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Liquefaction of lignin in hot-compressed water to phenolic feedstock for the synthesis of phenol-formaldehyde resins

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Abstract

The corn stalk lignin was liquefied in hot-compressed water without any other additives to obtain the degraded liquids (DL) with liquefaction yields of 45.9-61.4 wt.%, under 3.4 MPa and 260℃. The degradation liquids， mainly composed of small molecular phenols as high as

84.6 wt.%, were put to use as substitutes for phenol to modify phenol-formaldehyde resin. The degradation liquids modified phenol-formaldehyde resins (DLPFs) possessed the highest adhesive strength (1.32±0.10 MPa) than the lignin-phenol-formaldehyde resin (LPF, 0.72±0.20 MPa) and typical phenol-formaldehyde resin (PF, 0.77±0.26 MPa). The free formaldehyde contents of the DLPFs were all lower than the requirement of the corresponding standard (≤0.3 wt.%), even when 60% of phenol was replaced by DL (0.232 wt.%). The curing behavior analysis showed that the introducing of DL notably decreased the curing activation energy. The results demonstrated that the DLs were very suitable substitution for phenol in preparation of DLPFs. The adhesive strengths of DLPFs were considerably improved compared with typical PF. The thermal curing kinetic analysis revealed that the values of activation energy were decreased obviously with the introduction of DL.

Keywords: A. resins；B. adhension; D. Chemical analysis; D. Mechenical testing; E. cure

1. Introduction

Lignin is one of the most abundant natural polymers, only less than cellulose, which occupies 10-30% by weight and 40% by energy biomass-based lignocellulosic materials [1]. A large amount of technical lignins are produced as by-products in pulping and paper industry as well as the emerging biomass refinery industry [2]. Many researchers, including our research group focus on separation of the main components in lignocellulosic resources in environment-friendly ways, such as steam explosion, extraction with recyclable solvents, ultrasonic or microwave assisted methods [3], and developing high value added products or high performance composites based on the isolated components separately [4-6]. The isolated natural cellulosic fibers have been identified with proper properties as reinforcement material in the field of bio-composites through extensive characterization and analyzation [7]. There are some natural cellulosic fibers have been adopted as reinforcements in polymer based composites, including bamboo fiber [8], and hemp fiber [9] etc., and both the oriented bamboo fiber and hemp fiber reinforced composites have perfect mechanical property with low weight. The hemp fiber reinforced composites even meet the requirement of ultra-light aviation [9]. Besides, the lignin cellulosic material, *e.g.* the date palm wood flour has been used as filler of linear low-density polyethylene to increase the flexural strength and flexural modulus considerably, without significant influence on the tensile strength of the composites [10]. Pretreated cellulosic fibers are also successfully applied in functional composites, such as sound absorber material [11], and building material [12].

As lignin contains phenolic –OH functional group, as well we its highly crossed, three-dimensional structure resembles phenol formaldehyde (PF) resin well, it is involuntarily taken as replacement for phenol to prepare PF resin. Lignin has performed satisfactorily as a partial substitution of phenol in PF resins, especially after purification, and activation treatment including methylolation [13] or phenolation [14]. There are investigations on polymerization of liquefied agricultural residues or wood with formaldehyde with different catalysts [15-17], and other researchers have liquefied various lignins in phenol to prepare lignin-based PF resins [18-21]. Although they reported that the resol resins readily synthesized from the oily liquid products from wood or agricultural residues had pretty good performance compared with the typical PF resin, it is obvious that the complicated compositions in the liquefied biomass are not beneficial for the properties of the resins. According to the phenol-liquefied lignin derived PF resins, the lignin was activated mainly through dissolving and phenolation, but the network of the lignin had not been efficiently broken and activated.

In recent years, chemical depolymerization of lignin for getting bio-oil and fine chemicals has been developed greatly. It has been summarized and classified into five types of treatments, including base-catalyzed, acid-catalyzed, metallic catalyzed, ionic liquids-assisted, and supercritical fluids-assisted lignin depolymerization [22]. In another reviewed paper, the authors summarized oxovanadium complexes as catalysts to converse lignin models and extracts into small molecular ketones by selective aero oxidation [23]. The supercritical fluids have attracted researchers` interest to assist lignin depolymerization. Ethanol, methanol as well as mixed supercritical fluids, such as carbon dioxide/acetone/water have been applied to treat lignin. According to our earlier research, lignin can be efficiently depolymerized in subcritical water (or named hot-compressed water) [24-25], which points to liquid water between 100℃ and the critical point (374.2℃, 22.1MPa). The characteristics of the subcritical water change from gas-like to liquid-like with the variation of temperature and pressure, including density of hydrogen bonds, dielectric constant, ionization, and so on.

To obtain highly activated compounds from lignin, and then take them into preparation of LPF resins, the lignin was conducted to degradation liquefaction in hot-compressed water. The degradation liquids were put to replace phenol partially for synthesis of DLPF. The adhesive strengths of the prepared DLPFs were increased considerately than typical PF resin. Furthermore, the cure kinetic mechanisms of the DLPFs were investigated with dynamic and isothermal differential scanning calorimetry (DSC) to exhibit lower activation energies compared with LPF and typical PF resin, which was different from the reported liquefied wood/phenol/formaldehyde resins [26]. To further understand how the degradation liquefaction benefits the performance of DLPF resins, the chemical structures of the water soluble degradation liquids were comparable analyzed with original lignin and solid residues after degradation using FTIR, and GC-MS analysis was applied to manifest the chemical compositions of the low molecular degradation products.

2. Experimental Section

2.1 Materials

Lignin was supplied by Shandong Shengquan group Co. Lt. It was isolated from corn stalk under high pressure with pH of 5.35, containing 1.24% ash and with an electrical conductivity of 200 μS/cm. Lignin was crushed and sieved with a sieve of 60 meshes to get the lignin powder, and then dried at 105 ºC in an oven overnight before use. Single poplar veneer was purchased from Chengdu and its moisture content was kept at 8.2 wt.% for use. The phenol, formaldehyde solution (37-40 wt.%), ethyl acetate and sodium hydroxide and other reagents, of analytical grade, were purchased from Chengdu Kelong Chemical Reagent Co. and used without further purification.

2.2 Degradation liquefaction of lignin in hot compressed water

In this work, the degradation liquefaction of lignins was carried out in a 1L autoclave reactor (GSH-1) equipped with a mechanical stirrer and a water-cooling system. In a typical run, 20 g lignin and 200 g deionized water were added into the autoclave. After being securely sealed, the reactor was piped in nitrogen to get a certain pressure when necessary before being heated to a destined temperature and pressure. After the degradation was stopped, the reactor was cooled to room temperature, and the reaction mixture was filtered. The solid residue was rinsed thoroughly with water and ethyl acetate separately. The recycled solid residue (SR) was dried and weighed to calculate liquefaction ratio of lignin with substraction method, and all the liquid phases were combined and concentrated with vacuum rotation vaporization for DLPF preparation.

2.3 Preparation of PF, LPF and DLPF resins

Phenol-formaldehyde (PF) resins were synthesized by batch copolymerization. The phenol and formaldehyde are in molar ratio of 1:1.8 with 10 wt% NaOH as catalyst. The mixture was heated to 80℃, and kept for 4 h. After cooling down, the reaction mixture was vacuum evaporated under 50℃ to regulate the viscosity to be 150-200 mPa·s to get the viscous PF resin.

Lignin-phenol-formaldehyde (LPF) and degradation lignin-phenol-formaldehyde (DLPF) resins were synthesized in the similar way as PF, only using lignin or liquefied lignin to replace phenol in certain percentage. The experimental process of the liquefaction of lignin for the synthesis of DLPF was shown in Figure 1.

2.4 Gas chromatography - Mass spectrometry(GC-MS)

The obtained liquefied lignin was extracted thoroughly with ethyl acetate and the chemical compositions of the extraction were analyzed with GC-MS (HP 6890/5973 equipped with DB-5 MS column). The column temperature was set at 80 ºC, using helium as the carrier gas. The inlet temperature was 280 ºC with a shunt mode. The heating rate was set at 5 ºC/min from 60 to 140 ºC, 3 ºC/min from 260 to 300 ºC successively and kept at the end temperature for 12 min.

2.4 Fourier transform infrared spectroscopy (FT-IR)

The original lignin, the portion of liquefied products left in aqueous phases after being extracted with ethyl acetate and the prepared PF and LDPF resins were subjected to FT-IR (Nicolet 5700, USA) analysis to detect their chemical changes. All spectra were recorded over 4 scans, in the wave number range from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}.

2.5 Properties analysis of PF, LPF and LDPF resins

The properties of the prepared resins, including non-volatile contents, viscosity, free formaldehyde levels, pH values were determined with standard methods in accordance with GB/T 14074-2006. The non-volatile contents were determined through evaporation of the resin samples at 120℃ for 120 min before weighting and calculating. The viscosity was measured by 4 cup viscometer method at 25℃. The free formaldehyde level was determined with hydroxylamine hydrochloride standard method.

Adhesive strength was tested in accordance with GB/T 17657-1999. This test method is applicable for an adhesive used as a non-gap-filling adhesive suitable for use only in those joints where the surfaces to be jointed may be brought into close contact by means of adequate pressure. Single poplar veneers with moisture content of 8.2 wt.% were used for testing of adhesive strength. The prepared resins were applied uniformly to the inside surface of the two veneers at a spread rate of 120 g/m^2. The glued plywoods were then cold-pressed under a load of 0.5 MPa for 0.5 h, followed by being hot-compressed at 140℃ under a load of 1.0 MPa for 7min, and cold-pressed under 0.5 MPa for 7 min again. After conditioning for 72 h at room temperature (27±2℃), the plywood sheet was cut into specimens for adhesive strength test. Dry strength of the specimens was measured with a Universal Testing Machine (RGM-4020) at a loading rate of 5 mm/min. At least 5 replicates were tested and the average values were recorded.

2.6 Differential scanning calorimetry (DSC)

The thermal curing property of the prepared resins were evaluated with a differential scanning calorimetry (NETZSCH STA 449C, Germany) under N_2 flow of 50 mL/min. The samples contained in aluminum crucibles were heated from 30 to 250℃ at the rate of 5-20℃/min, during which, the DSC curves were recorded.

3. Results and discussion

3.1 Degradation liquefaction of lignin in hot-compressed water

The liquefaction of lignin was conducted in water under 260℃, 3.4 or 16.9 MPa, and periods of time from 10 to 30 min to get low molecular phenols in high yield. As shown in Table 1, the highest liquefaction yield of 61.4 wt.% was obtained under conditions of 260℃, 3.4 MPa and 10 min. It should be pointed out that, the liquefaction yields were not modified by the volatile productions, because which has not been detected properly. Since it has been reported that some volatile organic compounds may also be produced during the hydrothermal degradation process [27]. The liquefaction yields decrease with both the elongation of the reaction time and the increase of the pressure from 3.4 to 16.9 MPa by pre-folding 6 MPa N_2. Previous study displayed that the intermediates would undergo condensation with the proceeding of depolymerization [28-30]. The liquefaction yields under 16.9 MPa were all less than that under 3.4 MPa, which made it clear that the properties of water had obvious effect on the degradation. Under higher pressure, the dielectric constant of water decreases, which may results in higher solubility to organic intermediates [31] and then the condensation reaction becomes easier.

Besides the liquefaction yields, we pay more attention to the phenolic compositions contained in the degradation liquids, which act as reactants in preparation of PF resin. The degraded liquids were extracted with ethyl acetate, and the extracts were analyzed by GC-MS, the other water soluble fractions of liquid productions were analyzed with FTIR.

As shown in Table 2, the major compounds contained in ethyl acetate extracts are phenolic compounds such as 2-methoxy-phenol (from 11.63 to 22.02 wt.%), 2,6-dimethoxy-phenol (from 16.19 to 29.85 wt.%), 3,5-dimethoxy-4-hydroxyacetophenol (from 15.03 to 34.47 wt.%). With increasing reaction time, the phenol and some mono-substituted phenolic compounds such as 2-methoxy-phenol were detected, while the contents of 2,6-dimethoxy-phenol and 3,5-dimethoxy-4-hydroxyacetophenol decreased considerately. As to total phenolic compounds, it was apparently increased from 74.88 to 84.65 wt.% as the reaction time increased from 10 to 20 min, and then decreased slightly to 83.35 wt.% with continuous increasing the reaction time to 30 min under 3.4 MPa. Since the contentions of total phenolic compounds in the degradation liquids under 16.9 MPa were almost the same as which under 3.4 MPa, while the liquefaction efficiencies decreased as shown in Table 1. So, the three degradation liquids under 3.4 MPa were furtherly conducted in DLPF preparation.

The degradation products left in water phases after extracted with ethyl acetate were then condensed and analyzed with FTIR. The four samples obtained under conditions of 3.4 and 16.9 MPa for 10 and 30 min were comparable collected in Figure 2. The peaks at around 3400 and 2900 cm^{-1} belong to stretch vibrations of –OH and C-H respectively. The absorption at 1670 cm^{-1} is according to the stretch vibration of carboxyl. The group of peaks between 1400 and 1600 cm^{-1} are ascribed to the skeleton stretches of aryl. The vibrations at 1120 and 1270 (spectra a, b, c) or 1294 (spectrum d)cm^{-1} are produced by C-O of guaiacyl and syingyl. The weak absorptions at 922 and 778 cm^{-1} (spectra a and b) or 942 and 789 cm^{-1} (spectra c and d) are corresponded to the C-C vibration with different substitutions. Based on the red shift of carboxyl from 1578 to 1565 cm^{-1} and the blue shifts of C-O of guaiacyl and syingyl from 1270 to 1294 cm^{-1} and the C-C vibration from 922 and 778 to 942 and 789 to the C-C vibration, respectively, it is suggested that with increasing the pressure and reaction time the products become more complex because of the condensation reaction. Because the substitution of aryl increased, the vibration of C-O of guaiacyl and syingyl, and C-C bend of aryl became difficult, while the stretch of carbonyl connected with aryl became easier because of more conjugation.

3.2 Preparation and characterization of LPF and DLPF

The three lignin degradation liquefaction products under 3.4 MPa and different treating time (Experiments 1, 2, and 3 in Table 1) were furtherly conducted in DLPF preparation to replace 25 wt.% of phenol. The typical PF and lignin phenol formaldehyde (LPF) resin (25 wt.% of phenol was replaced by lignin). The prepared DLPF, LPF, and PF resins were carefully analyzed according to the standard methods (GB/T 17657-1999), and the pH, viscosity, non-volatile contents, free formaldehyde, and adhesive strength of the plywood were summarized in Table 3.

Although lignin contains phenolic –OH functional groups, and the highly crossed, three-dimensional structure resembles phenol formaldehyde (PF) resin very well, its low reactivity decreased the performance of LPF resin compared with typical PF. By comparing with PF (in Table 3), the free formaldehyde of LPF increased to 0.181 from 0.052 wt.%, and the adhesive strength decreased from 0.92±0.26 to 0.72±0.20 MPa.

It is clear that, the viscosity of all DLPF resins was higher than that of the PF. The non-volatile content of DLPF10 was equal to PF, and which of the other two DLPFs was increased obviously as shown in Table 3. This is benefit to form a continuous bond line between two cementing limiting surfaces when application. The adhesive strength of all the DLPFs are increased continuously with the elongation of the degradation time. As shown in Table 3, the adhesive of LDPF30 is 1.40±0.21 MPa, which is much higher than both the PF (0.92±0.16 MPa) and LPF (0.72±0.20 MPa). While, the free formaldehyde content of DLPF30 was increased heavily to 0.132 wt.%, compared with the other DLPFs (0.104 wt.%). Under consideration of both the apparently decreasing of liquefaction yields (from 59.3 to 45.9 wt.%, with the degradation time increasing from 20 to 30 min, in Table 1) and the reason of environmental safety, the DLPF30 was not believed to be the best resins. So, DLPF20 was selected to furtherly inspect the effect of replacement amount of liquefied lignin (DL) to phenol on the properties of the synthesized resins, and the results were summarized in Table 4.

By increasing replacement amount from 25:75 to 60:40 in weight, all properties are keeping good enough as adhesives, except that the free formaldehyde increased considerably from 0.141 to 0.232 wt.% when the replacement amount was increased from 40:60 to 60:40 in weight, which was very close to 0.3 wt.% of the standard limitation. It has been proven that the degraded lignin liquids themselves have the adhesive property, which is in accordance with the point that lignin can take the actions of both phenol and formaldehyde in synthesis of PF resins [32-34]. To reduce the free formaldehyde of the DLPF resins, using less formaldehyde than the common level of 1:1.8 (molar ratio of phenol to formaldehyde) might take effect, which will be put into the future work as one of the important consideration.

3.3 Thermal curing kinetic analysis of DLPF compared with PF

To manifest the curing kinetics of such synthesized DLPF resin adhesives, DSC scans conducted at different heating rates. The curing characteristic temperatures could be determined from peak temperatures obtained from nonisothermal DSC measurements at various heating rates through linear-regression analysis. The intercept at the heating rate of 0℃/min was regarded as the characteristic curing temperature under the isothermal condition. The activation energy could also be obtained by using both the Flynn-Wall-Ozawa and Kissinger methods from the dependence of the peak temperatures on the heating rates. All of the detected peak temperatures and the calculated activation energies are summarized in Table 5. The DSC curves of the PF and DLPFs at heating rate of 5℃/min are shown as Figure 2.

As displayed in Figure 3, the exothermic peaks of all the DLPFs are almost the same as that of the PF adhesive, indicating that the reactivity of DLs is very close to PF. The data in Table

5 also made it clear that the curing temperatures of the DLPFs under the isothermal condition were very near to that of PF resin.

The activation energy values calculated by both the Flynn-Wall-Ozawa and Kissinger methods were very similar, although the values calculated with the Kissinger method (E_K) were always slightly lower than those with the Flynn-Wall-Ozawa method (E_O) for all the adhesives. Comparison of the activation energy values of DLPFs with that of the PF, we can definitely draw the conclusion that the DLs are of higher reactivity even than lignin. Which furtherly proved that the lignin degradation liquids with hot-compressed water as the only medium was very promising for synthesis of DLPF resin adhesive. The chemical structures of the cured DLPF resins were also analyzed to be completely in accordance with typical PF as shown in Figure 4.

The adsorptions at 1600, 1470 and 1433 cm^{-1} are ascribed to the skeleton stretch vibration of aryl. The peaks at 1278 cm^{-1}, belongs to the C-O vibration. The vibrations at 1206 and 1142 cm^{-1} are associated with the C-H bending. The peak at 1010 cm^{-1} is in accordance with the stretch vibration of ether group. The two peaks at 878 and 782 cm^{-1} represent the vibration of substituted aryl. To clearly show the delicate adsorptions in the region of fingerprint, the strong adsorptions belonging to stretch vibrations of –OH and C-H between 4000 and 2500 are missed out here. It is worth being pointed out that there was no peak of carboxyl has been detected in the FTIR spectra. That is to say all the carboxyl groups have completely or mostly reacted during the synthesis of DLPF resins.

3. Conclusion

Commercial available corn stalk lignin was degradation liquefied in hot-compressed water without any other additives, and the degradation liquids were conducted as partial substitution of phenol to synthesize DLPFs. The results demonstrated that the DLs were very suitable for preparing DLPFs, and the adhesive strength was considerably improved compared to PF. The curing kinetic analysis revealed that the values of activation energy were decreased obviously with the introduction of DL. The chemical structures of the cured DLPFs were completely in accordance with the typical PF according to the FTIR spectra. To decrease the free formaldehyde content of the DLPFs under high substitution of DL to phenol, increasing the ratio of phenol equivalent to formaldehyde is a reasonable method. Because the carboxyl groups of the DLs have been completely or almost reacted during the process, and no carboxyl group has been detected in the cured DLPF resins through FTIR analysis.

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Figure 1 The experimental process of the liquefaction of lignin for the synthesis of DLPF.

Figure 2 FT-IR spectra of water soluble fraction of degraded lignin under different conditions. (a) 260℃, 3.4 MPa, 10 min. (b) 260℃, 3.4 MPa, 30 min. (c) 260℃, 16.9 MPa, 10 min. (d) 260℃, 16.9 MPa, 30 min.

Figure 3 DSC profiles of PF (a) and DLPFs resins at 5℃/min, DLPF10 (b), DLPF20 (c), DLPF30 (d).

Figure 4 FT-IR spectra of various cured resins. (a) PF. (b) DLPF10. (c) DLPF20. (d) DLPF30.

Table 1 Recipes used in degradation liquefaction of lignin in hot-compressed water

Experiment	T (℃)	P (MPa)	T[*] (min)	Liquefaction yield (wt. %)
1	260	3.4	10	61.4
2	260	3.4	20	59.3
3	260	3.4	30	45.9
4	260	16.9	10	37.8
5	260	16.9	20	29.7
6	260	16.9	30	36.3

[*] As to the accuracy of our autoclave control system, 10 min is the minimum correct setting time.

Table 2 Compounds analysis of ethyl acetate extraction of the liquefied lignin by GC-MS

compound	Yield (wt.%) [a]					
	1	2	3	4	5	6
Phenol	0.25	0.36	8.66	6.86	8.63	8.64
2-Methoxy-phenol	-	-	11.63	16.48	18.40	22.02
4-Methyl-phenol	-	-	2.32	2.64	2.04	2.66
2-Methoxy-4-methyl-phenol	-	-	1.71	1.66	1.47	1.70
1,2-Benzenediol	1.33	-	1.13	-	-	-
3-Methoxy-2-benzenediol	2.27	-	3.86	3.52	5.72	3.30
4-Methyl-2-methoxy-phenol	-	-	3.23	5.15	4.33	5.29
2,6-Dimethoxy-phenol	16.19	29.85	18.20	22.06	20.17	26.28
4-Hydroxybenzaldehyde	2.02	1.41	-	-	-	-
3-Methoxy-4-hydroxy-benzaldehyde	9.94	6.45	4.85	0.97	0.78	-
4-Hydroxyacetophenone	1.64	2.33	-	-	-	-
3-Methoxy-4-hydroxy-acetophenone	4.66	5.64	3.34	2.24	2.15	-
3-Methoxy-4-hydroxy-phenylacetic acid	2.49	-	2.19	-	-	-
3,5-Dimethoxy-4-hydroxybenzaldehyde	3.74	-	1.85	-	-	-
3,5-Dimethoxy-4-hydroxyacetophenone	24.53	34.47	16.17	16.26	15.03	18.31
Total phenolic compounds	**74.88**	**84.65**	**83.35**	**76.41**	**79.83**	**88.70**

[a] The numbers are corresponding to which the experiments in table 1.

- No such compound was detected.

Table 3 Characterization and adhesive strength of the prepared PF, LPF and DLPF resins

Samples	Viscosity (mPa·s)	Non-volatile contents (wt. %)	Free formaldehyde (wt. %)	pH	Adhesive strength (MPa)
PF	75	48.7±0.2	0.052	10.8	0.92±0.16
LPF	180	43.6±0.2	0.181	11.0	0.72±0.20
DLPF10	150	48.6±0.3	0.104	11.2	0.94±0.16
DLPF20	240	57.2±0.4	0.104	11.2	1.09±0.12
DLPF30	210	55.2±0.4	0.132	11.1	1.40±0.21
GB/T 14732	≥60	≥35	≤0.3	≥7	≥0.7

Table 4 Properties of DLPF prepared with different replacement of phenol with liquefied lignin*

Sample	Ratio of DL to phenol (wt.:wt.)	Viscosity (mPa·s)	Non-volatile contents (wt. %)	Free formaldehyde (wt. %)	pH	Adhesive strength (MPa)
PF	0:100	75	48.7±0.2	0.052	10.8	0.92±0.16
1	25:75	240	57.2±0.4	0.104	11.2	1.09±0.12
2	40:60	220	51.8±0.4	0.141	11.2	1.04±0.24
3	60:40	240	52.0±0.4	0.232	11.1	1.19±0.22

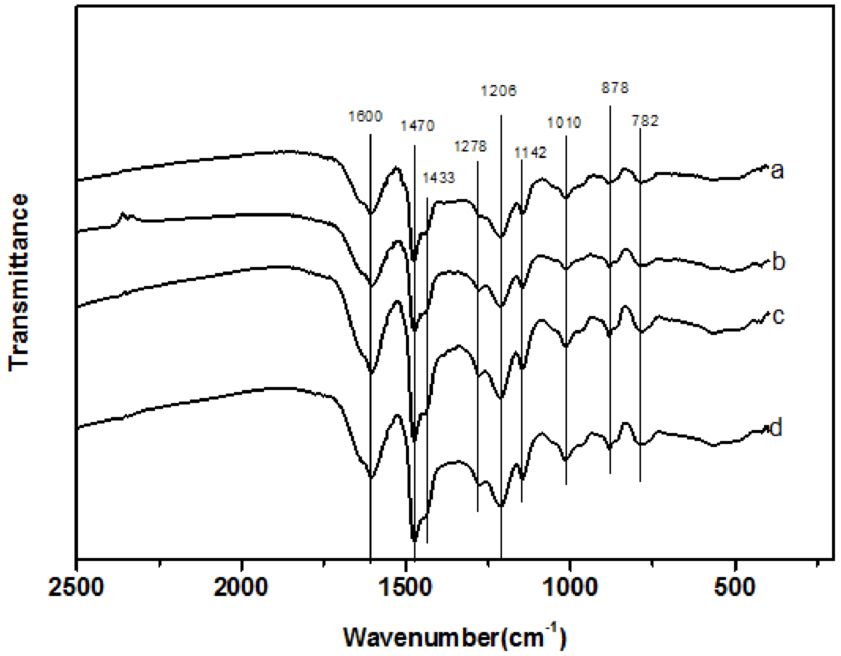
*All the DLPF samples were synthesized under the same conditions: 10 wt.% of NaOH, ratio of phenol and DL to formaldehyde in molar 1:1.8, reaction temperature 80℃ and reaction time 4h.

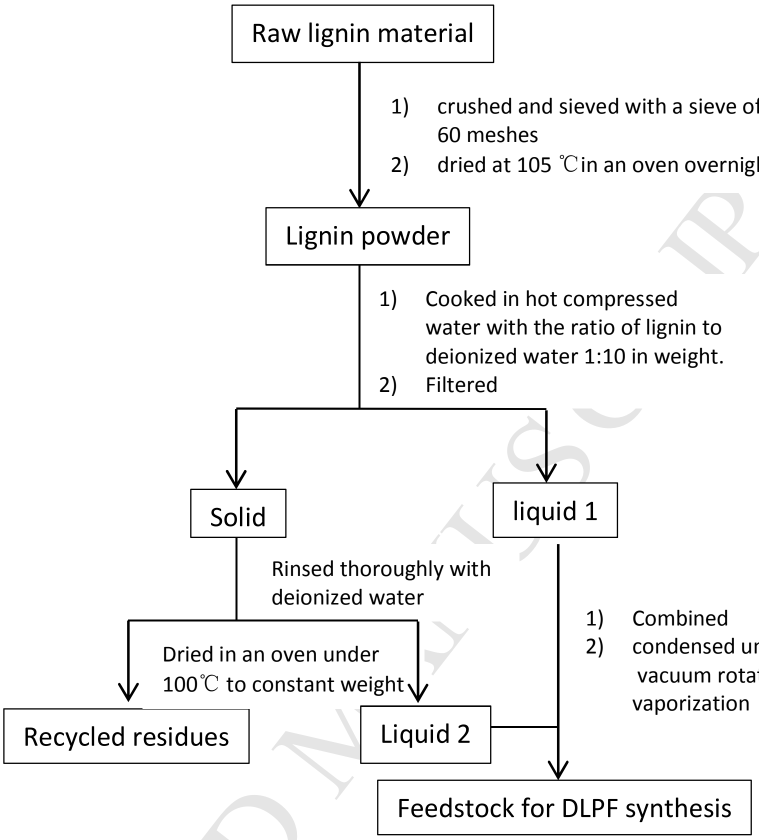
Table 5 Thermal cure kinetics parameters PF and DLPF resins

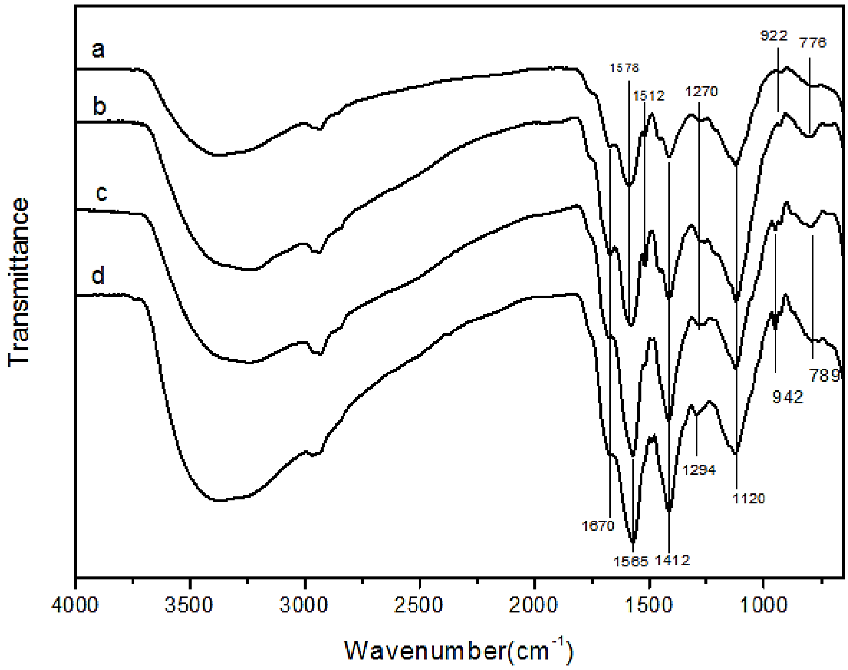
	T_p (℃)					
Sample	5℃min^{-1}	10℃min^{-1}	15℃min^{-1}	20℃min^{-1}	E_K (KJmol-1)[a]	E_O (KJmol-1)[b]
PF	123.9	134.9	138.9	142.8	93.4	95.1
DLPF10	124.1	129.4	140.5	144.8	78.2	80.8
DLPF20	124.9	134.8	139.6	145.5	88.7	90.9
DLPF30	12.1	135.6	139.9	144.0	67.4	68.6

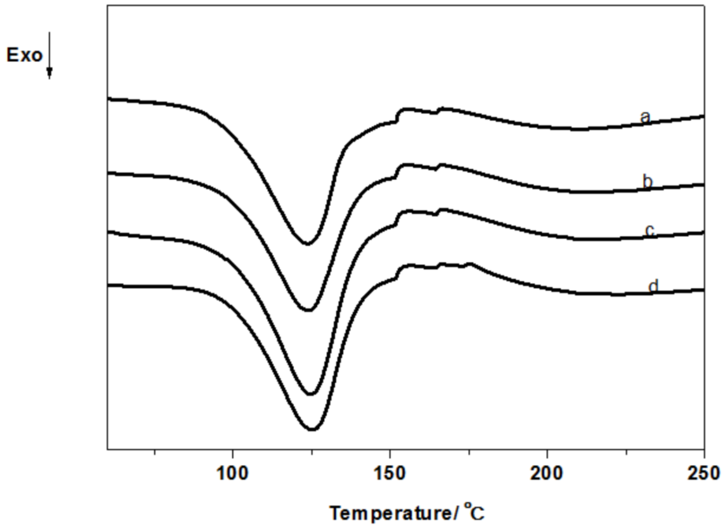
[a] E_K was calculated according to the Kissinger method.

[b] E_O was calculated according to the Fly-Wall-Ozawa method.


1600
1470
1433
1278
1206
1142
1010
878
782
a
b
c
d
Transmittance
2500
2000
1500
1000
500
Wavenumber(cm^{-1})


Raw lignin material
1) crushed and sieved with a sieve of 60 meshes
2) dried at 105 ℃in an oven overnight
Lignin powder
1) Cooked in hot compressed water with the ratio of lignin to deionized water 1:10 in weight.
2) Filtered
Solid
liquid 1
Rinsed thoroughly with deionized water
Dried in an oven under 100℃ to constant weight
1) Combined
2) condensed under vacuum rotation vaporization
Recycled residues
Liquid 2
Feedstock for DLPF synthesis


a
b
c
d
Transmittance
922
776
1578
1512
1270
942
789
1294
1120
1670
1565
1412
4000
3500
3000
2500
2000
1500
1000
Wavenumber(cm^{-1})


Exo
a
b
c
d
100
150
200
250
Temperature/ °C