

Phenolic Resol Resin from Phenolated Corn Bran and Its Characteristics

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ABSTRACT: To prepare phenolic resol resin, corn bran (CB) was liquefied in the presence of phenol and the liquefied CB was condensed with formaldehyde under alkaline condition. From NMR spectra of phenolated CB and phenolated CB-based resol resin, it was found that phenol was reacted with depolymerized CB components and the phenolated CB was methylolated by condensation with formaldehyde. Molecular weight distribution was divided into a high molecular weight zone, attributed mainly to phenolated CB, and a low molecular weight zone, which was attributed to the condensation reactants of formaldehyde and the unreacted phenol of liquefied CB. When reaction

conditions became severe, a high molecular weight zone was increased. Formaldehyde/unreacted phenol of liquefied CB molar ratio most affected the change of a low molecular weight zone. To reduce the viscosity of the phenolated CB-based resol resin, a milder condensation condition was required compared with that for preparing the conventional resol resin. Properties of the resol resin were comparable to those of conventional resol resin for plywood manufacture. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1365–1370, 2003

Key words: resins; adhesives; NMR

INTRODUCTION

There is growing interest in the wood industry to develop wood adhesives from renewable substances that would also satisfy environmental regulations. During the past several years, many attempts have been made to replace the petrochemical resins totally or partially with lignocellulose or its components such as carbohydrates, lignins, and tannins.^{1–5} Among these, the liquefaction technique was found to be very useful to use whole lignocellulose instead of its components.^{6–8} Shiraishi et al.⁹ reported on wood-phenol adhesives prepared from carboxymethylated wood, and both Pu et al.¹⁰ and Maldas et al.¹¹ reported on the liquefaction of wood in phenol under acid or alkaline catalysts and its application to adhesives. Ono et al.¹² also reported that the adhesive was obtainable from waste paper by means of phenol liquefaction. These studies showed that properties such as glueability of phenolated product-based resol resin were comparable to those of commercial phenolic resol resin.

In our previous reports, the phenol liquefaction of corn bran (CB), which is a by-product of the production process of cornstarch, has been described.^{13,14} The obtained phenolated CB was successfully applied to novolak-type phenolic resin. In this study, we tried to

prepare the phenolic resol resin from phenolated CB and investigate its characteristics.

EXPERIMENTAL

Materials

Corn bran was donated by Sanwa Starch Ltd. Co. (Japan). It was dried in an oven at 105°C for 24 h and then kept in a desiccator at room temperature before use. Phenol, formaldehyde, and sulfuric acid were reagent grade and obtained from Nakalai Tesque (Japan). All chemicals used were obtained from commercial sources.

Liquefaction of CB

Liquefaction of CB was conducted by use of a stainless-steel autoclave at high pressure (above 1 MPa) and temperature (200°C). After charging CB (2 g), phenol (6 g), and the catalyst (0.18 g), the autoclave was dipped into a brine bath and allowed to stand for 10–60 min. When the reaction was completed, the autoclave was cooled and the resulting reaction mixture was poured into methanol. The diluted solution was stirred for 20 min and was then filtrated through a glass-fiber filter under reduced pressure. The methanol-insoluble residue was dried to a constant weight at 105°C for 24 h and weighed for the determination of the percentage residue. The filtrated methanol soluble part was analyzed by a high performance liquid chromatograph (Shimadzu LC-10A, Kyoto, Japan), equipped

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with a UV absorbance detector (SPD-10A) to quantify the unreacted phenol. An ODS-II reverse-phase column (Shimadzu) was used and the mobile phase was methanol/water (1/2 v/v) with a flow rate of 1.0 mL/min. Hence, the methanol-insoluble residue and the combined phenol were calculated by the following two equations:

$$R (\%) = (W_r/W_0) \times 100$$

and

$$CP (\%) = (W_1 - W_2)/(W_0 - W_r) \times 100$$

where R is the residue percentage, W_0 is the weight of the starting CB, W_r is the weight of the CB residue, CP is the amount of the combined phenol, W_1 is the starting weight of the phenol, and W_2 is the weight of unreacted phenol.

Preparation of phenolated CB-based resol resin

The obtained liquefied CB, 37% aqueous formaldehyde, and sodium hydroxide were added in a 500-mL round-bottom flask, equipped with a reflux condenser, stirrer, and thermometer. The mixture was stirred and heated in an oil bath at 55–85°C for 1–4 h. The unreacted phenol content in the obtained resin was measured by high performance liquid chromatography mentioned earlier. The viscosity of the resin was measured by use of a Brookfield viscometer (Tokmec Inc., Japan) at 25°C and 60% relative humidity.

Gel permeation chromatography

Molecular weight distribution was investigated by GPC (Nippon Bunko GPC-900, Japan) in a solvent system of tetrahydrofuran with 0.4% trichloride acetic acid and 0.045% sulfuric acid as the mobile phase. The solvent flow rate and pressure were 1.0 mL/min and 7.0 MPa, respectively.

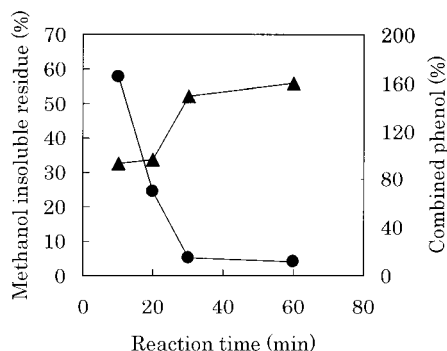


Figure 1 Liquefaction of CB by the high pressure temperature method. ●, Methanol insoluble residue; ▲, combined phenol.

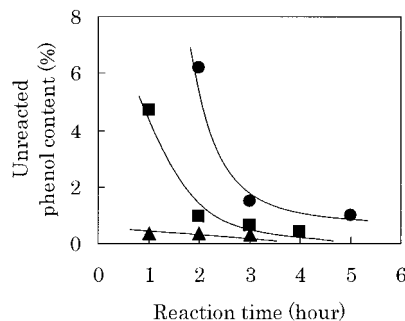


Figure 2 Effects of reaction temperature and time on the unreacted phenol content of resol resin. Unreacted phenol content at zero time of reaction, 37.3%; F/UP molar ratio, 2; ●, 55°C; ■, 70°C; ▲, 85°C.

NMR spectroscopy

^{13}C -NMR measurements were carried out by use of a Bruker AC300 spectrometer (Bruker Instruments, Billerica, MA). The analysis was conducted in acetone- d_6 for phenolated CB and in methanol- d_4 for methyloated phenolated CB resin.

RESULTS AND DISCUSSION

The liquefaction of corn bran was effectively conducted by the high pressure temperature method. As shown in Figure 1, methanol-insoluble residue and combined phenol of phenolated CB were decreased and increased abruptly at initial reaction time (30 min), respectively. The liquefied CB obtained at 200°C for 30 min was used to prepare a phenolic resol resin and was soluble in alkaline aqueous solution. The residue and combined phenol content were 5.3 and 149.6%, respectively.

Figure 2 shows the effects of reaction temperature and time on the unreacted phenol content of resol resin. It can be seen that the unreacted phenol content is decreased at an early time as the reaction temperature becomes high. In detail, the unreacted phenol content was decreased abruptly by increasing from 2 to 3 h and from 1 to 2 h of reaction time at 55 and 70°C, respectively. However, the unreacted phenol content at 85°C was below 1% within 1 h of reaction time. The effects of formaldehyde/unreacted phenol (F/UP) of liquefied CB molar ratio on the unreacted phenol content of the resol resin were also investigated and are shown in Figure 3. The unreacted phenol content was decreased with increasing the F/UP molar ratio. It is natural that the reaction of formaldehyde with the unreacted phenol remained after phenolation of CB should be enhanced by increasing the amount of formaldehyde, resulting in low unreacted phenol content. The F/UP molar ratio above 1.5 was necessary to obtain an unreacted phenol content below 3%.

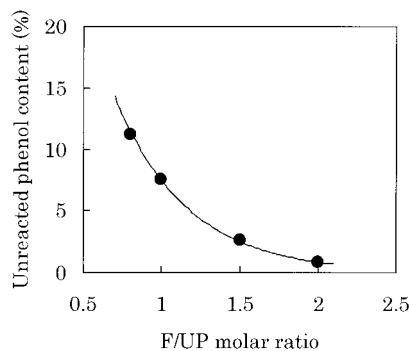


Figure 3 Effects of F/UP of liquefied CB molar ratio on the unreacted phenol content of resol resin. Reaction temperature, 70°C; time, 2 h.

Not only the reaction of the unreacted phenol of liquefied CB with formaldehyde, but also the reaction of phenolated CB with phenolic moieties (149.6% of combined phenol content) with formaldehyde would be caused in this condensation reaction. Ono et al.³ reported that phenol reacts with newsprint compo-

nents during liquefaction and the obtained phenolated newsprint also reacts with formaldehyde. We also examined whether phenol was reacted to liquefied CB components and the phenolated CB was methylolated by the condensation with formaldehyde.

Figure 4 shows NMR spectra of liquefied CB with unreacted phenol [Fig. 4(A)], phenolated CB after the removal of unreacted phenol [Fig. 4(B)], and methylolated resin obtained from phenolated CB without unreacted phenol [Fig. 4(C)]. There are peaks over the range from 100 to 160 ppm attributed to aromatic ring carbons. In particular, the peaks at 158 and 155 ppm are attributed to the carbon with a hydroxy group in the unreacted phenol and the phenol substituted by CB components, respectively. By removal of unreacted phenol, the peak at 158 ppm disappeared, whereas that at 155 ppm was clearly observed, as shown in Figure 4(B). From this result, it was proved that the phenol combined with the CB component. The combined phenol content of 149.6% is also proof of the reaction of phenol and the liquefied CB component.

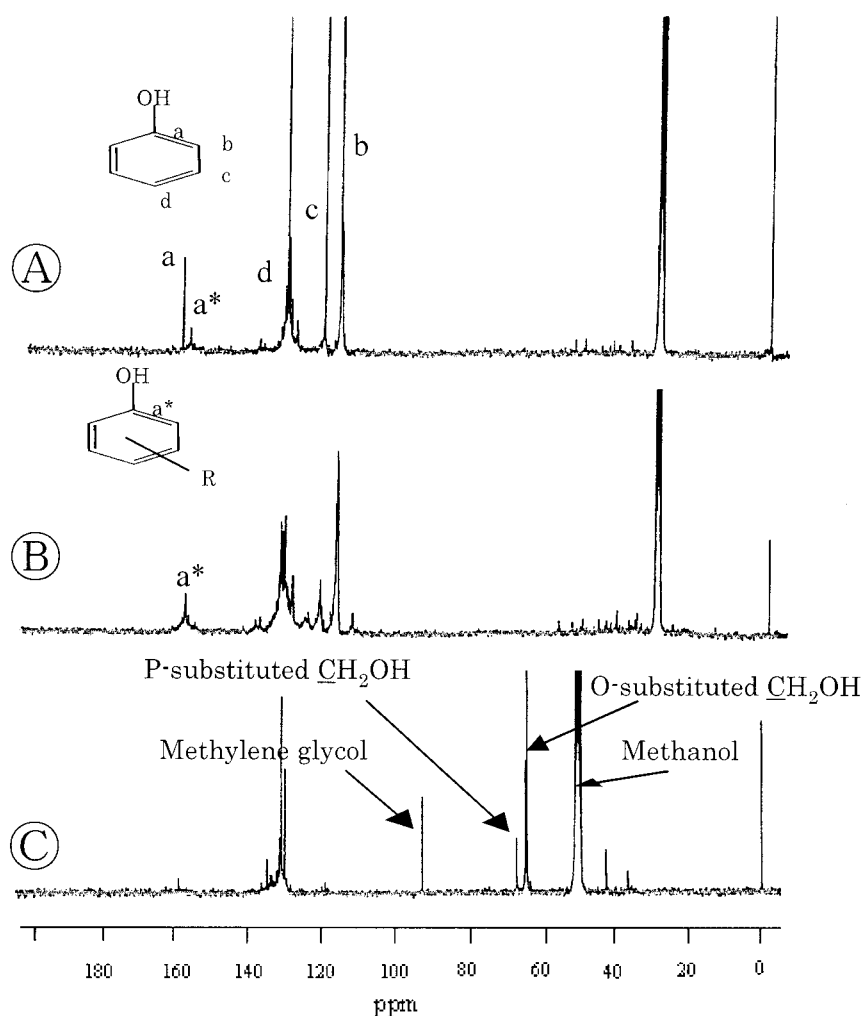


Figure 4 NMR spectra of liquefied CB with unreacted phenol (A), phenolated CB without unreacted phenol (B), and methylolated resin obtained from phenolated CB without unreacted phenol (C).

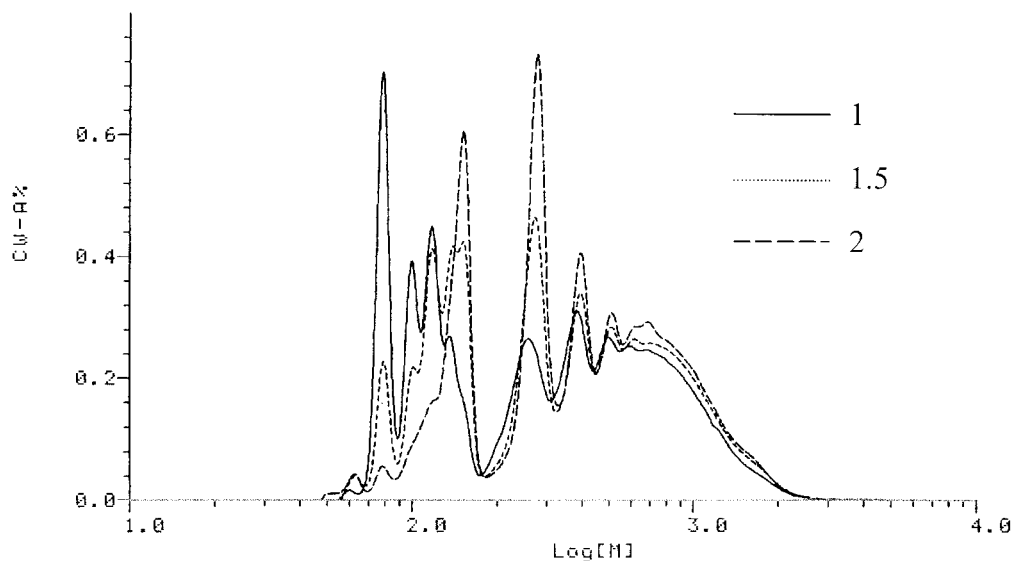


Figure 5 Effects of F/UP of liquefied CB molar ratio on the molecular weight distribution. Reaction temperature, 70°C; time, 2 h.

Figure 4(C) shows the peaks between 50 and 100 ppm, which are not observed in the spectrum of Figure 4(A) and (B). These peaks are attributed to *p*-substituted and *o*-substituted methylol groups and methylene glycol. This result indicates that phenolated CB reacts with formaldehyde.

Molecular weight distribution

Figure 5 shows the effects of F/UP molar ratio on the molecular weight distribution of the reaction products of phenolated CB and formaldehyde. It can be seen that every curve shows two distinct zones, that is, a low molecular weight zone with molecular weight up to about 300, and a high molecular weight zone with

molecular weight higher than about 300. Based on the curve of the phenolated CB without condensation,¹⁴ it can be found that the high molecular weight zone is mainly attributed to phenolated CB and the low molecular weight zone is composed of the main reaction products of unreacted phenol and formaldehyde. The *o*- or *p*-hydroxymethyl phenol, bis(hydroxymethyl) phenol, tris(hydroxymethyl) phenol, and diphenylmethane derivatives would be contained in a low molecular weight zone.

In a high molecular weight zone, the molecular weight distributions showed a negligible change with an increase of F/UP molar ratio. However, there are drastic changes in a low molecular weight zone. It was found in a low F/UP molar ratio that the low molec-

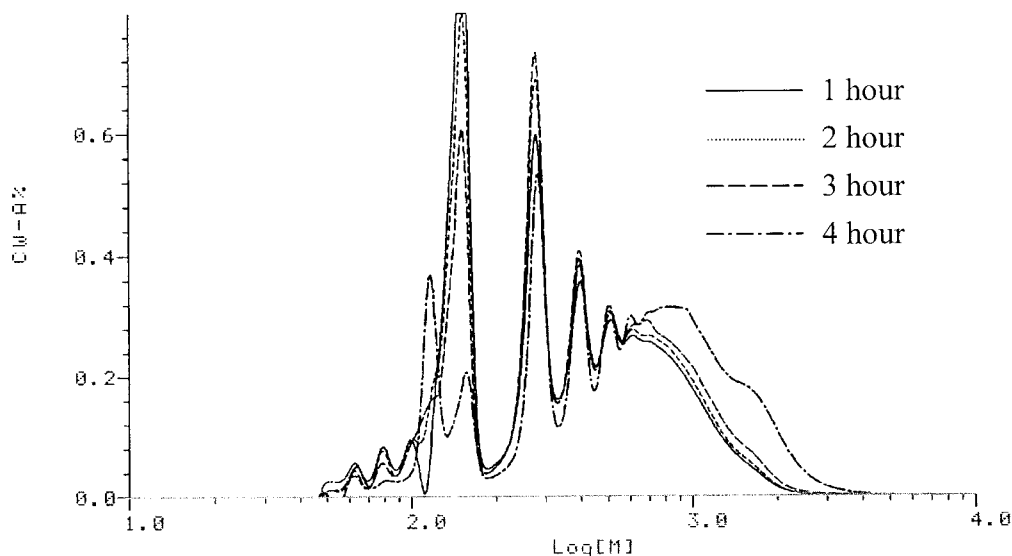


Figure 6 Effects of reaction time on the molecular weight distribution. Reaction temperature, 70°C; F/UP molar ratio, 2.

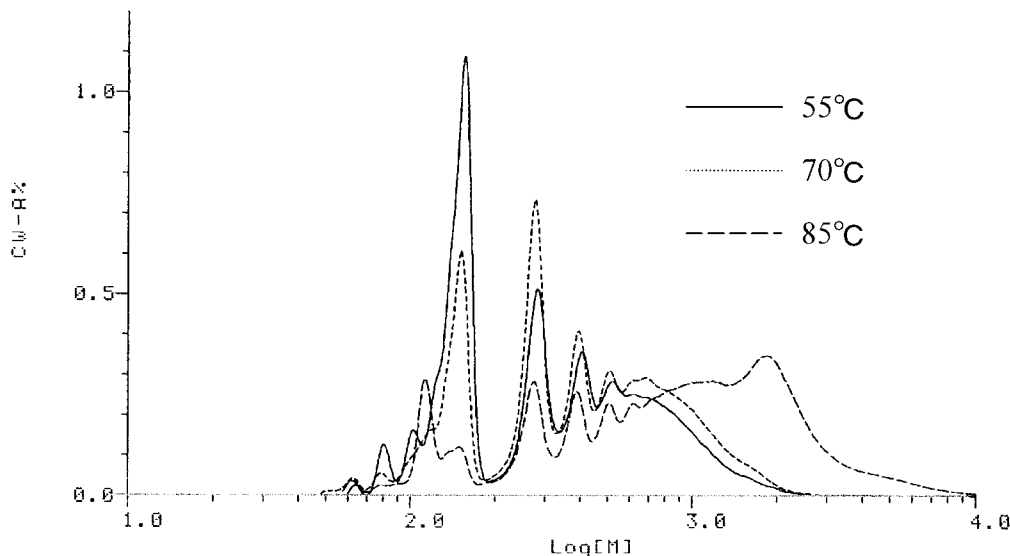


Figure 7 Effects of reaction temperature on the molecular weight distribution. Reaction time, 2 h; F/UP molar ratio, 2.

ular weight substances such as *o*- or *p*-hydroxymethyl phenol, bis(hydroxymethyl) phenol, and tris(hydroxymethyl) phenol were abundantly formed. However, these substances were decreased by further addition of formaldehyde.

Figure 6 shows the molecular weight distributions of the resol resin obtained at 70°C as a function of the reaction time. The high molecular weight zone increased by increasing reaction time, indicating that phenolated CB components participated in the reaction with formaldehyde. The decrease of the low molecular zone indicates that the condensation of unreacted phenol and formaldehyde progressed by increasing the reaction time.

Figure 7 shows the temperature dependency on the molecular weight distribution. The influence of reaction temperature was similar to that of reaction time. A low molecular weight zone was decreased, whereas a high molecular weight zone increased by increasing the reaction temperature. However, as the reaction

temperature increased from 70 to 85°C, a high molecular weight zone abruptly increased. The corresponding weight-average molecular weight and changing trends are summarized in Figure 8. As discussed earlier, molecular weights increased with increasing both reaction temperature and time. In particular, the resin obtained at 85°C showed higher molecular weight than that of the others. This drastic increase of molecular weight causes the high viscosity of the resin, considered as a defect in processing.

Figure 9 shows the change of viscosity as a function of reaction temperature. It was found that the viscosity of resin obtained at 85°C was much higher than that of the others. Lee et al. and Shiraishi et al. reported that because the phenolated wood has higher reactivity toward formaldehyde, milder condensation conditions are required for preparation of resol resin compared with those of the conventional methods. It is also considered to be the same in the case of the condensation of phenolated CB and formaldehyde.

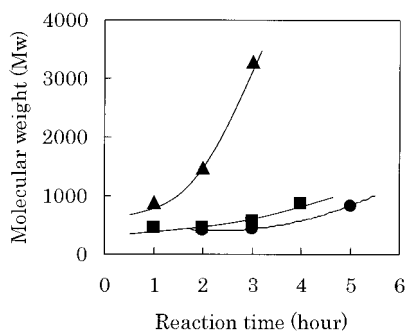


Figure 8 Effects of reaction temperature and time on the weight-average molecular weight. Molecular weight at zero time of reaction, 352; F/UP molar ratio, 2; ●, 55°C; ■, 70°C; ▲, 85°C.

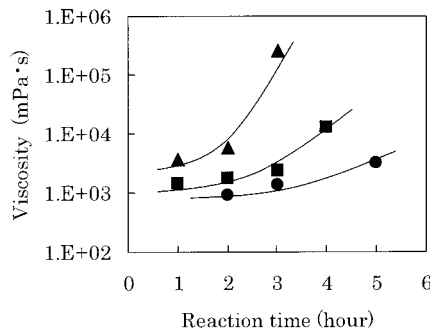


Figure 9 Effects of reaction temperature and time on the viscosity. F/UP molar ratio, 2; ●, 55°C; ■, 70°C; ▲, 85°C.

TABLE I
Properties of Phenolated CB-Based Resol Resin, Phenolated Newsprint-Based Resol Resin,
and Conventional Resin for Plywood Manufacture

Property	Phenolated CB-based resol resin ^a	Phenolated newsprint-based resol resin ^b	Conventional resin for plywood manufacture ^c
Dry solids content (%)	52	40–43	44 ± 1
PH	10	10	7–12
Viscosity (mPa · s)	1300	600–1200	700 ± 200(20°C)
Gel time (min)	16 (130°C)	—	33 (100°C)
Content of free phenol (%)	<2%	—	0.1

^a Reaction temperature, 55°C; time 3 h.

^b From reference 12.

^c From reference 15.

Properties

Some properties of phenolated CB-based resol resin, representatively obtained by this experiment; phenolated newsprint-based resol resin; and conventional resin for plywood manufacture are summarized in Table I. Although the viscosity of phenolated CB-based resol resin was somewhat higher than that of conventional phenolic resin, there were only negligible differences among them. It is thought that the phenolated CB-based resol resin can be sufficiently used as the wood adhesive, when it is prepared under milder reaction conditions to obtain low viscosity.

The evaluation as the wood adhesive and the experiments related to the application to phenolic foam are also in progress and will be reported in the near future.

CONCLUSIONS

Phenolated CB-based resol resin was successfully prepared by condensation of phenolated CB and formaldehyde. The effects of reaction conditions on the molecular weight distribution, viscosity, and unreacted phenol content of the resol resin were clarified. Moreover, it was proven from NMR spectra that the phenolated CB was methylolated by formaldehyde. The obtained resin had properties comparable to those of conventional resol resin for plywood manufacture, so it can be used practically as a wood adhesive.

At present, there is increasing interest in the wood industry to develop a novel adhesive from renewable

resources. The author expects that the present work will be a useful contribution to the wood industry. Furthermore, it is advantageous in the use of waste biomass and the solution of environmental problems.

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