

# Acid-Catalyzed Liquefaction of Waste Paper in the Presence of Phenol and Its Application to Novolak-Type Phenolic Resin

SEUNG-HWAN LEE,<sup>1</sup> YOSHIKUNI TERAMOTO,<sup>2</sup> NOBUO SHIRAIISHI<sup>2</sup>

<sup>1</sup> GreenBio Institute, Shimokamo Morihonmachi 15, Sakyo-ku, Kyoto 606-0805, Japan

<sup>2</sup> Division of Forest and Biomaterials Science, Kyoto University, Kitashirakawa Oiwake-cho, Sakyo-ku, Kyoto 606-8502, Japan

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**ABSTRACT:** Liquefaction of waste paper (WP) was performed in the presence of phenol with an acid catalyst. Newspaper (NP) was liquefied more easily than box paper (BP) or business paper (BNP). Differences in the degree of liquefaction were due to different chemical compositions. That is, NP had a relatively high lignin content, which is known to be easily liquefied, whereas BP and BNP were mainly composed of cellulose with a crystalline structure, which is difficult to liquefy. The acid concentration and phenol/WP ratio were more important factors in the regulation of liquefaction than reaction temperature. The changes in the apparent molecular weight depending on the reaction time were more significant for phenolated NP, with high lignin content, than for phenolated BP. The obtained phenolated products showed thermal flow properties and reactivity as good as those of phenolated wood and commercial Novolak resin. Thermosetting moldings were obtained from phenolated products, and their flexural properties and thermal stability were comparable to those of phenolated wood and commercial Novolak resin. Flexural properties were further improved by the cocondensation reaction between the unreacted phenol of phenolated products and formaldehyde.  
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**Key words:** waste; resin; molding

## INTRODUCTION

With an increasing worldwide resource shortage and environmental problems, many policies for recycling of waste materials have been proposed and are currently being performed in many countries to solve these problems. Recyclable waste materials include huge amounts of waste biomass and waste plastics. At present, waste paper (WP)

is actively recycled and regenerated. WP recycling rose from a level of 20% in 1968 to a level of 25–30% in the 1980s and was projected to approach 35% by the end of the year 2000 throughout the world.<sup>1</sup> The highest recycling levels are for corrugated cartons, newspaper (NP), and business paper (BNP).<sup>2</sup>

However, there are also some problems in systems for the use of recycled WP, including high collection cost, decrease in quality, low price, and limited market for the regenerated paper.<sup>3,4</sup> Therefore, methods to increase the economic efficiency of paper recycling are needed. The liquefaction technique, which was

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Correspondence to: S.-H. Lee (lshykh@hotmail.com).

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developed for the utilization of waste biomass,<sup>5-9</sup> may be useful for the development of new techniques for the use of WP. In this study, we attempted to liquefy some kinds of WP in the presence of phenol, and the obtained liquefied products were applied to Novolak-type phenolic resins.

## EXPERIMENTAL

### Materials

WPs used in the liquefaction were donated by Yokohama City, and the wood sample was 20–80 mesh wood meals of birch (*Betula maximowiczii regel*). Wood flour used as filler for molding was of 200 mesh pass size from Hitachi Chemical Co. (Tokyo, Japan) Flour 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 (CP), was high performance liquid chromatography (HPLC) grade, and tetrahydrofuran (THF), used as an eluting solvent for gel permeation chromatography, was extra-pure grade, containing 0.03% stabilizer (2,6-di-*t*-butyl-4-methylphenol). All other chemicals, purchased from commercial sources, were reagent grade.

### Liquefaction and Preparation of the Phenolated Resin

WP (50 g, oven dried), phenol (100–250 g), and sulfuric acid (3–13.5 g) were charged into a three-necked glass flask (500 mL) equipped with a reflux condenser and stirrer. Liquefaction was carried out under constant stirring (200 rpm) and reflux at 130–170°C for 20–180 min. Wood (50 g, oven dried), used as reference, was also liquefied under phenol (150 g) with sulfuric acid (4.5 g) at 150°C for 20–120 min. The resulting reaction mixture was washed out with methanol into a beaker. The diluted solution was filtrated through a glass-fiber filter under reduced pressure. The methanol-insoluble part was dried to constant weight at 105°C for 24 h and weighed for the determination of the percent residue (*R*). To quantify the unreacted phenol, the methanol-soluble part was analyzed by HPLC. Hence, *R* and *CP* were calculated by the following equations:

$$R (\%) = (W_r/W_0) \times 100 \quad \text{and}$$

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

where  $W_0$  is the weight of starting WP,  $W_r$  is the weight of the WP residue,  $W_1$ , the starting weight of phenol, and  $W_2$ , the weight of unreacted phenol.

The methanol-soluble part was neutralized with MgO. Methanol was then distilled off at 50°C, and unreacted phenol was removed at 180°C by vacuum distillation for preparation of the phenolated resin.

### Cocondensation of Unreacted Phenol of Liquefied Products and Formaldehyde

After liquefaction, the calculated amount of formalin (37% aqueous solution) was added into the liquefied products to maintain the mole ratio of unreacted phenol to formaldehyde at 1/0.8. The cocondensation reaction was conducted at 105°C under reflux for 80 min. The obtained cocondensed mixture was diluted with acetone and then neutralized with magnesium oxide (MgO). Finally the cocondensed mixture was concentrated by pressure-reduced evaporations at 50 and 180°C to remove acetone and unreacted phenol, respectively.

### Apparent Molecular Weight

The apparent molecular weight of the phenolated WP was determined with a gel permeation chromatograph equipped with a differential refractometer R401 detector (Tosoh, Tokyo, Japan). THF was used as the mobile phase at a flow rate of 1.0 mL/min with 7.0 MPa of pressure. The molecular weights were calibrated by monodisperse polystyrene standards.

### Thermal Flow Property and Reactivity

A flow tester (CFT-500A, Shimadzu, Kyoto, Japan) was used to measure the thermal flow properties of the phenolated WP. The starting temperature and heating rate were 50°C and 10°C/min, respectively. The apparent melt viscosity was determined at 115°C under a pressure of 5.0 MPa.

The reactivity of the phenolated WP with hexamethylenetetramine (HMTA) as a curing agent was examined with a Curelastometer (Nigohshouji, Tokyo, Japan) at 180°C for 10 min. The curing time at which the torque of the resin attained 90% of its maximum value [ $T_c(90)$ ] was used as a standard parameter for the description of the curing behavior of the phenolated WP.

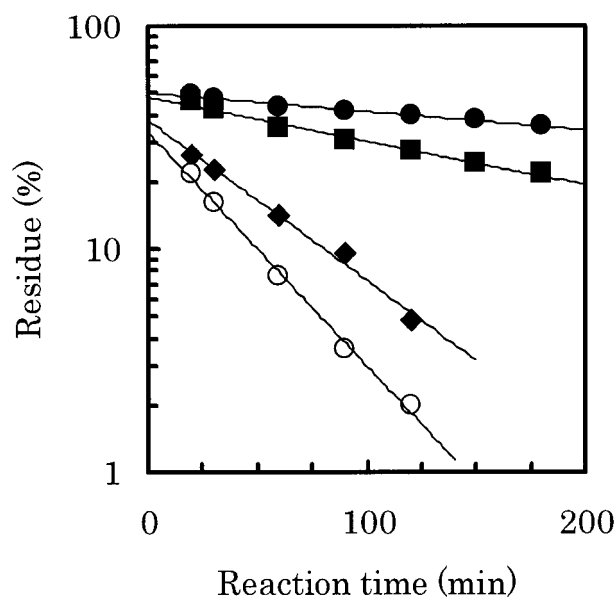
### Preparation and Flexural Properties of Thermosetting Molding

A formulation containing the phenolated WP (37.7 wt %), wood flour filler (49.5 wt %), HMTA (curing agent, 9.4 wt %), calcium hydroxide (accelerating agent, 2.4 wt %), and zinc stearate (lubricating agent, 1.0 wt %) was used. Except for the phenolated WP, all the other ingredients were premixed in a mortar for about 2 min, followed by the addition of an acetone solution of the phenolated WP, and then the mixing was continued until a uniform mixture was obtained. The resulting mixture was dried in an oven at 70°C for 1 h and then reground into powder and kept in a desiccator before measurement.

About 5 g of the compound powders was compression-molded into test specimens with dimensions of 80 × 10 × 4 mm. We accomplished the molding by preheating for 1 min and degassing, followed by molding under a pressure of 50 MPa at 180°C for 5 min. The flexural properties of the molded specimens were measured with an autograph (AGS-5kNG, Shimadzu). Flexural strength and modulus were calculated by the Shikibu program, and flexural toughness was calculated on the basis of the area under the stress-strain curve.

### Thermogravimetric Analysis (TGA)

We obtained the powder of the thermosetting molding by freezing and crushing under liquid



**Figure 1** Liquefaction of (●) BP, (■) BNP, (◆) NP, and (○) wood (temperature = 150°C, phenol/WP ratio = 3/1, catalyst concentration = 3%).

**Table I** *ks* of Liquefaction and Minimal Residue at Final Liquefaction Time Point

Sample	$k$ ( $\times 10^{-3}$ min)	Minimal Residue (%)
BP	1.9	35.3
BNP	4.5	21.9
NP	16.5	4.8
Wood	24.1	2.0

nitrogen with a cryogenic sample crusher (JFC-300, Japan Analytical Industry Co., Ltd., Tokyo, Japan). TGA was performed on a thermal gravimetric analyzer (TA instrument TGA 2950, New Castle, DE). The powder of the molding was put into an aluminum capsule and located automatically in the TGA instrument. We conducted degradation under air atmosphere by increasing the temperature from 30 to 900°C at a heating rate of 10°C/min.

## RESULTS AND DISCUSSION

### Liquefaction

In WP and wood, the progression of liquefaction over time was investigated at 150°C, and the results are shown in Figure 1. The amount of methanol-insoluble residue decreased linearly with reaction time on a logarithmic scale in all samples, indicating that the liquefaction during this period progressed according to pseudo first-order kinetics:

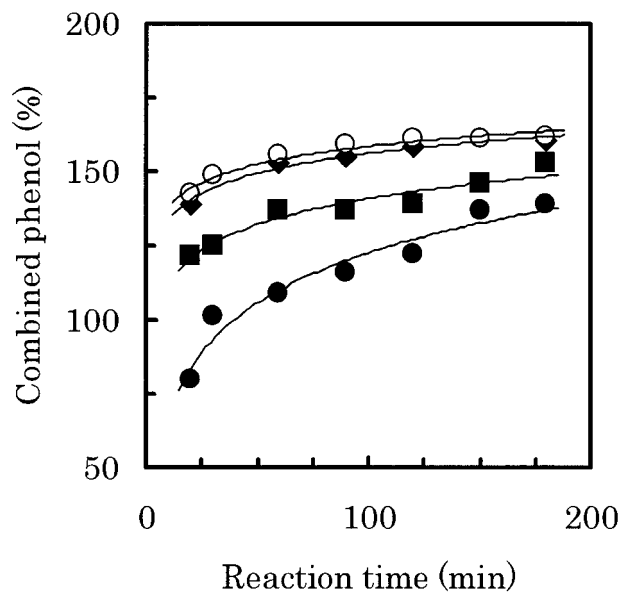
$$dc/dt = -kc \quad \text{or} \quad \ln c = \ln c_0 - kt$$

where  $c$  is the residue percentage,  $k$  is the apparent rate constant for liquefaction, and  $c_0$  is the initial content of the component liquefied obeying this formula, which can be estimated by extrapolating the linear portion to zero time.

The obtained  $ks$  and minimal residues at final liquefaction time (180 min) are summarized in Table I. The liquefaction rate was in the order

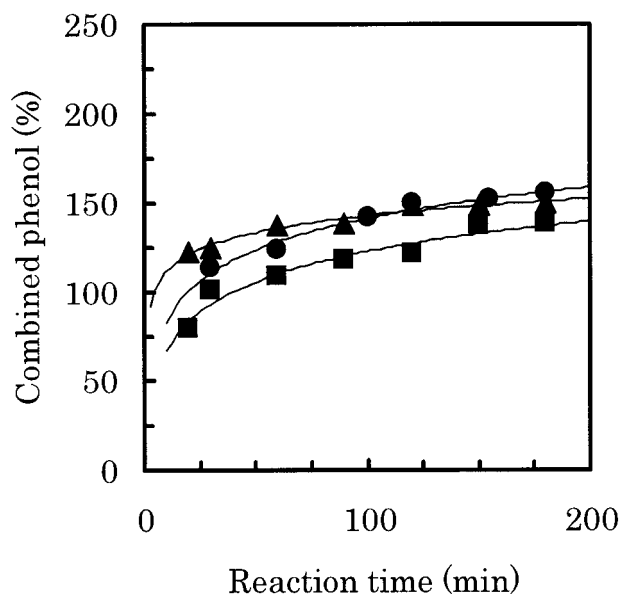
**Table II** Compositions of WP and Wood

Component	BP	BNP	NP	Wood
Lignin (%)	15.0	10.2	21.7	23.5
$\alpha$ -Cellulose (%)	60.9	64.7	54.7	53.8
Ash (%)	13.3	5.5	3.8	0.43



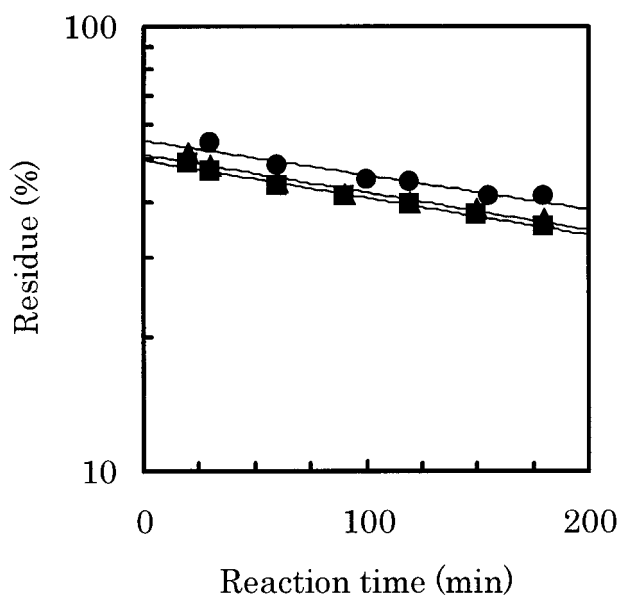
**Figure 2** Effects of reaction time on the CP contents of liquefied (●) BP, (■) BNP, and (◆) NP and (○) wood (temperature = 150°C, phenol/WP ratio = 3/1, catalyst concentration = 3%).

wood, NP, BNP, and box paper (BP); that is, wood and NP were more easily liquefied than BP or BNP. These differences in degree of liquefaction might be attributable to their different chemical compositions. Wood is mainly composed of cellulose, hemicellulose, and lignin. These three com-

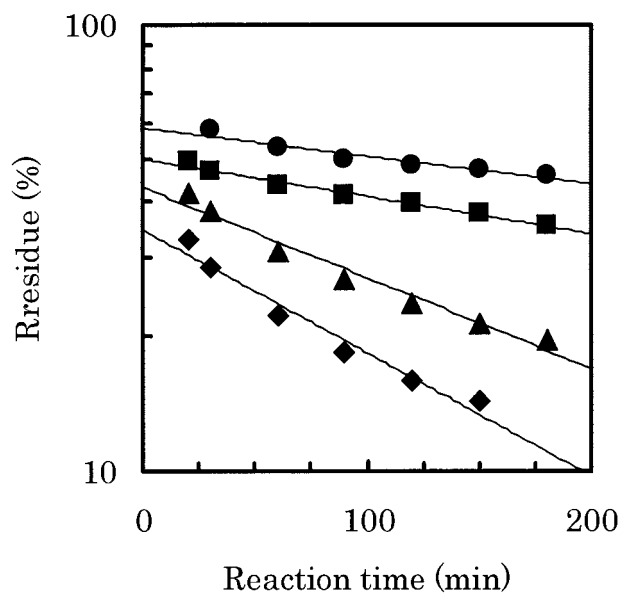


**Figure 4** Effects of reaction temperature on the CP contents of liquefied BP (phenol/BP ratio = 3/1, catalyst concentration = 3%): (●) 130, (■) 150, and (▲) 170°C.

ponents show marked differences in accessibility and reactivity during chemical reaction, especially in the chemical pulping process.<sup>10</sup> Lignin and hemicellulose can be removed selectively by treatment with some organic reagents. More severe conditions are required to depolymerize cel-



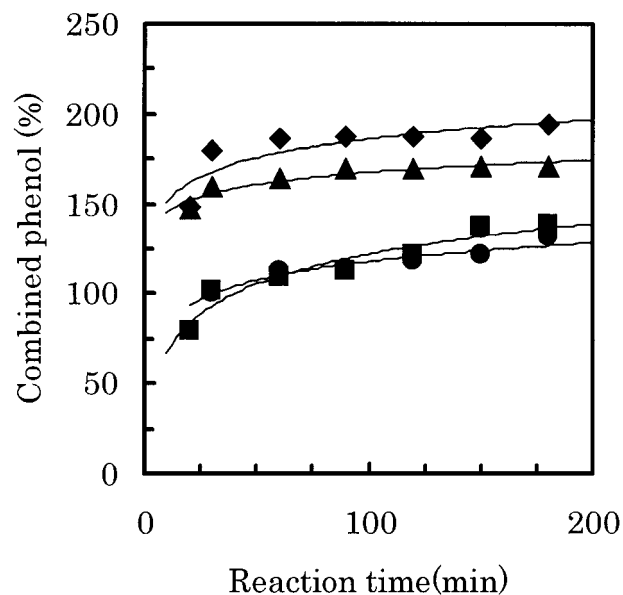
**Figure 3** Effects of reaction temperature on *c* of liquefied BP (phenol/BP ratio = 3/1, catalyst concentration = 3%): (●) 130, (■) 150, and (▲) 170°C.



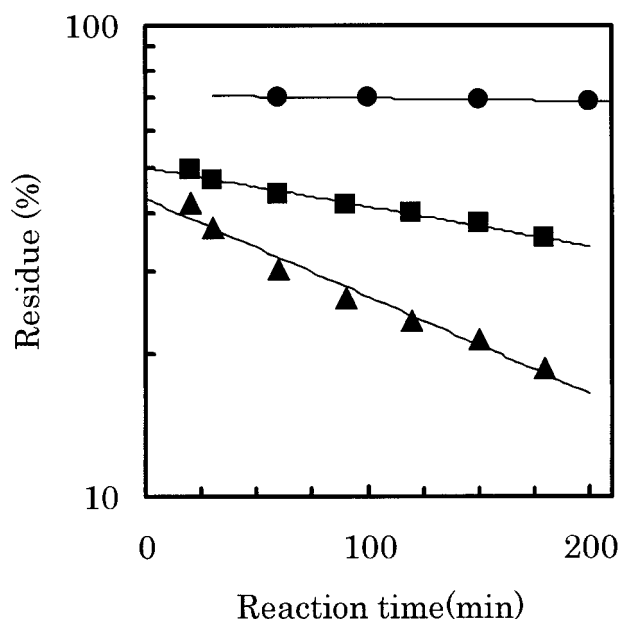
**Figure 5** Effects of catalyst concentration on *c* of liquefied BP (reaction temperature = 150°C, phenol/BP ratio = 3/1): (○) 2, (■) 3, (▲) 6, and (◆) 9%.

lulose with its high crystalline structure, as compared to lignin and hemicellulose. The chemical compositions of all samples are summarized in Table II. It is obvious from Table II that wood and NP have higher lignin contents than BP and BNP. Therefore, BP and BNP with high levels of cellulose would be expected to be more difficult to liquefy than NP and wood. The liquefaction rate of BP was very slow, and the amount of residue within the liquefaction time was markedly higher than for the other samples. This was because BP contains high levels of inorganic additives such as clay, talc, and so on, resulting in high ash content. Figure 2 shows the combined amount of phenol plotted as a function of reaction time. The CP content increased with increasing reaction time in all samples. However, there were also differences in the degree of CP content among the samples; that is, wood and NP had higher levels of CP content than BP and BNP. As discussed previously, the former had high contents of lignin with high reactivity to phenol.

As BP was the most difficult to liquefy among all of the samples, liquefaction of BP was investigated under several conditions. Figure 3 shows the effects of reaction temperature on  $c$ . Because the boiling temperature of phenol is 180°C, liquefaction was conducted below 180°C. The slopes of the lines were relatively similar at three different

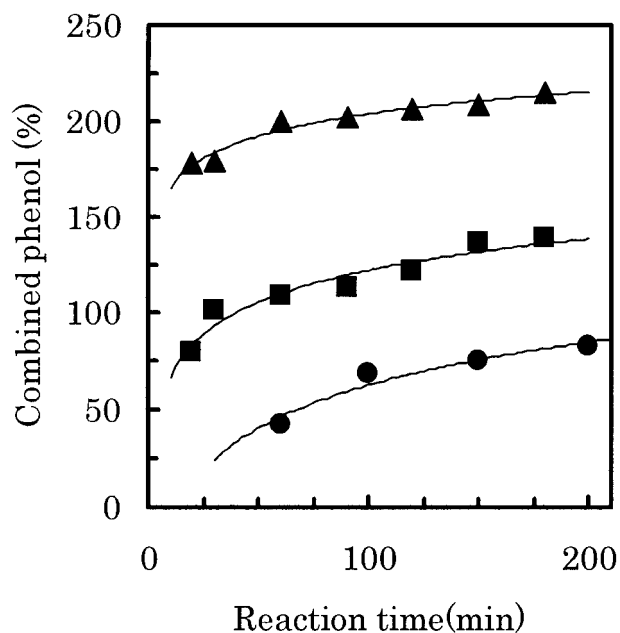


**Figure 6** Effects of catalyst concentration the CP contents of liquefied BP (reaction temperature = 150°C, phenol/BP ratio = 3/1): (○) 2, (■) 3, (▲) 6, and (◆) 9%.



**Figure 7** Effects of phenol/BP ratio on  $c$  of liquefied BP (temperature = 150°C, catalyst concentration = 3%): (●) 2/1, (■) 3/1, and (▲) 5/1.

reaction temperatures. Moreover,  $c$  did not decrease to less than 30%, even though the reaction temperature was increased to 170°C. This indicates that liquefaction could not be improved by



**Figure 8** Effects of phenol/BP ratio on the CP contents of liquefied BP (temperature = 150°C, catalyst concentration = 3%): (●) 2/1, (■) 3/1, and (▲) 5/1.

**Table III Apparent Molecular Weights and Polydispersities of Phenolated WP and Wood and Commercial Novolak Resin as a Function of Reaction Time**

Sample	Reaction Time (min)	$M_n$	$M_w$	$M_w/M_n$
BP	30	491	620	1.26
	60	500	617	1.23
	120	505	632	1.25
NP	30	536	719	1.34
	60	569	785	1.38
	120	633	989	1.56
Wood	30	559	733	1.31
	60	586	808	1.38
	120	643	991	1.47
Commercial Novolak resin	—	837	2553	3.05

an increase in the reaction temperature regardless of the length of the reaction time. In Figure 4, the CP content is plotted as a function of reaction time at different reaction temperatures. Likewise, the reaction temperature had little effect on the CP content. Figures 5 and 6 show the dependence of acid concentration on  $c$  and CP content, respectively. In Figure 5, the slope of the lines became steeper when acid concentration was changed from 3 to 9%.  $c$  decreased to less than 20% at acid concentrations of 6 and 9%. CP content was markedly increased to more than 150% when acid concentration increased from 3 to 6%, as shown in Figure 6. As a result, an acid concentration above 6% was necessary to obtain a  $c$  as low as 20% and a CP content of more than 150% within the reaction time investigated. The effects of the phenol/BP ratio on  $c$  and CP content are shown in Figures 7 and 8, respectively.  $c$  decreased and CP content increased as the liquid ratio increased, respectively. Increasing the phe-

nol/BP ratio to 5/1 increased the CP content to more than 200%. Specifically, the largest CP amount was 215%, which was obtained at a phenol/BP ratio of 5/1 in 180 min. In conclusion, the acid concentration and phenol/BP ratio influenced liquefaction to a greater extent than reaction temperature.

#### Apparent Molecular Weights

The apparent molecular weights [number-average molecular weight ( $M_n$ ) and weight-average molecular weight ( $M_w$ )] and polydispersities ( $M_w/M_n$ ) of phenolated WP, wood, and commercial Novolak resin are summarized in Table III. As shown in Table III, the apparent molecular weights and polydispersities of phenolated WP and wood increased with increasing reaction time. However, the changes depending on the reaction time were not significant in BP in comparison to the other samples. Degraded lignin causes

**Table IV Thermal Flow Properties of Phenolated WP, Phenolated Wood, and Commercial Novolak Resin**

Sample	CP (%)	$M_w$	Softening Temperature (°C)	Flow Temperature (°C)	Melt Viscosity (Poise)
BP	122.0	632	75.1	98.0	5406
BNP	152.8	651	75.3	98.2	4420
NP	160.2	997	109.7	132.2	—
Wood	161.0	1008	112.0	138.0	—
Commercial Novolak resin	—	2553	90.3	110.0	72

Reaction temperature = 150°C; time = 120 min; melt viscosity measured at 115°C.

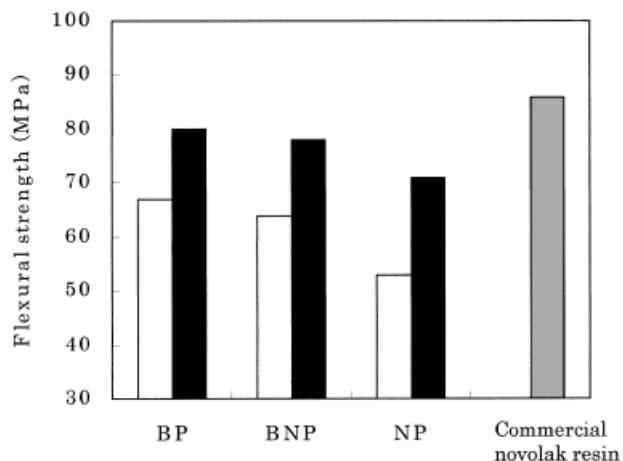
**Table V**  $T_c$  of Phenolated WP and Commercial Novolak Resin by Measurement with a Curelasterometer

Sample	CP (%)	$T_c(90)$ (min)
BP	122.0	2.25
BNP	138.8	2.13
NP	158.9	1.92
Wood	151.0	1.97
Commercial Novolak resin	—	1.74

a condensation reaction to occur very easily.<sup>11</sup> This result suggests that liquefied NP and wood components underwent more recondensation than liquefied BP components with little lignin. The  $M_w/M_n$  values obtained for the phenolated WP and wood were smaller than that for the commercial Novolak resin. In other words, the phenolated WP and wood have rather narrow molecular-weight distributions compared to the commercial Novolak resin.

#### Thermal Flow Properties and Curing Reactivity

Table IV shows the thermal flow properties of phenolated WP together with those of phenolated wood and commercial Novolak resin. As shown in Table IV, the phenolated BP and BNP had softening temperatures ranging from 75.1 to 75.3°C, flow temperatures from 98.0 to 98.2°C, and melt viscosities from 4420 to 5406 poise. These ranges were better values than those of phenolated wood and comparable with those of commercial Novolak resin. However, the phenolated NP displayed high softening (109.7°C) and flow temperatures (132.2°C). This result can be explained in terms of NP's high values of CP and molecular weight. The amount of CP and molecular weight

**Figure 9** Flexural strength of moldings from (□) phenolated WP and (■) phenolated WP/formaldehyde condensed resins.

affect the flow behavior of phenolated product;<sup>5,12,13</sup> that is, higher values of both CP and molecular weight, which restrict molecular motion, are associated with higher flow temperature and melt viscosity.

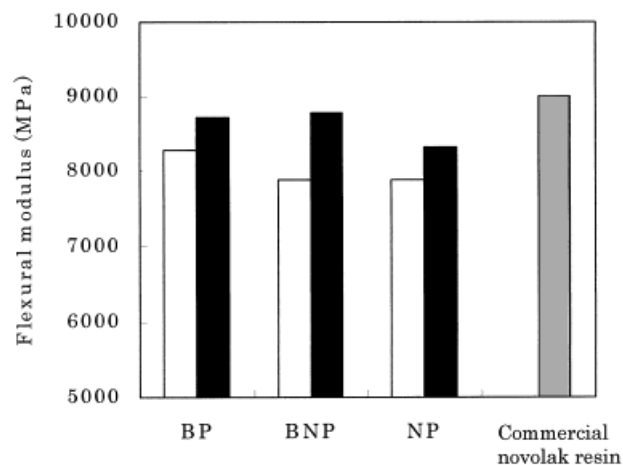
Table V shows the reactivity of phenolated WP with HMTA.  $T_c(90)$ 's of all phenolated WPs with sufficient amounts of CP (>100%) were comparable to that of phenolated wood but were slightly inferior to that of the commercial Novolak resin.

#### Flexural Properties of Thermosetting Moldings

Thermosetting moldings were successfully obtained from phenolated WPs by hot-pressing at 180°C. Moldings exhibited a broad range of flexural properties (Table VI), for example, flexural strengths ranging from 59 to 64 MPa, moduli ranging from 7873 to 8080 MPa, and toughness ranging from 26 to 29 MPa. These flexural properties were similar to those of the moldings

**Table VI** Flexural Properties of Moldings Obtained from Phenolated WP, Wood, and Commercial Novolak Resin

Sample	Flexural Strength (MPa)	Flexural Modulus (MPa)	Flexural Toughness (MPa)
BP	63	8080	28
BNP	64	7873	29
NP	59	7890	26
Wood	67	7396	33
Commercial Novolak resin	86	9005	37



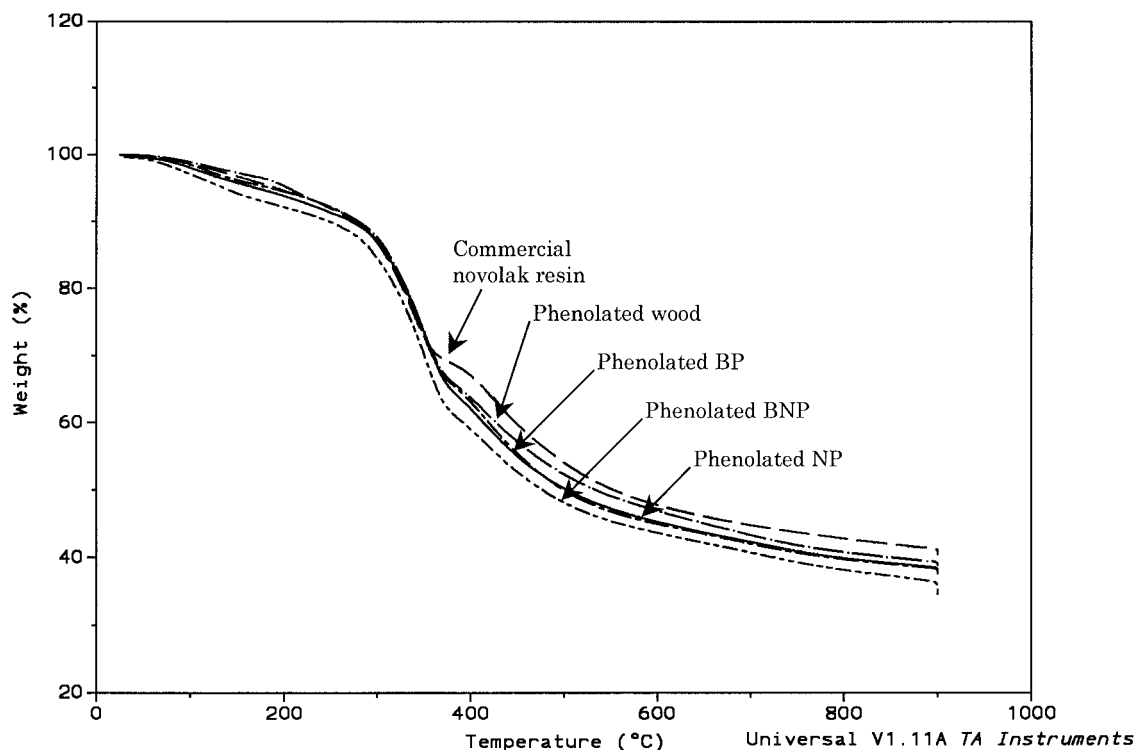
**Figure 10** Flexural moduli of moldings from (□) phenolated WP and (■) phenolated WP/formaldehyde co-condensed resins.

made from phenolated wood but were somewhat inferior to those of commercial Novolak resin. For further improvement of flexural properties, the cocondensation reaction between formaldehyde and the unreacted phenol of phenolated WP was conducted. The cocondensation reac-

tion between formaldehyde and the unreacted phenol of phenolated products can enhance the thermal and mechanical properties before cocondensation.<sup>6,14</sup> The results are shown in Figures 9 and 10. The flexural strengths of all samples after cocondensation reactions were enhanced to more than 10 MPa, and the moduli of the moldings were also higher than that of the moldings before cocondensation reaction. Furthermore, these moldings contained the solid residue and neutralization salt, the former of which remained after liquefaction and the latter of which was produced by neutralization of liquefied products. These results indicate that the total utilization of the liquefied WP was possible by condensation reaction without the removal of solid residue and neutralization salt.

### Thermal Stability of Moldings

Figure 11 shows the thermogravimetric curves of the moldings from phenolated WP in comparison to those from phenolated wood and commercial Novolak resin. As shown in the Figure 11, the phenolated WP-based moldings withstood a



**Figure 11** TG curves of the moldings from the phenolated WP, phenolated wood, and commercial Novolak resin.



temperature of about 350°C without significant degradation and then started degrading thermally with further increases. This thermal degradation temperature was quite close to that of the phenolated wood. However, commercial Novolak resin-based moldings withstood slightly higher temperatures than the other samples. This might have been due to the higher reactivity of the commercial Novolak resin in comparison to the others.

## CONCLUSIONS

Phenolated products were obtained from WP and applied to thermosetting Novolak resin. The liquefaction of BP was most difficult, but a lower *c* and a sufficient amount of CP could be achieved, depending on the reaction conditions. The phenolated WP showed relatively good thermal flow properties and reactivity. Also, thermosetting moldings were prepared from these phenolated products, and their flexural properties were as good as those of phenolated wood. Moreover, it was possible to further improve the flexural properties through a condensation reaction between the unreacted phenol and formaldehyde. The phenolated-WP-based moldings had thermal stabilities comparable to those made from phenolated wood. In conclusion, the results of this study show that the

phenol liquefaction technique may be useful for the utilization of WP.

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