

Properties of Phenol-Formaldehyde Resins Prepared from Phenol-Liquefied Lignin

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ABSTRACT: In this study, alkaline lignin (AL), dealkaline lignin (DAL), and lignin sulfonate (SL) were liquefied in phenol with sulfuric acid (H₂SO₄) or hydrochloric acid (HCl) as the catalyst. The phenol-liquefied lignins were used as raw materials to prepare resol-type phenol-formaldehyde resins (PF) by reacting with formalin under alkaline conditions. The results show that phenol-liquefied lignin-based PF resins had shorter gel time at 135°C and had lower exothermic peak temperature during DSC heat-scanning than that of normal PF resin. The thermo-degradation of cured phenol-liquefied

lignin-based PF resins was divided into four temperature regions, similar to the normal PF resin. When phenol-liquefied lignin-based PF resins were used for manufacturing plywood, most of them had the dry, warm water soaked, and repetitive boiling water soaked bonding strength fitting in the request of CNS 1349 standard for Type 1 plywood. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 4782–4788, 2012

Key words: lignin; liquefaction; phenol-formaldehyde resin; plywood

INTRODUCTION

Lignocellulosic biomasses are renewable natural resources that are composed mainly by organic polymers such as cellulose, hemicellulose, and lignin. Solvent liquefaction is an effective method to fully convert them from solid to liquid, and the liquefied products can be used as raw materials for various polymers. Phenol is a widely used solvent for liquefying lignocellulosic biomasses. During liquefaction, both carbohydrate and lignin will undergo hydrolysis, degradation, and decomposition reactions to become small fragments or monomolecular compounds, after which, they react with phenol to form derivatives.^{1,2} These phenol-liquefied products have the ability to react with formaldehyde; and so, most utilization studies focus on the preparation of PF resins.^{3–9}

There is an enormous amount of lignin produced from the pulping industry worldwide. However, most of it is treated as a waste, although some is burned to generate energy. Nevertheless, because of the phenolic structure of lignin, it can react with formaldehyde and be used as the raw material for preparing PF resins. Many articles have indicated that lignin-based PF resins can be used as the binder for particleboard, oriented strandboard, plywood, etc.^{10–12}

However, PF resins prepared from reacting lignin with formaldehyde have some drawbacks compared with normal PF resins. They have lower reactivity due to the larger molecular structure and less reactable position of lignin, and so, using a higher temperature, and a longer time would be demanded to achieve a complete curing.^{13,14} Therefore, some modification may be necessary for lignin to increase its reactivity for use for preparing PF resins. Khan et al.¹⁵ prepared lignin–phenol adducts as the first step, followed by reaction with formaldehyde to form lignin-based PF adhesives. They found that up to 50% of the phenol can be substituted by lignin, it gives a better bonding strength than that of the control PF adhesive. Cetin and Özmen¹⁶ indicated that particleboards bonded with phenolated-lignin formaldehyde resins had physical and mechanical properties similar to those bonded with commercial PF.

Lignin is defined as a polyphenolic material that is polymerized with phenylpropanoid monomer. However, lignin obtains from different plant species, pulping process, and recovering methods from the pulping liquor used to produce lignin can have various properties that influence the suitability for preparing PF resins.^{17,18} Furthermore, an advanced change in the properties of lignin will occur during the period of liquefaction.¹⁹

In this study, various lignins that liquefied with different conditions were used as raw materials to prepare the lignin-based PF resins. The hot-curing behavior, bonding strength, and heat resistance of

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cured resins were investigated and were compared with normal PF resin.

EXPERIMENTAL

Materials

Three kinds of lignin, i.e., alkaline-lignin (AL; reagent grade; Tokyo Chemical Industry, pH 9.27), dealkaline-lignin (DAL; reagent grade; Tokyo Chemical Industry, pH 4.12), and lignin sulfonate (SL; commercial technical lignin; pH 8.45) were used as raw materials. Bark powder of Taiwan acacia (*Acacia confusa*) with the dimension passing 200 mesh were used as the filler for manufacturing plywood. Chemicals such as phenol (C_6H_5OH ; P), hydrochloric acid (HCl), sulfuric acid (H_2SO_4), formalin (37% $HCHO_{(aq)}$), methanol (CH_3OH), sodium hydroxide (NaOH), and hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) were reagent grade and used without further purification.

Liquefaction of lignin

Lignin was liquefied in phenol with 5% of H_2SO_4 or HCl as the catalyst. The liquefaction reaction was conducted in a 1000-mL four-neck round-bottom glass reactor equipped with a stirrer, a thermometer, and a reflux condenser at $130^\circ C$ for 60 min.

Properties of liquefied lignin

The viscosity and pH of liquefied lignins were measured at $25^\circ C$ using a pH-meter and a Brookfield viscometer, respectively. The Stiasny number defined as the formaldehyde-condensable polyphenols was measured by the Wissing method.²⁰

Synthesis of resol-type PF resins

Lignin-based PF resins were prepared with the phenol-liquefied lignin as the raw material. The molecular weight of phenol (94 g/mol) was used to calculate the amount of liquefied lignin needed. The molar ratio of formaldehyde/phenol-liquefied lignin/NaOH was set as 1.8/1/0.35. To prepare resin, the liquefied lignin, formalin, and one-third of the $NaOH_{(aq)}$ were put into the round-bottom reactor equipped with stirrer, thermometer, and reflux condenser and heated at $85^\circ C$ for 10 min followed by gradually adding the remaining two-thirds of $NaOH_{(aq)}$ dropwise. After all the $NaOH_{(aq)}$ had been added, the reaction proceeded at $85^\circ C$ until the viscosity of the resin exceeded 200 cps. In addition, phenol and the mixture of AL lignin/phenol with a weight ratio of 1/2.5 were used as raw materials to

prepare PF resins with the process similar to that of liquefied lignin.

Properties of synthesized PF resins

Properties of PF resins were measured according to CNS 12001 standard. Solid content was measured by drying resins in an oven at $135^\circ C$ for 60 min, viscosity was measured with a Brookfield viscometer at $25^\circ C$, and pH was measured by a pH-meter at $25^\circ C$. The gel time was measured by putting 10 g of resin in a glass tube with a thin wire, and then immersed it in a $135^\circ C$ oil bath. The time at which the tube could be lifted up by pulling the wire was identified as the gel time. The free formaldehyde was measured using the hydroxylamine hydrochloride method. For this test, 10 g of resin was diluted with 150 mL of distilled water, followed by adjusting the pH to 4. Then, 50 mL of hydroxylamine hydrochloride with pH of 4.0 was added and reacted about 5 min. The sample was titrated using a 0.5 N $NaOH_{(aq)}$ until the pH value reached 4.0.

DSC thermosetting analysis of PF resins

The thermosetting properties of PF resins were determined by differential scanning calorimetry (DSC; Perkin-Elmer DSC-7) with a large-volume O-ring sealed stainless steel sample pan. The sample was heated from $30^\circ C$ to $200^\circ C$ with a heating rate of $10^\circ C/min$ under a nitrogen environment.

TGA thermo-degradation of cured PF resins

For thermal gravimetric analysis (TGA; Perkin-Elmer Pyris 1 TGA-7), about 5 mg of cured PF resin was put into a platinum sample pan and heated from 50 to $750^\circ C$ at a heating rate of $10^\circ C/min$ under a nitrogen atmosphere with a flow rate of 20 mL/min. Curves of weight loss and derivative weight loss (DTG) were plotted.

Properties of plywoods bonding with PF resins

Three-layer plywood with the dimension of $30 \times 30 \times 0.4 \text{ cm}^3$ was made with Lauan veneer with the thickness of 1 mm and 2 mm for face veneer and core veneer, respectively. The PF resins used were blended with 15% of bark powder to adjust the viscosity to 1000–2000 cps. The rate of glue applied for a single glue line was 200 g/m^2 and sheets were cold pressed under 0.3 MPa for 10 min, followed by hot-pressed at $135^\circ C$ for 3.5 min at a pressure of 1.0 MPa. The plywood were stored at $20 \pm 1^\circ C$ and $65 \pm 2\%$ R.H. for one week to regulate the moisture content. The specimen dimensions and testing methods were according to the CNS 1349 standard.

TABLE I
Properties of Phenol-Liquefied Lignin

Lignin ^a	Liquefaction conditions		Visc. (cps)	pH	Stiasny number (%)
	P/L ^b (w/w)	Catalyst			
AL	2.5	H ₂ SO ₄	23360	5.59	97.6
AL ^c	2.0	H ₂ SO ₄	1140	5.69	93.2
AL ^c	1.5	H ₂ SO ₄	4940	5.56	92.7
AL	2.5	HCl	1425	5.60	102.6
DAL	2.5	H ₂ SO ₄	145	2.50	100.5
DAL	2.5	HCl	70	2.85	99.8
SL	2.5	H ₂ SO ₄	18940	3.92	103.5
SL	2.5	HCl	1166	4.49	106.3

^a AL, DAL, SL were alkaline lignin, dealkaline lignin and lignin sulfonate, respectively.

^b P and L were phenol and lignin, respectively.

^c Liquefied with phenol/water (9/1; wt/wt) as the solvent.

The tensile shear bonding strength was measured using a universal strength testing machine (Shimadzu UEH-10) at a loading speed of 1 mm/min. This included the dry, warm water soaking and repetitive boiling water soaking bonding strength. Wood failure of testing samples was estimated by naked eye from the glueline of destroyed specimens. Eight specimens were tested for each condition. Formaldehyde emissions were measured with the acetylactone method. For this testing, ten specimens with the dimension of 15 × 5 cm² were put into a desiccator that had the capability of 10 L and contained 300 mL of distilled water in the bottom. After 24 h at 20°C, the concentration of formaldehyde absorbed in the distilled water was determined by the acetylactone method with the ultraviolet spectroscope (UV) with the wavelength of 415 nm.

RESULTS AND DISCUSSION

Properties of phenol-liquefied lignin

Table I shows the properties of phenol-liquefied lignin. It indicates that lignin could be completely

dissolved in phenol after liquefaction. But the viscosity and the pH of phenol-liquefied lignin depended on the kind of lignin and the condition of liquefaction. Of the samples, DAL lignin had the lowest viscosity and AL lignin had the highest. Comparing HCl and H₂SO₄, using H₂SO₄ as the catalyst for liquefaction had higher viscosity than that of HCl. This might because the decomposed lignin undergoes a re-condensation reaction under acid liquefaction conditions²¹. The stronger acidity of H₂SO₄ promoted greater re-condensation than HCl, resulting in a higher viscosity. By decreasing the weight ratio of phenol to lignin, the viscosity of the liquefied product increased significantly (not shown in Table). But it was decreased when 10% of phenol was replaced with water, probably because the water could inhibit the recondensation of lignin²². The liquefied AL lignin had higher pH than DAL and SL lignin. All of the liquefied lignins had a Stiasny number over 92.7%. In our previous article, it indicated that phenol-liquefied lignins had the weight average molecular weight of about 4000, and some of phenol could combine with liquefied lignin.²³

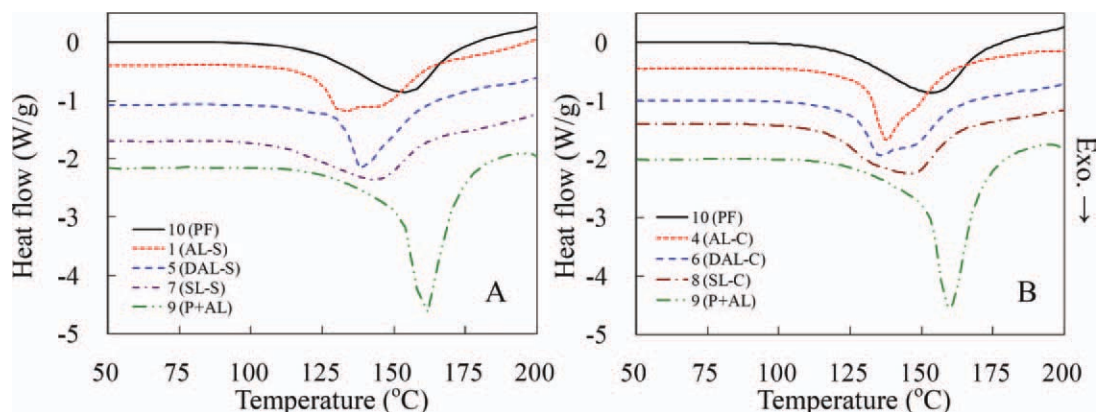


Figure 1 DSC curves of various kinds of PF resins. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
Synthesis Conditions and Properties of Prepared PF Resins

Resin	Liquefied lignin			Synthesis conditions			Properties of resins				
	Type	P/L ^a	Catalyst	F/P/NaOH ^b (Molar ratio)	Temp. (°C)	Time (min)	Solid content (%)	pH	Visc. (cps)	Gel time (min)	Free formaldehyde (%)
1	AL	2.5	H ₂ SO ₄	1.8/1/0.35	85	60	49.9	10.96	243	9.2	0.91
2	AL ^c	2.0	H ₂ SO ₄	1.8/1/0.35	85	60	48.1	11.26	282	10.5	2.58
3	AL ^c	1.5	H ₂ SO ₄	1.8/1/0.35	85	40	48.5	11.14	266	8.3	3.59
4	AL	2.5	HCl	1.8/1/0.35	85	60	50.5	10.57	288	11.2	1.02
5	DAL	2.5	H ₂ SO ₄	1.8/1/0.35	85	60	49.4	9.93	334	8.2	1.20
6	DAL	2.5	HCl	1.8/1/0.35	85	60	50.6	10.84	249	11.2	0.89
7	SL	2.5	H ₂ SO ₄	1.8/1/0.35	85	60	50.8	10.21	264	12.0	0.57
8	SL	2.5	HCl	1.8/1/0.35	85	60	50.5	10.52	207	9.5	0.60
9 ^d	-	-	-	1.8/1/0.20	90	40	51.7	10.12	292	13.0	0.92
10 ^e	-	-	-	1.8/1/0.35	90	90	51.4	11.30	254	14.0	0.07

^a The weight ratio of phenol to lignin.
^b P represented phenol-liquefied lignin or phenol.
^c AL liquefied with phenol/water (9/1; wt/wt) as the solvent.
^d Prepared from the mixture of phenol with AL lignin (2.5/1; w/w).
^e Prepared from phenol.

Properties of PF resins prepared

Table II lists the synthesis conditions and properties of PF resins prepared. It took 90 min to reach viscosity over 200 cps for the normal PF (Resin 10) that prepared by reacting phenol with formaldehyde at 90°C. However, a lower temperature and a shorter time to reach this viscosity was needed for resins using phenol-liquefied lignin as raw materials. The normal PF resin had solid content of 51.4% and pH of 11.30. PF resins prepared from phenol-liquefied lignin had lower solid content and pH than that of normal PF resin, which had solid content between 48.1% and 50.8% and pH between 9.93 and 11.26. The gel time for normal PF resin was 14.0 min when heating at 135°C, whereas phenol-liquefied lignin-based PF resins had shorter time for gelling,

indicating they had higher reactivity than that of normal PF resin.

Resin 9, prepared from the mixture of phenol and AL lignin, had a faster viscosity increase during the

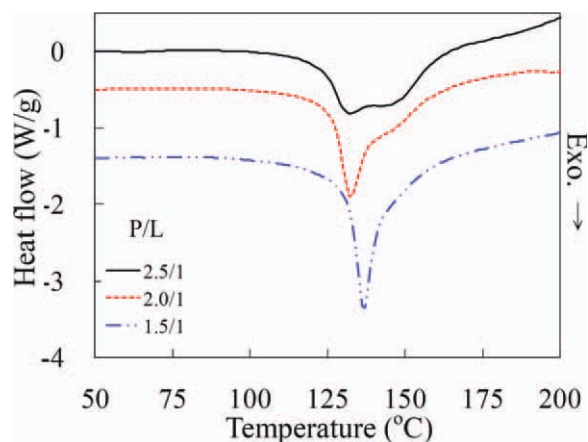


Figure 2 DSC curves of PF resins prepared from phenol-liquefied AL lignin with various P/L weight ratios. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

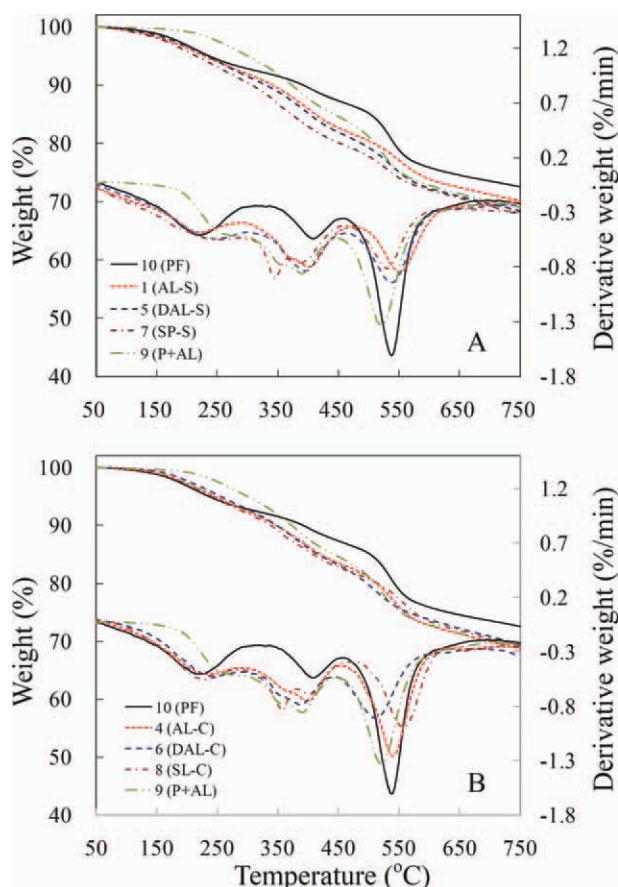


Figure 3 TGA and DTG curves of various kinds of PF resins. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

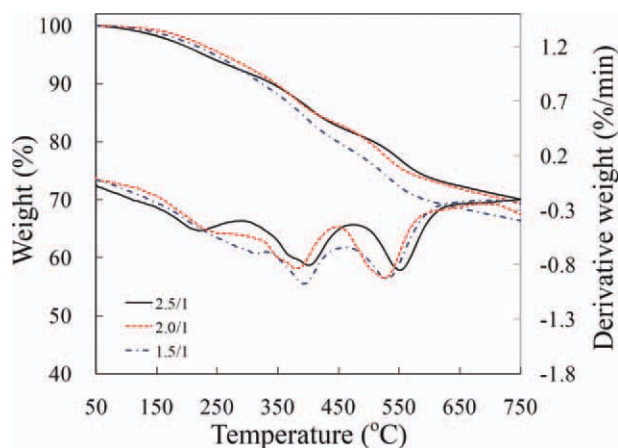


Figure 4 TGA and DTG curves of PF resins prepared from phenol-liquefied AL lignin with various P/L weight ratios. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

period of synthesis, but its gel time was similar to the normal PF resin. This is because it was synthesized under a lower NaOH content, which induced a resin with higher increase of viscosity because it was less hydrophilic, but did not really promote the molecular growth.

Resins 2 and 3 that prepared with the liquefied-lignin having the weight ratio of phenol to AL as 2.0/1 and 1.5/1, respectively, had more free formaldehyde than others. Because lignin had less free position in the aromatic nuclei and considerably lower reactivity than that of phenol,¹³ the higher free formaldehyde might due to their less content of phenol in the liquefied-lignin and the lower Stiasny number that shown in Table I.

DSC thermosetting analysis of PF resins

Figure 1 shows DSC thermosetting curves of various PF resins. All of them shows an obvious exothermic

peak due to the curing reaction. The normal PF resin had the onset temperature of 120°C and peak temperature of 154°C. In contrast, the peak temperature dropped for phenol-liquefied lignin-based resin in both Figure 1(A,B), indicating it had higher reactivity than that of the normal PF resin. Of the various phenol-liquefied lignin, AL lignin had the lowest peak temperature and SL lignin had the higher peak temperature. On the other hand, Resin 9, prepared from the mixture of phenol and AL lignin, had a sharp exothermic peak with higher peak temperature and larger peak area than the normal PF resin. These results indicate that this resin underwent less degree of condensation during the period of synthesis and had less reactivity. Therefore, it needs a higher temperature to complete its curing reaction during the period of DSC heat scanning.

Figure 2 shows DSC curves of PF resins prepared from lignin liquefied with various weight ratios of phenol to lignin. The resin prepared from lignin that was liquefied with the weight ratio of 2.5/1 had a broader exothermic peak but lower peak height, indicating its curing reaction occurred over a wider temperature range. Nevertheless, with decreased weight ratio of phenol to lignin (2.0/1 and 1.5/1), the exothermic peak became sharper within a narrow temperature range. It might be because they had higher free formaldehyde content as shown in Table II, which cause a drastic crosslinking reaction during DSC heat scanning. But due to the lower reactivity and less free position for lignin than that of phenol,¹³ the crosslinking reaction finished at early time.

TGA thermo-degradation analysis of cured PF resins

Figure 3 shows the TGA and DTG curves of cured PF resins. The normal PF resin had better heat resistance than that of phenol-liquefied lignin-based PF,

TABLE III
Bonding Strength of Plywood Made with Various PF Resins

Resin	Liquefied lignin			Bonding strength (MPa) ^a			Formaldehyde emission (mg/L)
	Type	P/L	Catalyst	Dry	Warm water soaking	Repetitive boiling water soaking	
1	AL	2.5	H ₂ SO ₄	1.23 ± 0.31 (60)	0.91 ± 0.15 (60)	0.58 ± 0.16 (15)	0.39
2	AL	2.0	H ₂ SO ₄	1.22 ± 0.15 (50)	1.04 ± 0.15 (35)	0.73 ± 0.11 (15)	1.11
3	AL	1.5	H ₂ SO ₄	1.19 ± 0.15 (85)	0.92 ± 0.14 (65)	0.54 ± 0.22 (20)	1.41
4	AL	2.5	HCl	1.42 ± 0.19 (50)	1.22 ± 0.15 (55)	1.10 ± 0.24 (50)	0.56
5	DAL	2.5	H ₂ SO ₄	1.30 ± 0.12 (50)	1.06 ± 0.30 (20)	1.04 ± 0.18 (20)	0.46
6	DAL	2.5	HCl	1.23 ± 0.16 (75)	0.95 ± 0.22 (90)	0.83 ± 0.18 (50)	0.59
7	SL	2.5	H ₂ SO ₄	1.24 ± 0.15 (90)	1.05 ± 0.17 (80)	0.81 ± 0.22 (50)	0.16
8	SL	2.5	HCl	1.36 ± 0.25 (60)	0.92 ± 0.34 (25)	0.87 ± 0.25 (20)	0.40
9	-	-	-	1.25 ± 0.24 (75)	0.96 ± 0.17 (70)	0.96 ± 0.14 (35)	0.98
10	-	-	-	1.42 ± 0.22 (100)	1.23 ± 0.16 (80)	1.02 ± 0.12 (65)	0.12

^a () indicates the percentage of wood failure.

less weight loss during the period of heating, and higher char content at 750°C. The thermo-degradation of these resins can be divided into four temperature regions, i.e., lower than 300°C, 300–450°C, 450–600°C, and higher than 600°C, with the most drastic thermo-degradation occurred at temperature between 500 and 550°C.

For temperatures below 300°C, the weight loss included the evaporation of formaldehyde, water, phenol, and cresol those formed by the breaking of methylol groups, the condensation reaction between methylol groups, and the methylene bridge breakdown. For temperatures between 350°C and 450°C, the weight loss might be due to the loss of water that produced from the condensation reaction between phenolic OH and methylene and between two hydroxyl functional groups. For temperatures between 450°C and 600°C, crosslinking of methylene with carbon-hydrogen crosslinks causes hydrogen elimination. Furthermore, the water and the hydrogen produced would react with the methylene group, which would release carbon monoxide and methane, respectively. When the temperature exceeded 600°C, the continuous weight loss is mainly caused by the dehydrogenation of the benzene ring structure^{24,25}.

Comparing various kinds of phenol-liquefied lignin-based PF resins, those using HCl-catalyzed lignin as the raw material had better heat-resistance and higher char content at 750°C than that with H₂SO₄-catalyzed lignin. They had similar thermo-degradation behavior for various kinds of lignin. In contrast, when H₂SO₄-catalyzed lignin was used, AL-lignin had better heat-resistance than the others.

Figure 4 shows TGA and DTG curves of PF resins that were prepared from phenol-liquefied AL lignin that was liquefied with various weight ratios of phenol to lignin. Resins prepared with lower weight ratio, i.e., more lignin content in the liquefied lignin, had more weight loss at higher heating temperature and lower char content at 750°C.

Bonding strength of PF resins

Table III shows the shear bonding strength and formaldehyde emissions of plywoods made with various PF resins. The CNS 1349 standard requests the bonding strength of Lauan plywood should exceed 0.7 MPa. The normal PF resin had dry, warm water soaked, and repetitive boiling water soaked bonding strengths of 1.42, 1.23, and 1.02 MPa, respectively. All phenol-liquefied lignin-based PF resins had dry and warm water soaked bonding strength fitting this standard. In addition, most of the phenol-liquefied lignin-based PF resins, except Resin 1 and Resin 3, had the repetitive boiling water soaked bonding strength that conformed to the

standard; and of these, Resins 4 and 5 had bonding strengths similar to that of normal PF resin.

The formaldehyde emissions for F1, F2, and F3 plywoods as identified in the CNS 1349 standard were lower than 0.3, 0.5, and 1.5 mg/L, respectively. Plywoods made with normal PF resin and Resin 7 were graded as F1 plywood, while Resins 1, 5, and 8 were graded as F2 plywood. In contrast, plywoods made with Resins 2 and 3 had higher formaldehyde emissions, which might be because more free formaldehyde existed in the resin.

CONCLUSIONS

In this study, lignin was liquefied in phenol with H₂SO₄ or HCl as the catalyst. The phenol-liquefied lignin-based PF resins could be prepared with lower temperature and shorter time than the normal PF resin. In addition, phenol-liquefied lignin-based PF resins had higher reactivity than the normal PF resin; they had shorter gel time at 135°C and lower exothermic peak temperature during DSC heat-scanning. But the resin prepared from a mixture of phenol and AL lignin had a higher exothermic peak temperature and a larger peak area than that of normal PF resin. The thermo-degradation of PF resins were divided into four temperature regions, i.e., lower than 300°C, 300–450°C, 450–600°C and higher than 600°C; and the most drastic thermo-degradation occurred between 500°C and 550°C. Phenol-liquefied lignin-based PF resins had dry, warm water soaked, and repetitive boiling water soaked bonding strength fitted the request of CNS 1349 standard, except for Resins 1 and 3.

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