

Liquefaction and Product Identification of Corn Bran (CB) in Phenol

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ABSTRACT: The liquefaction of corn bran (CB) was successfully conducted by using three different liquefaction conditions. Among them, catalyzed liquefaction at high pressure and temperature (180–220°C) using phenol was the most effective for the liquefaction of CB. Both the phenol/CB ratio and the catalyst content affected the extent of the liquefaction. The decomposed components of CB did not show high reactivity toward phenol when liquefied without a catalyst. Thermal-flow properties of the phenolated CB and flexural properties of the phenolated CB-based moldings were influenced by the amount of combined phenol and were comparable to those of the commercial novolak or phenolated wood. The effect of molding time and filler content on the flexural properties is also presented. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 311–318, 2000

Key words: liquefaction; corn bran; phenol; novolak; molding

INTRODUCTION

The utilization of biomass has recently attracted considerable attention because of its biodegradability, availability, and renewable nature. It has been found that liquefaction is one of the useful methods for utilizing biomass.^{1–10} The liquefaction of lignocellulosic biomass and the properties of the resulting liquefied materials have been intensively investigated. Shiraishi and coworkers found that the lignocellulosic biomass, such as wood, can be liquefied in the presence of phenol or alcohols using acid catalysts at temperatures of 120–180°C or without catalysts at temperatures around 250°C^{1–10} and that the obtained liquefied products are successfully used to prepare novolak-type phenolic resins,^{11–15} polyurethane foams,^{16–18} and adhesives.¹⁹

On the other hand, there is also growing interest in using the underutilized biomass. In the 1997 and 1998 Earth Meetings held in Kyoto and Buenos Aires, it was recognized that the combustion of biomass is an important factor of carbon dioxide production. New policies have been adopted all over the world to reduce the CO₂ emissions.

In this connection, food industries are said to generate a large amount of agricultural residues. For instance, corn bran (CB) is an abundant by-product of the production process of corn starch. Although minor outlets are currently in application (e.g., animal feedstock), new technologies are required to transform such residues in attractive value-added products.

Therefore, it was the objective of this work to transform CB into phenol-based materials by thermochemical liquefaction in the presence of phenol. Still, this is the first time that a food-industry by-product, poor in cellulose and lignin, was attempted to be liquefied by this means.

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EXPERIMENTAL

Materials

The CB used in the liquefaction was donated by the Sanwa Starch Ltd. Co. (Nara, Japan). The wood flour used as a filler for molding is a 200-mesh pass size from Hitachi Chemical Co. (Tokyo, Japan). It was dried in an oven at 105°C for 24 h and then kept in a desiccator at room temperature before use. Methanol, used for the measurement of the amount of combined phenol, was of HPLC grade, and tetrahydrofuran (THF), used as an eluting solvent for gel permeation chromatography (GPC), was of extra pure grade containing 0.03% of a stabilizer (2,6-di-*t*-butyl-4-methylphenol). All other chemicals, purchased from commercial sources, were of reagent grade.

Liquefaction of CB and Preparation of the Phenolated CB Resin

Liquefaction was conducted using sulfuric acid as a catalyst. The amount of the catalyst used in the liquefaction was expressed as a weight percentage based on the weight of phenol. Liquefaction at a moderate temperature (150°C) was carried out under constant stirring and reflux. When the reaction was completed, the resulting reaction mixture was poured into methanol. The diluted solution was stirred for 20 min and then was 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 percent residue. The filtrated methanol soluble part was analyzed by HPLC to quantify the unreacted phenol. 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 , the weight of the starting CB; W_r , the weight of the CB residue; CP , the amount of the combined phenol; W_1 , the starting weight of the phenol; and W_2 , the weight of unreacted phenol (free phenol). Subsequently, the methanol-soluble fraction was neu-

tralized with MgO. Methanol was then distilled off at 50°C and free phenol was removed at 180°C by vacuum distillation.

The high-pressure-temperature (around 250°C) liquefaction was conducted in a stainless-steel autoclave (TVS-1 type of Taiatsu Glass Industry Inc.) with a 10 MPa pressure-proof. After charging CB, phenol, and the catalyst, the autoclave was dipped into a hot brine bath at a controlled temperature (180–250°C) and allowed to stand for 10–60 min. The amount of the methanol-insoluble residue and the combined phenol were determined as mentioned above.

Molecular Weight Distribution

The molecular weight of the phenolated CB was determined using a gel permeation chromatograph equipped with a differential refractometer R401 detector. THF was used as the mobile phase at a flow rate of 1.0 mL/min with 7.0 MPa pressure. The refractive index versus the elution volume was obtained for each sample and correlated to that of the polystyrene standard.

Thermal-flow Properties

The thermal-flow properties of the phenolated CB, after distillation of the free phenol, were measured by a flow tester CFT-500A (Shimadzu) with a die having an orifice of 1 mm (diameter) and 10 mm length. The start temperature and heating rate were fixed to 50 and 10°C/min, respectively, to measure the flow temperature. Apparent melt viscosity was determined in the same apparatus at 130°C under a pressure of 5.0 MPa.

Preparation of Phenolated CB Moldings and Measurement of the Flexural Properties

Phenolated CB (37.7%) was mixed mechanically with wood flour filler (49.5%), hexamine (9.4%), Ca(OH)₂ (2.4%), and Zn stearate (1%). The obtained mixture was molded at 170–180°C under 50 MPa pressure for 1–30 min. The flexural properties of the molded specimens were measured using an Autograph AGS-5kNG (Shimadzu). The flexural strength and elasticity modulus were calculated by the included Shikibu program, and flexural toughness was calculated on the basis of the area under the stress-strain curve.

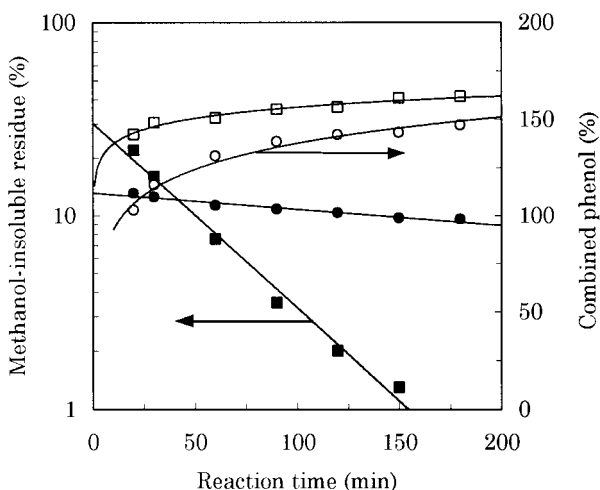


Figure 1 Kinetics of the liquefaction process of CB and wood. Reaction temperature, 150°C; phenol/CB or wood ratio, 3; catalyst content, 3%; atmospheric pressure. (●, ○) CB; (■, □) wood.

RESULTS AND DISCUSSION

Liquefaction Kinetics

The progression of liquefaction was studied at 150°C in the presence of phenol and the H_2SO_4 catalyst, which are the general liquefaction conditions used for lignocellulosics. The effects of reaction time on the amount of the methanol-insoluble residue and on the combined phenol of the phenolated CB are presented in Figure 1 and compared to those of wood liquefaction. In both cases, it was found that the solid residue amount decreases linearly with the reaction time in a semilog scale, indicating that the liquefaction during this period progressed according to pseudo-first-order kinetics. On the other hand, the amount of combined phenol increases as the reaction time increases. It was observed that the rate constant of liquefaction of CB ($1.9 \times 10^{-3}/\text{min}$) was about 10 times lower than that of wood ($22.1 \times 10^{-3}/\text{min}$). In other words, the liquefaction rate of CB is much slower than that of wood. Moreover, the combined

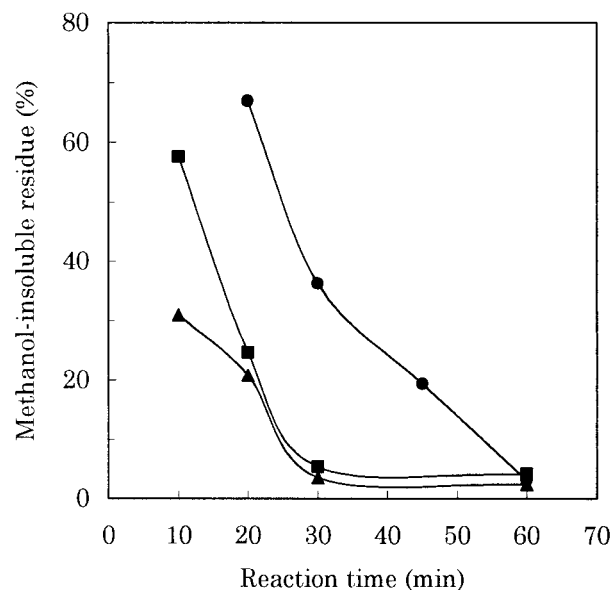


Figure 2 Effect of reaction time and temperature on the methanol-insoluble residue of CB. Phenol/CB ratio, 3; catalyst content, 3%; high pressure. (●) 180°C; (■) 200°C; (▲) 220°C.

phenol in wood is always higher than in CB. The lower reactivity of CB may be attributed to its composition. Indeed, CB is composed mainly of nitrogen free extracts (Table I), which include starch, saccharides, pectin, and organic acids.²⁰ It was found that the liquefaction of starch or other polysaccharides is easier than that of lignocellulosic materials because the latter has a semicrystalline structure with high hydrogen bonding. However, other components (crude protein, crude fat, crude fiber, and ash) may form a protective layer of corn, reducing the accessibility of the main components. Therefore, as an attempt to increase the yields of the CB liquefaction, more severe conditions were tested.

Catalyzed Liquefaction of CB at High Pressure and Temperature (180–220°C)

Figures 2 and 3 show the effect of the reaction time on liquefaction at different temperatures in

Table I Composition of CB

Composition	Crude Protein	Crude Fat	Nitrogen-free Extract	Crude Fiber	Crude Ash
Content (%)	7.5	4.4	65.0	10.0	2.1

Data summarized from ref. 20.

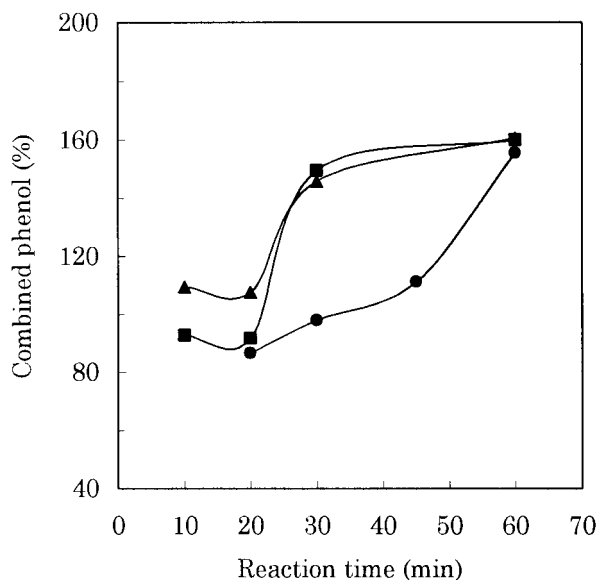


Figure 3 Effect of reaction time and temperature on the combined phenol of CB. Phenol/CB ratio, 3; catalyst content, 3%; high pressure. (●) 180°C; (■) 200°C; (▲) 220°C.

high-pressure-temperature conditions (autoclave). The methanol-insoluble residue decreases significantly within 60 min at 180°C and within 30 min at 200°C and 220°C; then, it levels off. The methanol-insoluble residue varied between approximately 70 and 4% based on the reaction temperature and time. Likewise, the amount of combined phenol increases rapidly within the same periods and then levels off. Liquefaction of CB is complete within 30 min at a temperature higher than 200°C.

As shown in Figure 1, the methanol-insoluble residue at 150°C did not decrease below 10% even at longer reaction times when compared to the high-pressure-temperature conditions, in which the methanol-insoluble residue decreases to less than 5%. From these results, it is suggested that the liquefaction of some CB components are greatly dependent on the temperature and pressure.

Figures 4 and 5 show the molecular weight distribution curves of the phenolated CB as a function of reaction temperature and time. When increasing these factors, all the molecular weight distributions shifted downward. Moreover, both low and high molecular weight parts were diminished with increasing the reaction temperature and time. As the reaction temperature and time increased from 180°C and 10 min to 200°C and 30

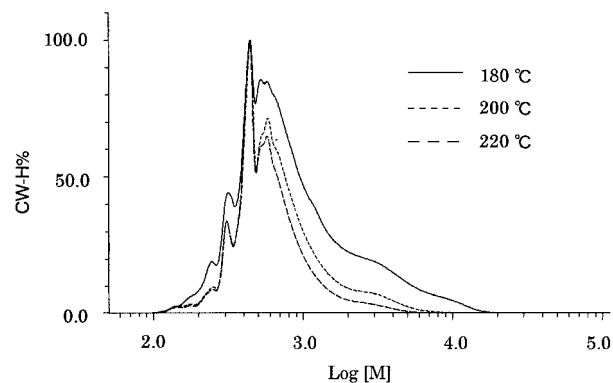


Figure 4 Molecular weight distribution curves of CB liquefied at 180–220°C.

min, the high molecular weight part was drastically diminished. After this point, the molecular weight distribution became stable. The corresponding weight-average molecular weight (M_w), the polydispersity (M_w/M_n), and their changing trends are summarized in Figure 6. It was found that the molecular weight decreases as the reaction time increases to 30 min and then levels off when the liquefaction temperature is higher than 200°C, which is very consistent with the results shown in Figures 2 and 3.

Furthermore, the extent of liquefaction can vary with different catalyst contents (Table II). The methanol-insoluble residue was decreased with both an increasing catalyst content and phenol/CB ratio. The amount of combined phenol can be almost doubled when the catalyst concentration was changed from 1 to 3%. However, a further increase in the catalyst content has no effect on the amount of the combined phenol. The same increasing trend of the combined phenol amount

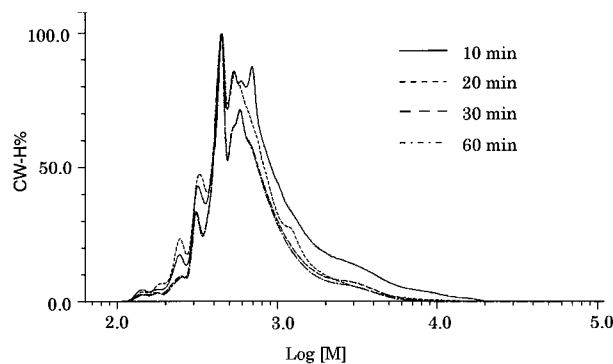


Figure 5 Molecular weight distribution curves of CB liquefied at 200°C for different reaction times.

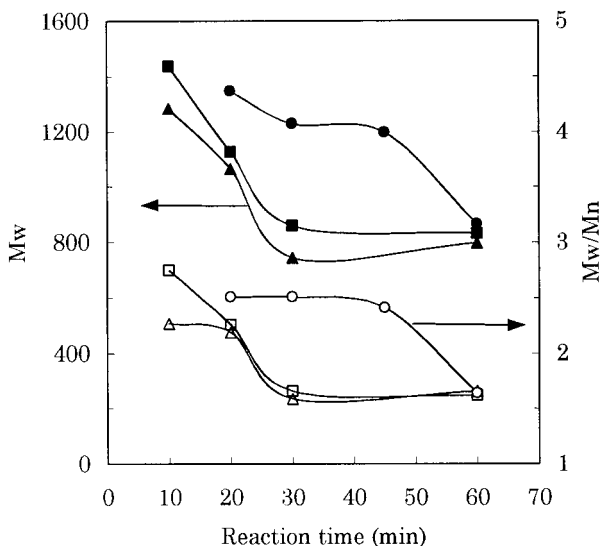


Figure 6 Effect of reaction time on the molecular weight and polydispersity of CB liquefied at 180–220°C. Phenol/CB ratio, 3; catalyst content, 3%. (●, ○) 180°C; (■, □) 200°C; (▲, △) 220°C.

was observed when the phenol/CB ratio was increased (Table III).

Noncatalyzed Liquefaction of CB

We considered that avoiding the addition of a catalyst would render this process more attractive. Therefore, we tested the noncatalyzed liquefaction of CB at a higher temperature (250°C) to compensate the absence of a catalyst. The patterns of the curves (Fig. 7) are similar to those obtained at 180–220°C in the presence of a catalyst. The methanol-insoluble residue decreases and the combined phenol content increases significantly within 20 min and then it levels off. However, there is a considerable dif-

Table II Effect of Catalyst Concentration on the Methanol-insoluble Residue and Combined Phenol of the Liquefied CB

Catalyst Content (%)	Methanol-insoluble Residue (%)	Combined Phenol (%)
1	14.7	82.2
3	5.6	149.6
5	3.4	150.3

Reaction temperature, 200°C; reaction time, 30 min; phenol/CB ratio, 3.

Table III Effect of Phenol/CB Ratio on the Methanol-insoluble Residue and Combined Phenol of the Liquefied CB

Phenol/CB Ratio	Methanol-insoluble Residue (%)	Combined Phenol (%)
1	36.7	75.4
2	17.7	93.8
3	5.6	149.6
5	1.7	183.1

Reaction temperature, 200°C; reaction time, 30 min; catalyst content, 3%.

ference between the two reaction conditions in the amount of the combined phenol, that is, the maximum value of the combined phenol obtained in the noncatalyzed conditions is only approximately 60%, which is just one-third of the value obtained in the catalyzed reaction condition. Such results demonstrate that there are differences in the liquefaction mechanism among these three methods of liquefaction depending on the temperature. The catalyzed liquefaction, conducted at 150°C as well as 180–220°C, are known to be governed by heterolytic, ionic reactions,²¹ resulting in higher amounts of combined phenol than is the case for noncatalyzed high-temperature (250°C) liquefaction.

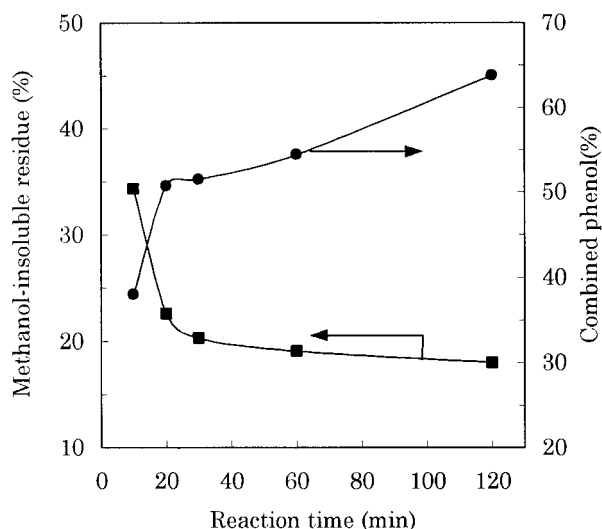


Figure 7 Effect of reaction time on the methanol-insoluble residue and combined phenol of CB liquefied at 250°C without catalyst. Phenol/CB ratio, 3; high pressure.

Table IV Comparison of the Thermal-flow Properties of the Phenolated CB with Various Amounts of Combined Phenol

Phenol/CB Ratio	Catalyst Content (%)	Combined Phenol (%)	T_s^a (°C)	T_f^b (°C)	Melt Viscosity ^c (poise)	M_w
1	3	75.9	85.0	107.5	1662	741
3	2	114.2	90.8	110.7	2397	721
3	3	158.0	98.7	120.8	4629	784
Novolak	—	—	90.3	110.0	—	—
Phenolated wood ^d	—	69	—	125	—	—
	—	88	—	160	—	—

^a Softening temperature.^b Flow temperature.^c Measured at 130°C and at constant shear stress of 1.225×10^6 dyn/cm².^d From ref. 1.

The latter are known to be proceeded by homolytic, radical reactions.²²

Thermal Flow and Flexural Properties

The thermal-flow property is one of the most important factors in the process of the phenolated materials. It is expected that molecular weight and the combined phenol amount influence the flow properties. In our case, the fully liquefied products showed similar molecular weights (Table IV). Therefore, the changes in flow properties will be attributed only to the amount of combined phenol. Different combined phenol amounts were obtained by changing the catalyst content and the phenol/CB ratio at the same temperature (200°C) and reaction time (30 min).

As shown in Table IV, the softening and flow temperatures became higher with an increasing amount of the combined phenol. The same phenomenon was observed for the apparent melt viscosity. This behavior can be explained by the fact that steric hindrance and hydrogen bonding in the phenolated CB molecules can be increased by the combined phenol groups. Indeed, hydroxyphenylation causes branching of the molecules of the phenolated CB, which results in restricted molecular motions.^{1,15}

The softening temperatures and the flow temperatures of the phenolated CB are very close to those of the commercial novolak resin. Moreover, such values are lower than those of phenolated wood with comparable combined phenol amounts obtained in previous reports.^{1,15} In other words, the processability of the phenolated CB obtained

in the present study is better than that of the phenolated wood, and, at the same time, it is comparable to that of a commercial novolak resin.

Figure 8 shows the effect of the amount of combined phenol on the flexural properties of the phenolated CB-based moldings. Generally, the greater the amount of combined phenol, the larger the crosslinking degree of the phenolated product-based molding, which results in greater flexural properties.¹² It can be seen that the optimum flexural properties of the phenolated CB-based moldings are reached at about a 110% amount of the combined phenol.

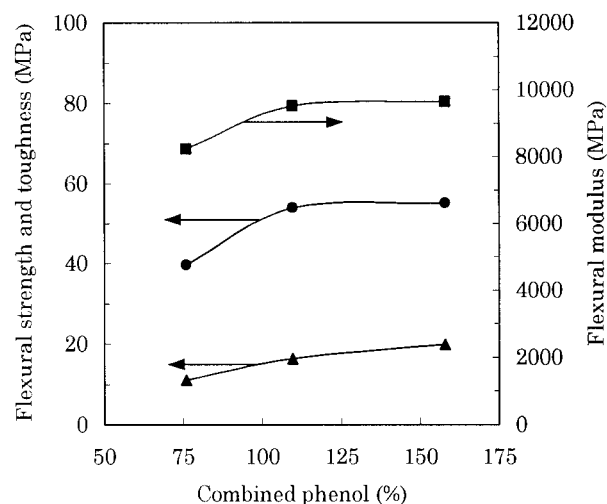


Figure 8 Effect of combined phenol amount on the flexural properties of the phenolated CB-based moldings. Molding temperature, 170–180°C; molding time and pressure, 5 min and 5.0 MPa. (●) Flexural strength; (■) modulus; (▲) toughness.

On the other hand, the curing behavior of the obtained phenolated CB-based resin can be indirectly evaluated by investigating the effect of the molding time on the flexural properties. As shown in Figure 9, all the flexural properties initially increase to a maximum with increase in the molding time, and then they level off. When comparing these data to those obtained in the previous report,¹² it is found that the curing behavior of phenolated CB-based resin is similar to that of the commercial novolak or phenolated wood.

Finally, we investigated the effect of the wood filler content on the flexural properties of the composite (Fig. 10). The increase of all the flexural properties with increasing filler content demonstrate that the phenolated CB resin can be further reinforced by the addition of fillers in the range of 30–60%.

CONCLUSIONS

The liquefaction of CB was achieved with yields comparable to those obtained with wood reported previously. Among the liquefaction conditions used in this study, the catalyzed liquefaction at high pressure and temperature (180–220°C) was the most effective for the liquefaction of CB. Under such conditions, the extent of liquefaction ad-

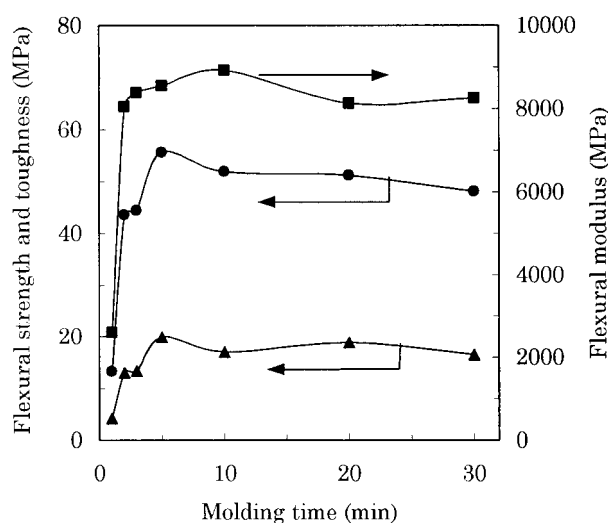


Figure 9 Effect of molding time on the flexural properties of the phenolated CB-based moldings. Amount of combined phenol, 158%; molding temperature and pressure, 170–180°C and 5.0 MPa. (●) Flexural strength; (■) modulus; (▲) toughness.

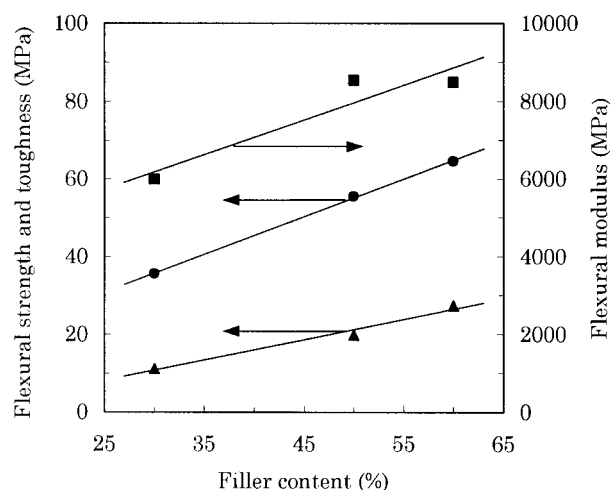


Figure 10 Effect of filler content on the flexural properties of the phenolated CB-based moldings. Amount of combined phenol, 158%; molding temperature, 170–180°C; molding time and pressure, 5 min and 50 MPa. (●) flexural strength; (■) modulus; (▲) toughness.

vanced rapidly (30 min) to high yields (1.7% residue). Moreover, the properties of the obtained phenolated CB were comparable to those of phenolated wood and commercial novolak resin. Also, their curing behavior was practically the same as that found in commercial novolak. The authors believe that these results open new opportunities for the utilization of biomass by-products considered generally as waste.

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REFERENCES

1. Lin, L.; Yoshioka, M.; Yao, Y.; Shiraishi, N. *J Appl Polym Sci* 1994, 52, 1629.
2. Maldas, D.; Shiraishi, N. *Polym-Plast Technol Eng* 1996, 35, 917.
3. Maldas, D.; Shiraishi, N. *Biomass Bioener* 1997, 12, 273.
4. Pu, S.; Shiraishi, N. *Mokuzai Gakkaishi* 1993, 39, 446.
5. Pu, S.; Shiraishi, N. *Mokuzai Gakkaishi* 1993, 39, 453.
6. Pu, S.; Shiraishi, N. *Mokuzai Gakkaishi* 1994, 40, 824.
7. Alma, M. H.; Yoshioka, M.; Yao, Y.; Shiraishi, N. *Mokuzai Gakkaishi* 1995, 41, 741.

8. Alma, M. H.; Yoshioka, M.; Yao, Y.; Shiraishi, N. *Mokuzai Gakkaishi* 1995, 41, 1122.
9. Yao, Y.; Yoshioka, M.; Shiraishi, N. *Mokuzai Gakkaishi* 1993, 39, 930.
10. Yao, Y.; Yoshioka, M.; Shiraishi, N. *Mokuzai Gakkaishi* 1994, 40, 176.
11. Lin, L.; Yoshioka, M.; Yao, Y.; Shiraishi, N. *J Appl Polym Sci* 1995, 53, 1563.
12. Lin, L.; Yoshioka, M.; Yao, Y.; Shiraishi, N. *J Appl Polym Sci* 1995, 55, 1563.
13. Lin, L.; Yoshioka, M.; Yao, Y.; Shiraishi, N. *J Appl Polym Sci* 1995, 58, 1297.
14. Maldas, D.; Shiraishi, N. *J Reinforc Plast Compos* 1997, 16, 870.
15. Alma, M. H.; Yoshioka, M.; Yao, Y.; Shiraishi, N. *Holzforschung* 1996, 50, 85.
16. Maldas, D.; Shiraishi, N. *Int J Polym Mater* 1996, 33, 61.
17. Yao, Y.; Yoshioka, M.; Shiraishi, N. *Mokuzai Gakkaishi* 1995, 41, 659.
18. Yao, Y.; Yoshioka, M.; Shiraishi, N. *J Appl Polym Sci* 1996, 60, 1939.
19. Maldas, D.; Shiraishi, N.; Harada, Y. *J Adhes Sci Technol* 1997, 11, 305.
20. Patrich, H.; Schaible, P. J. *Poultry: Feeds & Nutrition*; AVI: Westport, CT, 1981.
21. Lin, L.; Yao, Y.; Yoshioka, M.; Shiraishi, N. *Holzforschung* 1997, 51, 316–324.
22. Shiraishi, N. *Cell Commun* 1998, 5, 1–12.