.5:1	7:1
S5	28	56	168	12	1.2	2:1	7:1

Table 1. Formula and Processes Used for Preparation Different Grinding Wheels

Characterization

Scanning electron microscopy (SEM)

The samples with dimensions of 5 mm \times 5 mm \times 4 mm cut from the grinding wheels were observed using a Hitachi scanning electron microscope (model S 4800, Tokyo, Japan). The acceleration voltage of scanning electron microscope was 12.5 kv. The sample was subjected to gold sputtering surface treatment before testing.

Compression and Brinell hardness measurement

For the compression test, the samples (16-mm diameter and 10-mm height) were tested with a strength analysis instrument (Instron model 1193, Los Angeles, CA, USA) according to the standard ASTM D695-10 (2010). The rate of loading was 2 mm/min. Each result was the average value of four specimens.

For the Brinell hardness measurement, the measurement following GB/T 231.1-2009 (2009) standard was conducted using a strength analysis instrument (Instron model 1193, Los Angeles, CA, USA) with a steel ball with a 10-mm diameter and 2452 N loading. The rate of loading was 2 mm/min. The Brinell hardness was calculated from Eq. 1,

$$HB = \frac{3.18}{1000} \times \frac{F}{P} \tag{1}$$

where F is the force that determined the retained depression (N) and P is the depth of depression of the steel ball (mm). Each result was the average value of four specimens.

Wear resistance measurement

The wear resistance of a grinding wheel is characterized by using an angle grinder (Bosch GWS 1400, Foshan Bright River Electromechanical Equipment Co., Ltd., Foshan, China) with a speed of 10,000 rpm. The steel tube was cut off with a grinding wheel along the vertical direction of the tube length. The dimension of steel tubes for different grinding wheels was the same, with a length of 0.8 m, a diameter of 7 mm, and an inner diameter of

6 mm. The cutting time of the grinding wheel and the quality loss of the grinding wheel were measured during the cutting process. In addition, the commercial grinding wheels (PFG) were compared with alkali lignin-based grinding wheels. The percentage of mass loss from the grinding wheels was calculated by weighing the grinding wheels before and after the wear resistance test. The mass loss was calculated as follows in Eq. 2,

$$m = \frac{m_1 - m_2}{m_1} \times 100\%$$
(2)

where *m* is the mass loss (%), m_1 is the mass of the grinding wheel before steel cutting (g), and m_2 is the mass of the grinding wheel after steel cutting (g). Each result was the average value of four specimens.

¹³C Nuclear magnetic resonance (¹³C-NMR) and electrospray ionization mass spectrometry (ESI-MS)

A superconducting nuclear magnetic resonance (NMR) apparatus (Bruker-ADVANCE 600, Karlsruhe, Germany) was used to evaluate the samples. The resonance frequency was 150 MHZ. Then, 200 μ L of samples and 200 μ L deuterium generation solvent dimethyl sulfoxide (DMSO - d6) were mixed in NMR cuvettes. The inverse-gated decoupling method was applied by using the "zgig" pulse program. Test conditions were a 6 s relaxation delay time and scanning accumulative number of 512 times.

The mass spectrometry detection of LF resin was implemented using a Waters Xevo Triple Quadrupole-MS (Waters, Milford, USA) equipped with an electrospray ionization source (ESI). The mixture sample was dissolved in chloroform sequentially at a concentration of approximately 5 μ L/mL and injected into the ESI source plus ion trap mass spectrometer (Bruker Daltonics Inc., Billerica, USA) *via* a syringe at a flow rate of 5 μ g/s. The spectra were recorded in a positive mode, with a scan range of 0 Da to 1000 Da and ion energy of 0.3 eV.

Thermomechanical analysis (TMA) and thermogravimetric analysis (TGA)

The TMA measurement was implemented using a TMA device (Mettler-Toledo SDTA840, New York, USA) with STARe software (Mettler-Toledo, Version 14.0, New York, USA) for data treatment. All cured resins (17 mm \times 5 mm \times 5 mm) were tested using the same conditions of a heating rate of 20 °C min⁻¹ and the temperature range was 25 to 250 °C.

A TGA from NETZSCH (model TG 209 F3, Netzsch, Germany) was used to study the thermal stability of the cured lignin-furanic resin. The tests were conducted with temperatures that ranged from 30 to 900 °C and used a rate of 20 °C/min under a nitrogen atmosphere.

RESULTS AND DISCUSSION

Macroscopic Observations

Sample S1 was composed of lignin and furfuryl alcohol with the mass ratio of F/L being 1. Some cracks appeared during the curing of the resin, which were the consequence of the excessive remaining lignin. To increase the mass ratio of F/L, the amount of furfuryl alcohol was increased. The mass ratio (F/L) of S2 was increased to 1.5,

and the mass ratio (F/L) of S3 and S4 were increased to 2. Macroscopic observations of different grinding wheels (S2 through S5) observed by SEM photographs are shown in Fig. 2. It can be seen that the surface of S2 exhibited obvious pores, marked by red ring, which was not the case for the S3, S4, and S5 samples. For S2, the excessive lignin caused the mixtures to be filled with air and when the sample was cured, some big pores became present in the surface of S2. Meanwhile, compared with sample S4 and S5, some small pores appeared in the surface of S3. Indeed, the lignin-based grinding wheel prepared without lactic acid as a flexibilizer might present some pores during the curing process. For the sample of S5, the cured resin was friable and showed some cracks, as indicated by the red rectangle. This result indicated that the more Alu particles there were, the more easily they were to aggregate, which weakened the bonding of lignin-based resin with Alu particles.



Fig. 2. SEM images of different samples (0.45 mm to 0.8 mm): a) S2; b) S3; c) S4; and d) S5

Brinell Hardness and Compression

The results of the Brinell hardness and compression measurement of different grinding wheels are listed in Table 2. By using the same lignin-based resin, S3 was harder than S4 and S5. The sample S4 with fewer Alu particles (150%) was harder than S5 with 200% Alu particles, which indicated that excessive Alu may reduce hardness of the grinding wheel. The hardness of S3 was higher than that of PFG, showing that it could reach commercial standards and may even be better, using alumina with modified lignin-furfuryl alcohol to prepare an abrasive wheel. Meanwhile, it can be seen that the sample of S4 showed higher compressive resistance than S1, S2, and S3. The surfaces of S1 and S2 showed some cracks and pores according to the results of the macroscopic observations. Meanwhile, the addition of lactic acid increased the tenacity of S4 and improved the

ability for compressive resistance. This was the reason why S3 was harder and had less compressive resistance than S4. Especially when compared with PFG (135.67 \pm 1.52), the sample of S4 (171.25 \pm 1.37) also had an excellent compression resistance.

	S1	S2	S3	S4	S5	PFG
HB	2.36 ±	4.77 ±	8.38 ±	8.02 ±	7.33 ±	6.50±
(daN·mm-2)	0.034	0.032	0.041	0.028	0.031	0.038
Compressive	85.37 ±	123.35 ±	152.31 ±	171.25 ±	169.37 ±	135.67 ±
Strength (MPa)	1.15	1.09	1.21	1.37	1.30	1.52

Table 2. Brinell Hardness and Compression Results of All Grinding Wheels Tested

Abrasiveness of Grinding Wheels

The results in Fig. 3 show that the sample of S4 prepared with lignin-based resin had the best resistance to wear in all the samples. These findings were consistent with the results on the compressive test with the same lignin-based resin, where S4 presented less mass loss and shorter cutting time than S3. Meanwhile, compared with S4, the result of S5 showed a higher mass loss within a determined period to cut the metal tube. Apparently, some cracks were observed in the surface of S5 (Fig. 2d). Meanwhile, with the increase of Alu particle amounts, the wear ability was clearly improved, which was indicated by a shorter cutting time (2 s) for S5. With all these results considered, the best lignin resinbased wheel was the one with 150% Alu particles (S4). Moreover, the cutting time of S4 was shorter than that of PFG. In contrast, the PFG value of mass loss was higher than S4. Consequently, sample S4 presented an excellent abrasiveness property and could be competitive to the non-renewable PF resin-based grinding wheel.



Fig. 3. Mass loss and cutting time of grinding wheels

¹³C-NMR and ESI-MS Analysis

To investigate the reaction of lignin with furfuryl alcohol, the pure lignin and LF resin for the well-cured grinding wheel (S3) were determined by ¹³C-NMR. The NMR

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spectra obtained are shown in Fig. 4. Figure 4a shows that the peaks at the ranges of 0 to 38 ppm belong to the series of alkyl groups (Liang *et al.* 2017). The primitive unit of lignin is the benzene propane structure. Many cross compositions were found in the lignin structure. Meanwhile, the absorption peak of 62.86 ppm was assigned to the hydroxymethyl group. The chemical shift signal at 28.67 ppm was attributed to the hydroxyl methyl group of lignin. Moreover, these absorption peaks at 69.93 ppm and 74.84 ppm corresponded to the ether bond (RC-O-CR) (Liang *et al.* 2017). The peaks at 168.95 ppm, 171.82 ppm, and 174.62 ppm were ascribed to the carbonyl of carboxylic acid or carbonyl of ester (Blunt and Stothers 1977). Meanwhile, peaks at 181.94 ppm and 183.24 ppm were attributed to the structure of phenol oxidation-quinone.



Fig. 4. ¹³C-NMR results of pure lignin and lignin-furanic resin: a) pure lignin and b) lignin-furanic resin

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Fig. 5. Reaction mechanism between lignin and furfuryl alcohol

Compared with the spectra of LF resin (shown in Fig. 4b), some new absorption peaks at 30.57 ppm and 36.20 ppm were obviously detected. They were ascribed to the structure of methylene formed in the co-polycondensation between the lignin and furfuryl alcohol appearance. Previous studies (Slonim *et al.* 1985; Fan *et al.* 2009) showed that the self-polycondensation peak of phenol mainly appears at 41 ppm, and the peak of self-polycondesation of furfuryl was at 28 ppm. Hence, these new absorption peaks of methylene, such as those at 30.57 ppm and 36.20 ppm, can be attributed to co-polycondensation of lignin and furfuryl alcohol. Indeed, the reactivity of lignin is similar with that of phenol. The dehydration condensation reaction between lignin and furfuryl alcohol can be represented as shown in Fig. 5. The structure corresponding to the peak at 30.57ppm comes from the reaction mechanism in Fig. 5b, and that of 36.20 ppm comes from the reaction mechanism in Fig. 5b, and that of 36.20 ppm comes from the reaction mechanism in Fig. 5b, and that of 36.20 ppm comes from the reaction mechanism in Fig. 5b, and that of 36.20 ppm comes from the reaction mechanism in Fig. 5c Fig. 4b, the absorption peak at 30.57 ppm was considerably higher than that of the peak at 36.20 ppm.



Fig. 6. ESI-MS of lignin-furanic resin

The ESI-MS of LF resin that was prepared for the grinding wheel (S4) is shown in Fig. 6. The main chemical structures are shown in Table 3. These samples contain many furan ring substances, which can be easily detected in the positive ion mode of ESI-MS. Some peak values shown in Fig. 6 are based on the MW of the fundamental structures plus 23. From Fig. 6 the 255 Da, 285 Da, and 315 Da were probably the dehydration condensation products from the reaction of the three kinds of lignin units and single furfuryl alcohol. Additionally, 365 Da, 395 Da, and 475 Da were possibly assigned the structures from the reaction of furfuryl alcohol polymer and lignin, which indicated that the self-condensation of furfuryl alcohol occurred with the treatment of pTSA.

Experime	ntal (Da)	Chamical Spacias		
Experimental	Calculated	Chemical Species		
203	203			
255	255	но-Он		
285	285			
315	315			
365	365	но на		
395	395			
475	475			

Table 3	. The	Main	Ion Pe	aks of	FSI-MS	and	their	Assianr	nents
		mann				ana	u ion	/ toolgin	10110

Thermal Analysis

To research the heat resistances and curing properties of lignin-furanic resins, one of the LF samples (S4) was selected and compared to the laboratory prepared alkali lignin resin.

The glass transition temperature (T_g) of resins is the temperature at which a resin transforms from a glassy state into a rubbery state (Li *et al.* 2000). To obtain the T_g of LF

and lignin resin, the TMA was used and the spectra is shown in Fig. 7, which shows the T_g of LF resin (170 °C) was higher than that of lignin (123 °C). The results indicated that the lignin resin cross-linked by furfuryl alcohol increased the T_g of lignin. Moreover, the T_g of LF resin was higher than that of PF resin (144 °C) (Zhang *et al.* 2015). This means that the LF-based grinding wheel revealed itself to have excellent thermal resistance, which is beneficial for angle grinder applications.



Fig. 7. TMA spectra of lignin and lignin-furanic resins from 30 °C to 240 °C under nitrogen



Fig. 8. TGA thermograms of lignin and lignin-furanic resins from 40 °C to 800 °C under nitrogen

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The TGA curve of the cured LF resin and lignin obtained at the temperature range of 40 to 800 °C are shown in Fig. 8. It was clear that compared to the cured lignin, the sample of cured LF resin showed a better heat-resistance property. The sample of LFcured resin reached its 10% weight loss at 275 °C, which was higher than that of lignin (240 °C). Furthermore, the weight loss of LF-cured resin was 42% when the temperature was raised to 800 °C. It revealed itself as carbon precursors because it was still 58% weight at 800 °C.

CONCLUSIONS

- 1. It was possible to formulate a new easily-prepared grinding wheel with biobased resin, namely lignin-furanic resin. An acid catalyst (pTSA), 56 mL of furfuryl alcohol, 28 g of lignin, and 12 mL of lactic acid were pre-polymerized in a beaker. Then, the pre-polymer was mixed with aluminum oxide particles (150%) and transferred to a press machine at 150 °C under a pressure of 8 MPa for 1.5 h. As confirmed by SEM, no cracks or bubbles appeared in the new product.
- 2. Moreover, the grinding wheel prepared with lignin-furanic resin and aluminum oxide particles was harder than the PF grinding wheel and had high compression resistance. It presented an excellent abrasive property. The metal tube was cut by the wheel for 3 s with less weight loss.
- 3. The reaction of the dehydration condensation between lignin and furfuryl alcohol was established. As an environmentally friendly material, lignin-furanic resin showed a promising prospective for the advancement of the grinding wheel in the abrasive industry.

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