

## Application of Lignin-Modified Phenolic Resins to Brake Friction Material

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**ABSTRACT:** Lignin-modified phenolic resin (LPF) is prepared from methanol-soluble lignin by polymer blend methods (solvent blend and *in situ* polymerization) for application to environment-friendly brake friction material. The chemical structure of LPF is characterized by <sup>13</sup>C NMR, and TMA and DSC analyses are conducted to evaluate the thermal behaviors. Flexural tests and brake dynamometer tests of samples prepared from LPF by compression molding are carried out, and the results are compared with those for the samples prepared from commercial phenolic resin (PF). Results of the flexural test show that the addition of methanol-soluble lignin by solvent blend polymerization decreases the flexural strength. In contrast, *in situ* polymerized LPF exhibits flexural strength equivalent to that of PF. Results of the brake dynamometer test show that replacement of PF with methanol-soluble lignin increases the fade resistance of the brake friction material at elevated temperatures. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 310–315, 2013

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### INTRODUCTION

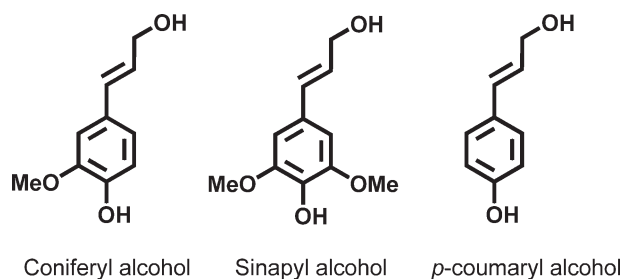
The effective utilization of biomass for material development has recently attracted much attention as an alternative to petrochemicals because of global warming and depletion of fossil resources. Lignocellulosic biomass, which consists of cellulose and lignin, is one of the most abundant renewable resources. Large amounts of lignin are produced as an industrial by-product of pulping processes. However, lignin has been mainly used in energy production because the chemical structure of lignin is complicated and the pulping process makes it even more complex.<sup>1</sup>

Native lignin is a biopolymer produced via enzymatic polymerization of three monolignols (coniferyl alcohol, sinapyl alcohol, and *p*-coumaryl alcohol) (Figure 1).<sup>2–4</sup> These monolignols form guaiacyl (G), syringyl (S), and *p*-hydroxyphenylpropane units (H), respectively, in the lignin chemical structure. Because lignin contains a large amount of phenol derivatives from monolignols, it is expected that lignin can be used as a replacement for commercial phenolic resin (PF) produced from fossil resources. Indeed, previous studies have investigated the replacement of phenolic resin with lignin.<sup>5–9</sup> Tejado et al. have reported the properties of novolac-type phenolic resins partially substituted with three types of lignin (kraft lignin, soda/AQ lignin, and sul-

fonated kraft lignin).<sup>10,11</sup> They investigated the thermal and mechanical properties of these resins; however, the effect of the preparation method on the properties and friction characteristics of the resins has not been investigated.

Most types of phenolic resins have been used as binding materials for industrial products.<sup>12</sup> Brake friction material uses novolac-type phenolic resin with hexamethylenetetramine (HMTA) as a curing agent.<sup>13</sup> In addition, reduction of environmentally harmful substances is generally required for ingredients of brake friction material.<sup>14,15</sup> Therefore, investigation of the use of lignin in place of phenolic resin may lead to the development of environment-friendly alternatives for brake friction materials. Previous studies have reported the effect of replacement of the phenolic resin component with lignin in the friction material.<sup>16,17</sup> However, friction material containing asbestos, an environmentally harmful substance, was used in these studies. In addition, the effect of substitution with more than 50 mass% lignin was not investigated.

In this study, we investigated the effect of methanol-soluble soda lignin as an alternative material to phenolic resin for brake friction material. The reaction of lignin model compound dihydroconiferyl alcohol (DCA) with HMTA was carried out to investigate the curing process of lignin-modified phenolic resin



**Figure 1.** Three monolignols that act as lignin precursors.

(LPF). LPF was then prepared by polymer blend methods (solvent blend and *in situ* polymerization) from methanol-soluble soda lignin. The chemical structures, average molecular weights, thermal properties, flexural strengths, and friction properties of the prepared LPF were investigated. Flexural tests and friction tests were carried out with molded composites prepared using LPF containing different amounts of lignin, and the results were compared to those of regular PF. It was found that resin and friction properties depended on both the method of preparation and the amount of lignin in the material. Interestingly, replacement of PF with LPF was found to improve fade resistance of the brake friction material, and investigations of this friction behavior are also discussed.

## EXPERIMENTAL

### Materials

Methanol-soluble soda lignin was extracted from soda lignin (Harima Chemicals) using methanol and was used for the preparation of LPF. Extraction yield of methanol-soluble soda lignin was 50%. The glass-transition temperature of methanol-soluble soda lignin was lower than that of normal soda lignin. The soda lignin was recovered from black liquor discharged in a pulping process that uses straw as a raw material. Random novolac-type phenolic resin was used for PF and as a reference for characterization. All solvents and chemicals were purchased from Wako Pure Chemical Industries and used as received.

### Reaction of DCA with HMTA

A mixture of DCA (100 mg, 0.55 mmol) and HMTA (13 mg, 0.092 mmol) was stirred at 70°C for 1 h, 120°C for 1 h, and 150°C for 1 h. The resultant substance was washed with distilled water and methylene chloride to remove the unreacted DCA. The organic residue was concentrated to give a yellowish compound, which was analyzed by <sup>13</sup>C NMR using a Bruker DRX-300 NMR spectrometer.

### Resin Preparation

Solvent-blended LPFs with different lignin contents, 25 mass% (LPF 1), 50 mass% (LPF 2), and 75 mass% (LPF 3), were

prepared from methanol-soluble soda lignin and commercial phenolic resin (PF) with methanol as the solvent. A mixture of lignin, PF, and methanol was stirred at room temperature for 1 h and the methanol was removed by drying at 80°C for 2 h under vacuum.

*In situ* polymerized LPFs (LPF 4 and LPF 5) were synthesized with methanol-soluble soda lignin, phenol, and formaldehyde (37% aqueous solution) with oxalic acid as the catalyst (Table I). A mixture of phenol and methanol-soluble lignin in methanol (2.0 g) was stirred at 80°C for 30 min in a three-neck flask equipped with a condenser and thermometer. After adding oxalic acid and formaldehyde to the flask, the mixture was stirred at 90–100°C for 3 h to promote the polycondensation reaction. Water and unreacted phenol were removed by distillation under vacuum, and then the flask was cooled to room temperature. Lignin content was calculated from the yield of LPF.

### Characterization of LPF and Lignin

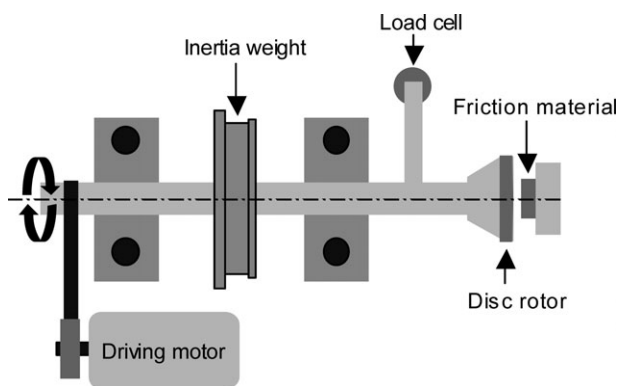
The chemical structure of LPF was characterized with <sup>13</sup>C NMR (JNM-LA400, JEOL, Japan) in deuterated methanol. The average molecular weight and molecular weight distribution were determined using a Waters gel permeation chromatography (GPC) system using THF as the eluant at a flow rate of 1 mL min<sup>-1</sup>. The GPC system was calibrated with standard polystyrene samples. The thermal cure behaviors of LPF with 10 phr HMTA were evaluated by differential scanning calorimetry (DSC, Thermo Plus DSC8230, Rigaku, Japan) at a heating rate of 10°C min<sup>-1</sup>. The glass transition temperature (*T*<sub>g</sub>) was measured on a thermomechanical analyzer (TMA, TMA-60, Shimadzu, Japan) at a heating rate of 5°C min<sup>-1</sup> under N<sub>2</sub> with a flow rate of 20 mL min<sup>-1</sup>. The fluidity of LPF containing 10 phr HMTA in the curing process was investigated at 150°C with a compression load of 49 kN. The area of the cured resin was measured after compression for 4 min. The flexural test was carried out using a universal tester (AGS-J, Shimadzu, Japan) at a crosshead speed of 1.0 mm min<sup>-1</sup>. Molded specimens consisting of LPF (20 mass%) and calcium carbonate (80 mass%) as a filler were used in the flexural test. These specimens were prepared by compression molding (150°C, 30 MPa, 10 min) followed by post curing (200°C, 3 h) in air atmosphere. Solid state crosspolarization/magic angle spinning (CP/MAS) <sup>13</sup>C NMR analysis was conducted for heat-treated lignin using a Bruker AVANCE DSX-300 NMR spectrometer.

### Friction Properties

Friction properties were investigated in a 1/10 scale brake dynamometer<sup>18</sup> with molded brake friction materials. Figure 2 shows a schematic diagram of the brake dynamometer. Cast iron (FC250) was used for the disk rotor and a standard dynamometer test procedure (JASO C406)<sup>19</sup> was used for the friction test.

**Table I.** Composition of *In Situ* Polymerized LPF

Resin	Methanol-soluble lignin (g)	Phenol (g)	Formaldehyde (g)	Oxalic acid (g)	Lignin content (mass %)
LPF 4	10	14.1	3.2	0.38	61
LPF 5	10	9.4	2.4	0.28	74



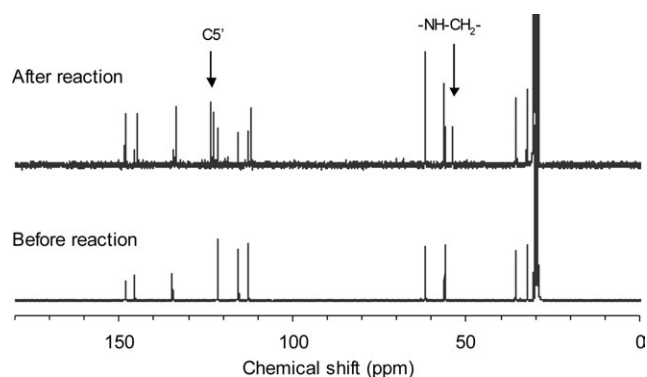
**Figure 2.** Schematic diagram of the 1/10 scale brake dynamometer.

The friction coefficient ( $\mu$ ), speed, and rotor temperature were recorded during the friction test. The wear rate of the friction material was calculated from thickness losses determined from measurements before and after the friction test. Table II shows the formulations of the brake friction materials examined in this investigation. The friction modifiers consisted of 20 vol% cashew dust, 27 vol % barium sulfate, 2 vol % zirconium oxide, and 20 vol % potassium titanate. LPF and PF containing 10 phr HMTA were used as binders for the friction materials. These friction materials were prepared by compression molding (150°C, 50 MPa, 10 min) of the mixtures of ingredients. The post curing was carried out at 250°C for 3 h in air atmosphere.

## RESULTS AND DISCUSSION

### Reaction of DCA with HMTA

Figure 3 shows the  $^{13}\text{C}$  NMR spectra of DCA before and after reaction with HMTA. The signal at 53.9 ppm in the spectrum taken after the reaction is attributed to the benzylamine-type methylene carbon ( $\text{NH-CH}_2\text{-Ar}$ ). The signal of the *o*-carbon ( $\text{C5}'$ ) substituted with the methylene carbon was observed at 123.7 ppm. This result confirmed that DCA produced a benzylamine-type species after reaction with HMTA (Scheme 1). Solomon et al. have investigated the reaction of xylenol as a model compound of phenolic resin in the curing process with HMTA and identified benzylamine species by NMR analysis as inter-



**Figure 3.** The  $^{13}\text{C}$  NMR spectra of DCA in deuterated acetone before and after reaction with HMTA.

mediates.<sup>20,21</sup> Therefore, this suggests that lignin-modified phenolic resins show the same curing process as phenolic resin.

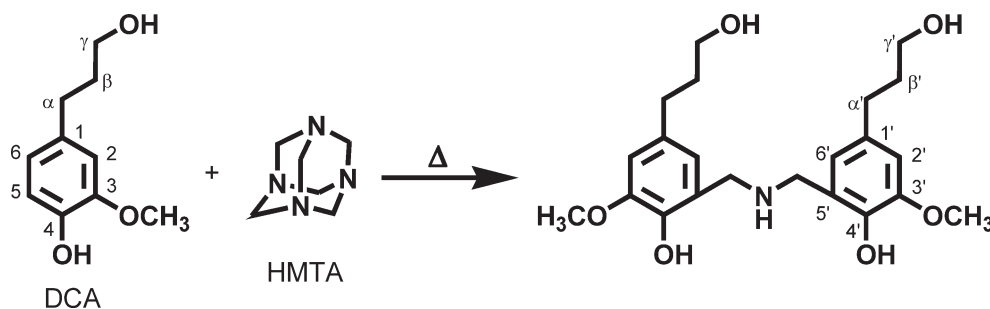
### Characterization of LPF

In the NMR spectrum of *in situ* polymerized LPF, characteristic signals of PF and lignin were observed. The  $^{13}\text{C}$  NMR spectrum of LPF 4 is shown in Figure 4. The diphenylmethane-type methylene carbons ( $\text{Ar-CH}_2\text{-Ar}$ ) were detected by signals at 41.1 ppm (*p-p'*), 35.7 ppm (*o-p'*), and 30.6 ppm (*o-o'*). In the aromatic carbon region between 115 and 160 ppm, the signals of carbons substituted with hydroxyl and methoxy groups (158.3–149.0 ppm), substituted aromatic carbons and unsubstituted aromatic *m*-carbons (134.2–127.9 ppm), unsubstituted aromatic *p*-carbon (120.5 ppm), and unsubstituted aromatic *o*-carbon (116.1 ppm) were observed.<sup>20,22</sup> The signals of the methoxy groups in the guaiacyl and syringyl units of lignin were observed at 57.0 ppm.

Figure 5 shows DSC thermograms of LPF and PF with 10 phr HMTA. The DSC thermograms exhibit a main exothermic peak at 100–180°C due to the curing reactions of HMTA with free *o*- or *p*-phenolic positions of the resins to form benzylamine species. The increase of lignin content in LPF decreased the enthalpy ( $\Delta H$ ) of the curing reaction (Table III). This result indicates that lignin, which is substituted with a methoxy group at the *o*-phenolic position, has fewer active sites for reaction with HMTA than PF.

**Table II.** Formulations of Friction Materials (vol %)

Ingredients	F-LPF 1	F-LPF 2	F-LPF 3	F-LPF 4	F-LPF 5	F-PF
LPF 1	18	-	-	-	-	-
LPF 2	-	18	-	-	-	-
LPF 3	-	-	18	-	-	-
LPF 4	-	-	-	18	-	-
LPF 5	-	-	-	-	18	-
PF	-	-	-	-	-	18
Graphite	5	5	5	5	5	5
Aramid pulp	8	8	8	8	8	8
Friction modifiers	69	69	69	69	69	69
Total	100	100	100	100	100	100



Scheme 1. Reaction of DCA and HMTA.

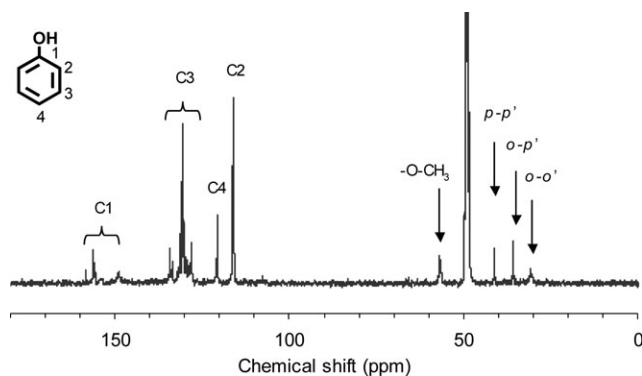


Figure 4.  $^{13}\text{C}$  NMR spectrum of LPF 4 in deuterated methanol.

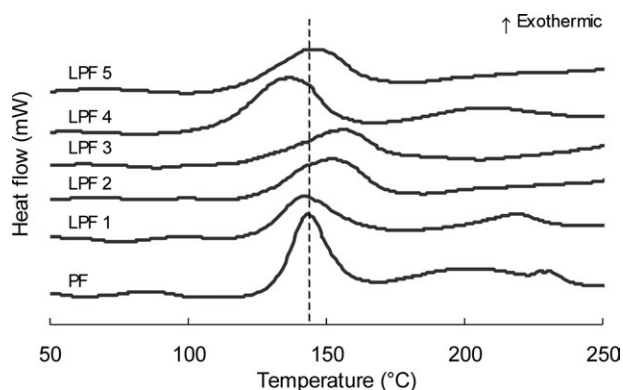


Figure 5. DSC thermograms of LPF and PF with 10 phr HMTA.

Solvent-blended LPF showed higher peak temperature ( $T_p$ ) and  $T_g$  values depending on the lignin content, while *in situ* polymerized LPF 5 showed values of  $T_p$  and  $T_g$  equivalent to those of PF (Table III). It is known that the first stage of the curing process of phenolic resins is melting followed by formation of an adduct with HMTA.<sup>21,23,24</sup> The results of the GPC analysis showed that *in situ* polymerized LPF has low average molecular weight and narrow polydispersity ( $M_w/M_n$ ), which means that it contains low-molecular-weight components that function as plasticizers. Therefore, the replacement of PF with lignin by solvent blend increases  $T_g$ , which inhibits the curing reaction of the resin.

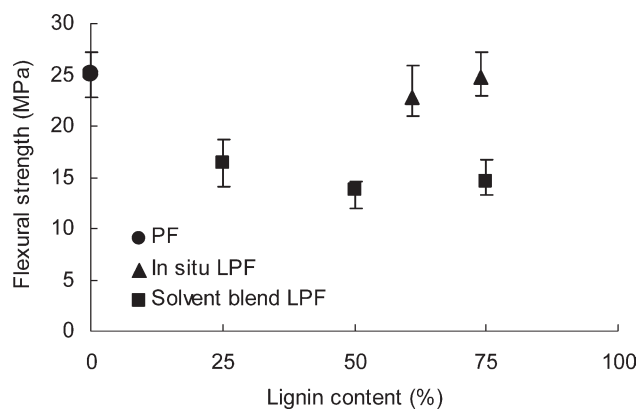
Figure 6 shows the relationship between flexural strength and lignin content of molded specimens prepared using LPF. The replacement of PF with lignin in solvent-blended LPF decreased flexural strength. This result suggests that lignin has reduced adhesion with calcium carbonate, which is attributed to the lower fluidity and crosslinking density of LPF resulting from its lower reactivity with HMTA. In contrast, *in situ* polymerized LPF exhibited flexural strength equivalent to that of PF. This is probably due to the improved reactivity with HMTA and the fluidity during the molding caused by the low-molecular-weight components of *in situ* polymerization LPF.

### Friction Properties

Table IV shows the lowest friction coefficient in the fade test component of the friction test, and the wear rates of the friction materials. Figure 7 shows variations of the friction coefficients during the fade test. Brake fade phenomenon is the reduction

Table III. Properties of LPF and PF Investigated by GPC, DSC, TMA, and Fluidity Test

	Solvent blend			In situ polymerization			Methanol-soluble soda lignin
	LPF 1	LPF 2	LPF 3	LPF 4	LPF 5	PF	
Lignin content (%)	25	50	75	61	74	0	-
$M_w$	6300	5170	3540	1430	1840	7200	1600
$M_n$	1160	1100	940	580	650	1260	810
$M_w/M_n$	5.4	4.7	3.7	2.5	2.8	5.7	2.0
$\Delta H$ ( $\text{J g}^{-1}$ )	93	76	73	76	73	186	-
$T_p$ ( $^{\circ}\text{C}$ )	142	152	156	136	145	143	-
$T_g$ ( $^{\circ}\text{C}$ )	89	106	123	52	79	78	126
Fluidity ( $\text{cm}^2$ )	43	32	28	102	60	91	-



**Figure 6.** Relationship between flexural strength and lignin content in LPF.

of the friction coefficient that occurs when the braking system is heated to elevated temperatures. F-PF exhibited significant brake fade, while F-LPF showed good fade resistance depending on lignin content. However, F-LPF exhibited an increased wear rate of the friction material. This is likely due to the lower strength of the friction material and thermal stability of LPF at high temperatures.

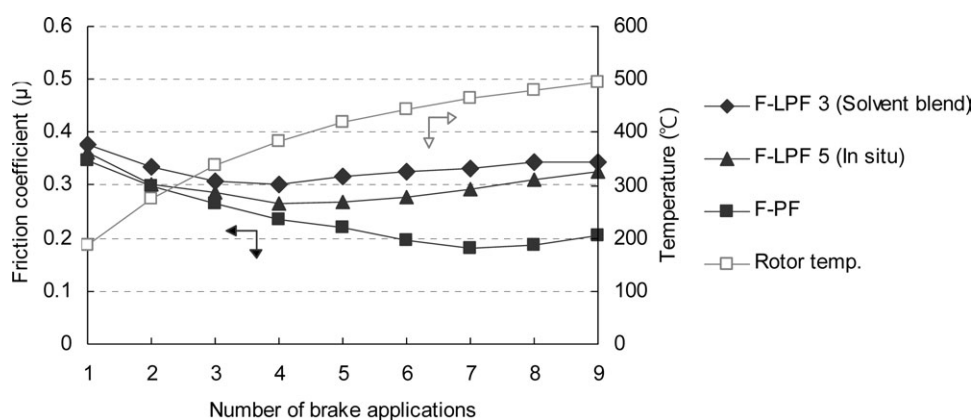
Inoue et al. have investigated the formation mechanisms of liquid-phase degradation products that cause the brake fade phenomenon on friction surfaces.<sup>25</sup> They reported that heat and

**Table IV.** Friction Test Results of F-LPF and F-PF

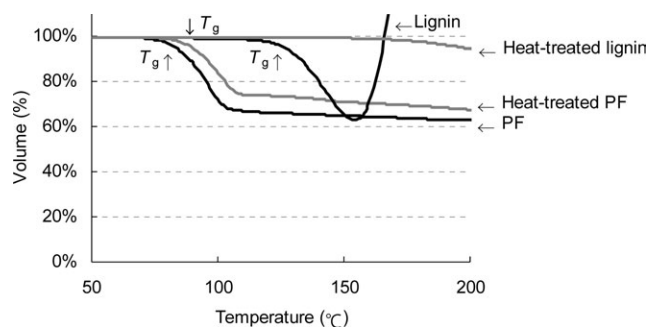
	F-LPF 1	F-LPF 2	F-LPF 3	F-LPF 4	F-LPF 5	F-PF
The lowest $\mu$ in the fade test	0.23	0.28	0.30	0.25	0.27	0.18
Wear rate of friction material (%)	5.3	7.6	10.1	6.8	7.9	4.9

shearing forces produced liquid-phase degradation products from cured phenol resin. Therefore, improvement of fade resistance by using LPF is probably attributed to the fact that the degradation products of LPF do not become liquid on the friction surface. Figure 8 shows TMA profiles of methanol-soluble soda lignin and PF without HMTA before and after heat treatment (250°C, 1 h). Although PF shows the glass transition at approximately 90°C even after heat treatment, no clear glass transition of methanol-soluble soda lignin after heat treatment is observed.

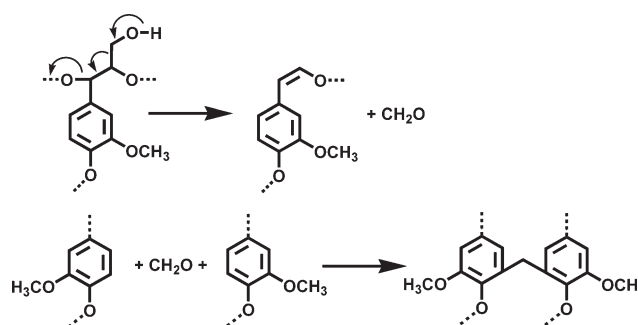
It is known that heat treatment affects the chemical structure of lignin through depolymerization by cleavage of  $\alpha$ - and  $\beta$ -aryl-ether linkages and recondensation, which is the same structural change that occurs in the pulping process (Scheme 2).<sup>26–28</sup> Figure 9 shows CP/MAS <sup>13</sup>C NMR spectra of methanol-soluble



**Figure 7.** Friction coefficient variations during fade test.

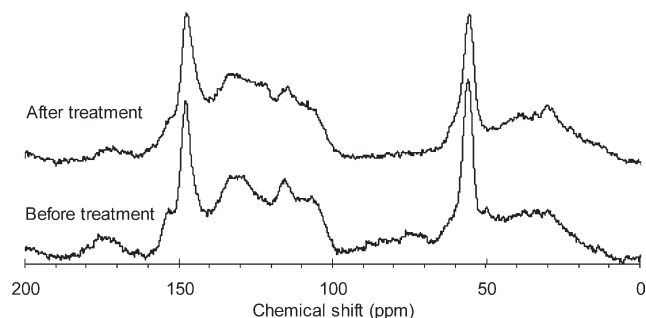


**Figure 8.** TMA profiles of methanol-soluble soda lignin and PF before and after heat treatment.



**Scheme 2.** Depolymerization and recondensation reactions of lignin.





**Figure 9.** CP/MAS  $^{13}\text{C}$  NMR spectra of methanol-soluble soda lignin before and after heat treatment.

soda lignin without HMTA before and after heat treatment. The broad signal assigned to substituted aromatic carbons such as C1 was observed between 120 and 140 ppm, while an increase of signals between 120 and 125 ppm was observed in the spectrum after heat treatment. This result confirms that heat treatment caused thermal crosslinking reactions of methanol-soluble soda lignin without HMTA.

These results from TMA and NMR analyses indicate that the degradation products of methanol-soluble soda lignin are not changed to the liquid phase owing to crosslinking reactions caused by friction heat on the friction surface. Therefore, LPF containing methanol-soluble soda lignin exhibited improved fade resistance in the friction test.

## CONCLUSIONS

Both replacement of PF with methanol-soluble soda lignin and the method used to prepare the polymer blend affect the resin and friction properties of brake friction materials. The addition of methanol-soluble soda lignin by solvent blend reduced reactivity with HMTA in the curing process and also reduced flexural strength, while *in situ* polymerized LPF showed flexural strength equivalent to that of PF. However, the results from the friction test showed that the replacement of PF with lignin improved fade resistance. The reason for this fade resistance is that the degradation products of lignin do not change to liquids on the friction surface because they undergo cross-linking reactions caused by friction heat. Although further development to improve the wear resistance is needed, lignin will be useful as an ingredient for brake friction material.

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