

Preparation and Properties of Phenolated Wood/Phenol/Formaldehyde Cocondensed Resin

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SYNOPSIS

A phenolated wood/phenol/formaldehyde cocondensed novolac-type resin was prepared with a two-stage procedure. Wood was first liquefied in the presence of phenol by using an acid catalyst to produce a phenolated wood, and after the liquefaction, formalin (i.e., formaldehyde aqueous solution) was added to conduct a cocondensation reaction for converting the remaining nonreacted phenol into resin components. It was found that this procedure can convert almost all the phenol remained after liquefaction into resin, and therefore significantly upgrades the practical value of the liquefaction technique. In addition, it can also greatly improve the thermofluidities of the phenolated wood resins and the mechanical properties of their molded products. As a result, the flow temperatures and melt viscosities of the cocondensed resins were much lower than those of the phenolated wood resins. However, these two properties were more or less similar to those of the conventional novolac resin, resulting in an excellent processability. The flexural properties of the molded products made from the cocondensed resins were much higher than those of the phenolated wood and also somewhat superior to those of the conventional novolac resin. Therefore, this preparation procedure is a prospective technique for preparing wood-based novolac resins.

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INTRODUCTION

The liquefaction of wood in the presence of phenol has been studied in this laboratory for many years.¹⁻⁵ Among all the usages of the resulting phenolated wood (i.e., liquefied wood), replacement of phenolic novolac resin as a thermosetting material is the most prospective one. The molded products prepared from the phenolated wood resins have been found to be comparable in mechanical properties to those of the conventional novolac resin, particularly when the amount of combined phenol in the phenolated wood reached a certain level.⁶ However, the flow temperatures and the melt viscosities of the phenolated wood resins were rather high in comparison to those of the conventional novolac resins, and the mentioned properties increased significantly with an increase in the amount of combined phenol. When the

amount of combined phenol was very large, the flow temperature was close to the crosslinking temperature of the phenolated wood resin with hexamine as a hardener.^{7,8} This drawback in thermofluidities not only creates difficulties in processing, especially in the injection molding, but also deteriorates the properties of the final molded products. On the other hand, in the manufacturing procedure of the phenolated wood resins, an excessive amount of phenol was necessary in the liquefaction in order to attain a satisfactory liquefaction. As a result, a quite large amount of phenol remained after liquefaction reaction, and it must be removed from the liquefied mixtures to obtain the final phenolated wood resins. Therefore, this treatment is an energy-consuming process, and will reduce the practical value of the technique. In order to overcome these two deficiencies, in this study, a cocondensation reaction of phenolated wood/phenol/formaldehyde was conducted after liquefaction of wood, by adding formaldehyde into the liquefied mixture, to convert the remaining phenol into cocondensed resin. It was ex-

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pected that the cocondensation reaction can also modify the structures of the phenolated wood components and therefore improve the thermofluidities (or processability) and mechanical properties of the phenolated wood resins.

EXPERIMENT

Materials

The wood sample used in the liquefaction was 20–80 mesh wood meals of birch (*Betula maximowiczii* Regel). It was dried in an oven at 105°C for 8 h and then kept in a vacuum oven at room temperature before use. Both wood powders (200 mesh pass), used as fillers for molded products, and a commercial novolac resin (Novolac, HP-700) were supplied by Hitachi Chemical Co. For comparison, the wood residues obtained from the liquefaction of wood were also used as the fillers for molded products after grinding into powders and allowing to pass a 200-mesh sieve. Hexamethylenetetramine (hexamine) was obtained from Mitsubishi Gas Chemical Co. All other chemicals were of reagent grade and were used without further purification.

Preparation of Phenolated Wood/Phenol/Formaldehyde Cocondensed Resins

The liquefaction of wood was conducted according to the method described in our previous paper.⁷ In this study, both phosphoric acid and oxalic acid were used individually as catalysts for the liquefaction. After the liquefaction reaction, the temperature of the liquefied mixtures was allowed to decrease from 160 to 105°C, and then the calculated amount of formalin (37% aqueous solution) was added into the liquefied mixtures. In all cases, the mole ratio of nonreacted phenol to formaldehyde was fixed at 1 : 0.8. The acid remained in the liquefied mixture acted as the catalyst for the cocondensation reaction among the phenolated wood, phenol, and formaldehyde. The cocondensation reaction was conducted at 105°C for 80 min under reflux. When oxalic acid was used as the liquefaction catalyst, additional oxalic acid might be added together with formalin solution in order to obtain a desirable acidity for the cocondensation reaction. After the desired reaction time, the cocondensed mixtures were diluted with acetone, and then filtrated through a glass filter paper (Toyo GA100). The filtrate was neutralized by magnesium oxide (MgO), and was finally concentrated by pressure-reduced evaporations (about 20

mmHg) at 50 and 165°C, successively, to remove the diluting solvent and nonreacted phenol to obtain the phenolated wood/phenol/formaldehyde cocondensed resins. The preparing procedure for the cocondensed resins is shown in Figure 1. The amount of combined phenol in the phenolated woods and nonreacted phenol remaining after liquefaction was determined and calculated as described in the previous paper.⁷ The conversion rate of nonreacted phenol to resin in the cocondensation reaction was calculated according to the following equation:

$$V_r = (W_2 - W_1)/W_p$$

where V_r is conversion rate of phenol, W_2 is the weight of the final cocondensed resins, W_1 is the weight of phenolated wood, and W_p is the weight of nonreacted phenol remaining after liquefaction.

Methods of Measurements

The molecular weights and polydispersities of the phenolated wood/phenol/formaldehyde cocondensed resins, phenolated woods, and a commercial novolac resin were determined in a liquid chromatography (6000A Waters Chromatography) using linearly linked Shodex GPC KF802 and KF803 columns and a differential refractometer detector (Waters R401). Tetrahydrofuran (THF) was used as the mobile

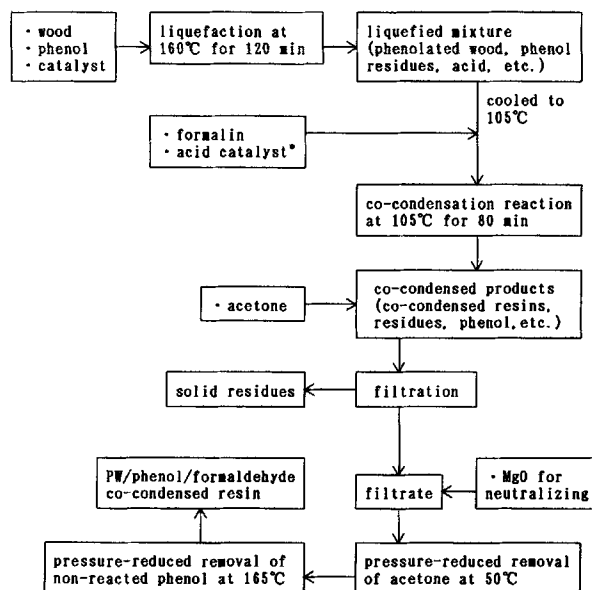


Figure 1 Procedure for the preparation of phenolated wood/phenol/formaldehyde cocondensed resins. *When phosphoric acid was used as a catalyst, the additional acid catalyst was not used.

Table I Liquefaction Conditions^a and the Compositions of the Liquefied Mixtures

Concentration of Catalyst (%)	Phenol to Wood Ratio	Compositions ^b of the Liquefied Mixture (%)				
		Residues	Phenolated Wood (CPh) ^c	Nonreacted Phenol	Acid Catalyst	
H ₃ PO ₄	4.5	2	8.0	39.4 (64%)	48.0	4.5
	1.7	3	9.8	21.5 (45%)	67.0	1.7
	2.5	3	7.6	25.8 (52%)	64.1	2.5
	5.2	3	2.9	36.4 (75%)	55.5	5.2
	6.0	3	1.7	39.3 (78%)	53.0	6.0
(COOH) ₂	4.5	3	12.7	15.5 (38%)	67.0	4.5
	6.0	3	12.5	16.0 (45%)	65.5	6.0
	4.8	4	12.6	13.0 (44%)	72.0	4.8

^a Liquefaction temperature, 160°C and time 120 min.

^b The compositions were calculated based on the total weight of the liquefaction mixture including the phenolated wood, nonreacted phenol, residues, and catalyst.

^c The data in the brackets express the amount of combined phenol (CPh) in the phenolated wood.

phase and the flow rate was 1 mL/min. The concentrations of the samples were 0.2–0.5 wt % in THF solutions and the injecting amount for measurement was 150 μ L. The molecular weights of the samples were calibrated by the monodisperse polystyrene standards.

The thermofluidities of all the samples were measured by the GFT-500A Flow Tester (Shimadzu Co.). A die with the dimensions of 1 mm \times 2 mm (diameter \times length) was used. The preheating time was 200 s for all the samples and a heating rate of 10°C/min was used for the measurement of flow temperature. The apparent viscosities of the samples were measured under a fixed shear stress of 6.129 $\times 10^6$ dyn/cm² at a temperature of 120°C.

Preparation of Molded Specimens and Measurement of Mechanical Properties

A formulation containing 37.7 wt % resins, 9.4 wt % hexamine, 49.5 wt % wood fillers, 2.4 wt % Ca(OH)₂ (calcium hydroxide), and 1.0 wt % zinc stearate was used to prepare molded specimens for mechanical tests. The compression molded specimens were prepared according to the method described in the previous paper.⁵ The molding cycles were 1 min preheating and degassing, 2 min molding under a pressure of 38 MPa at 185°C, and 10 min cooling under pressure.

The flexural tests of the molded specimens were conducted by using Autograph DCS-R-500 (Shimadzu Co.) according to the JIS K-6911. The cross-head speed for measurement was 2 mm/min. The specimens were conditioned at 20 \pm 0.5°C and 60% RH for at least 24 h before test. The flexural

strength, flexural modulus, and flexural toughness (or energy absorbed) were calculated according to the methods described in the previous paper.⁵

RESULTS AND DISCUSSION

Table I lists the compositions of the liquefied mixtures prepared under different liquefaction conditions using phosphoric acid or oxalic acid as the catalyst. This table reveals that a large amount of nonreacted phenol, ranging from 48.0 to 72.0% of the total mixtures, remained in the liquefied mixtures. Therefore, it is much more reasonable to convert directly the nonreacted phenol into resins *in situ* rather than to recycle it. Moreover, from this table it can also be found that solid residual contents in the liquefied mixtures are relatively low, ranging from 1.7 to 12.7%. Therefore the cocondensation reaction can be performed after the liquefaction process without removing the solid residues.

Phosphoric Acid Catalyzed Method

Phosphoric acid is a relatively strong acid. It was found that after the liquefaction and addition of formalin, the reaction mixtures usually have high acidity (pH \approx 1.0–1.5). Therefore, this acidity can successively be used to catalyze the cocondensation reaction. The effect of phosphoric acid concentration in the cocondensation reaction mixture on the conversion rate of phenol to resin is shown in Table II. It can be seen that with a lower acid concentration (i.e., 1.2%), a lower conversion rate (i.e., 57.4%) in comparison with that of industrial yield of the no-

Table II Effect of Phosphoric Acid Concentration of the Cocondensation Reaction Mixture on the Conversion Rate of Nonreacted Phenol

H ₃ PO ₄ concentration ^a (%)	1.2	2.5	3.2	3.7	3.8
Conversion rate of phenol (%)	57.4	88.0	90.1	92.5	94.0

^a The phosphoric acid concentration of the cocondensation reaction mixture (including liquefied mixture and formalin) was calculated based on the amount of phosphoric acid added in the liquefaction stage.

volac resin (about 107%) is obtained.⁹ With increasing the acid concentration from 1.2 to 2.5%, the conversion rate increases rapidly from 57.4 to 88%. With the further increase in the acid concentration, the rising tendency of the conversion rate becomes slower. Because the amounts of acid usually required in the liquefaction stage for obtaining a satisfactory liquefaction correspond to acid concentrations of 2.5 to 3.7% in the cocondensation stage, the above results indicate that the cocondensation reaction can be performed sufficiently without charging an additional acid after liquefaction stage. Moreover, the good conversion rate of phenol suggests that the presence of phenolated wood components does not inhibit the conversion of the nonreacted phenol to resin.

The thermofluidities, number average molecular weights, and polydispersities (M_w/M_n) of the resulting cocondensed resins are shown in Table III in comparison with those of the commercial novolac resin and phenolated wood resin (PW resin). Both flow temperature and melt viscosity of the cocondensed resin decrease monotonically with decreasing phenolated wood content (expressed as "PW content" in the tables) in the resin regardless of the

catalyst concentration used and the amount of combined phenol in the phenolated wood. It is important to notice that even at the highest phenolated wood content (62.5%), the cocondensed resin has a flow temperature and melt viscosity much lower than those of the mere phenolated wood resin, but close to those of the commercial novolac resin. It has also been found that an addition of commercial novolac resin into the phenolated wood by mechanical mixing can only proportionally improve the thermofluidities of the phenolated wood.¹⁰ Therefore, it can be assumed that the cocondensation reaction can lead to a substantial improvement in affinity of phenolated wood with the phenol-formaldehyde (PF) components, resulting in an effective external plasticization of the former with the latter. As a result, the flow properties of the cocondensed resins improve significantly. It is also important to notice that the liquefaction as well as cocondensation conditions are not controlling factors to obtain excellent thermofluidities, that is, all of the cocondensed resins obtained have satisfactory thermofluidities regardless of their preparing conditions and compositions. However, no attempt was made to prepare resins with phenolated wood content higher than

Table III Number Average Molecular Weights (M_n), Polydispersities (M_w/M_n), and Thermofluidities of the Novolac Resin, Phenolated Wood Resin, and Cocondensed Resins Prepared Using Phosphoric Acid as a Catalyst

H ₃ PO ₄ Concentration ^a (%)	PW Content ^b (%)	Combined Phenol ^c (%)	M_n	M_w/M_n	Flow Temperature (°C)	Melt Viscosities (Poise)
—	Novolac, HP-700		872	5.2	89.9	270
—	PW resin ^d	70	516	2.7	126.4	21450
3.7	62.5	75	682	5.0	95.1	1540
3.8	52.6	65	526	3.5	94.8	1201
3.0	50.0	63	540	3.5	90.0	463
2.45	50.0	55	—	—	89.8	465
1.2	37.0	45	434	2.8	89.0	259
3.7	35.7	70	588	4.4	80.2	252

^a The acid concentration of the cocondensation reaction mixture.

^b PW content means the phenolated wood content in the cocondensed resin.

^c The amount of combined phenol in the phenolated wood.

^d A pure phenolated wood resin prepared by the phosphoric acid catalyzed method.

62.5% in this study, because a further increase in the phenolated wood content can be obtained only by a decrease in the conversion rate of the non-reacted phenol, but this is not practically meaningful.

Table III also shows that the number average molecular weights of the cocondensed resins do not change regularly with the change in reaction conditions and the compositions of the resins, and they scatter within a relatively small range from 434 to 682. The polydispersities also reveal a scattering nature, ranging from 2.8 to 5.0.

The flexural properties of the molded specimens prepared from the cocondensed resins are shown in Table IV. It is obvious that the flexural strength and toughness of the molded specimens from the cocondensed resins are much larger than those of the specimens from the only phenolated wood, and also somewhat superior to those of the molded specimens from the commercial novolac resin, even at the highest phenolated wood content of 62.5%. With the decrease in the phenolated wood content from 62.5 to 35.7%, the properties mentioned do not change evidently. From Tables III and IV, it can be found that the influence of the amount of combined phenol on the mentioned properties under study is marginal, even though the amounts of combined phenol change from 45 to 75%. The above results indicate that the cocondensation not only improve the flow properties of the resins, but also significantly improve the mechanical properties of their molded products. It has also been proved in one of our previous studies that the phenolated wood resins have better interactions with wood fillers than those of the commercial novolac resin.⁶ Therefore, the superior properties of the molded products prepared

from the cocondensed resins could be attributed to the interaction of the phenolated wood components and the typical phenol-formaldehyde (PF) resin fragments.

Oxalic Acid Catalyzed Method

Oxalic acid is a weak catalyst in the liquefaction of wood, as a result of which the resulting liquefied mixtures possess smaller amounts of combined phenol and larger amounts of both residues and non-reacted phenol, as shown in Table I. Even though the liquefaction conditions were enhanced, neither the combined phenol nor the residual content change appreciably. It is worth mentioning that this phenomenon is similar to that of the organosolv pulping process, where the cellulose component is kept as intact as possible. In this study, the use of oxalic acid was proposed in consideration of the fact that it has low corrosivity to the equipment and the remaining residues (mainly cellulose) can also be used as fillers for the preparation of molded products thereafter. However, because of the low amounts of combined phenol, the properties of molded products prepared from these phenolated wood resins are usually much lower than those of the conventional novolac resins. Under these circumstance, the conversion of the nonreacted phenol into resin as well as the modification of the phenolated woods by this cocondensation reaction have a much more practical value.

As mentioned above, the liquefaction results cannot be improved significantly by the increase in the oxalic acid concentration, therefore, in this study, the amount of oxalic acid charged in the liquefaction stage was kept at a lower level. An additional amount

Table IV Flexural Properties of Molded Specimens Made from the Cocondensed Resins Prepared Using Phosphoric Acid as a Catalyst

PW Content ^a (%)	Combined Phenol ^b (%)	Flexural Strength (MPa)	Flexural Modulus (MPa)	Flexural Toughness (MPa, ×10 ²)
Novolac, HP-700	—	96.0	8012	58.0
PW resin ^c	70	75.0	8750	33.5
62.5	75	99.4	8846	57.0
52.6	65	97.2	8405	57.6
50.0	63	97.7	8287	59.1
50.0	65	97.5	8738	57.2
37.0	45	102.2	8308	65.0
35.7	70	102.6	8150	65.6

^a PW content means the phenolated wood content in the cocondensed resin.

^b The amount of combined phenol in the phenolated wood.

^c A pure phenolated wood resin prepared by the phosphoric acid catalyzed method.

of oxalic acid was added in the cocondensation reaction to obtain a greater conversion rate. The total concentration of acid in the cocondensation reaction mixture was calculated based on the sum of the two parts of acid. The effects of catalyst concentration on the conversion rate, molecular weight, and thermofluidity of the resulting cocondensed resins are shown in Table V. It is evident that the effect of catalyst concentrations on the conversion rates for oxalic acid follows a trend similar to that of the phosphoric acid catalyst, that is, with an increase in the oxalic acid concentration, the conversion rate increases gradually. When the total oxalic acid catalyst concentration reaches 4.2%, the conversion rate is more than 100%; this can be comparable to that of the industrial yield of the novolac resin. On the other hand, it is observed that with an increase in catalyst concentration, the number average molecular weight, flow temperature, and melt viscosity of the cocondensed resin increase monotonically regardless of the decrease in the phenolated wood content. However, the resins prepared with relatively low acid concentrations have low flow temperatures and melt viscosities comparable to those of the commercial novolac resin. This result is quite different from the case of the phosphoric acid catalyst where the thermofluidities of cocondensed resins are independent of the catalyst concentration, but decrease slightly with increasing the phenolated wood content. The explanation for the two different

behaviors resulted from the two acid catalysts requires further investigation.

For verifying whether the phenolated wood content also influences the above-mentioned properties, the cocondensed resins with various phenolated wood contents were prepared under a fixed acid concentration of 2.5% by changing the liquid ratio (i.e., ratio of phenol to wood) in the liquefaction stage. The results are shown in Table VI. It can be seen that the flow temperatures and melt viscosities of all the samples are close to those of the commercial novolac resin, and with a decrease in the phenolated wood content these properties do not change their values significantly. This result indicates that excellent resins can be obtained by using a relatively low oxalic acid concentration, and their properties are not influenced evidently by their compositions in the studied range.

The flexural properties of the molded specimens made from the cocondensed resins, prepared from the oxalic acid catalyzed method, are shown in Table VII. It is revealed that the flexural properties, except for the modulus, of all the samples are obviously higher than those of the commercial novolac resin and also much higher than those of the only phenolated wood resins. Moreover, the change in phenolated wood content does not influence these mechanical properties. These results also have good agreement with those of the phosphoric acid catalyzed method. Once again, this fact indicates that

Table V Effects of Oxalic Acid Concentration on the Conversion Rates, Number Average Molecular Weights (M_n), Polydispersities (M_w/M_n), and Thermofluidities of the Cocondensed Resins

Oxalic Acid Concentration ^a		Combined Phenol ^b (%)	Conversion Rate of Phenol (%)	PW Content ^c (%)	Properties of Cocondensed Resin			
A (%)	B (%)				M_n	M_w/M_n	Flow Temperature (°C)	Melt Viscosity (Poise)
0.0	0.4	40	28.6	49.0	—	—	—	—
0.0	0.9	40	34.5	44.2	—	—	—	—
2.2	0.0	35	70.2	28.0	515	4.3	80.5	255
2.5	0.0	36	79.6	25.5	519	4.1	89.0	414
3.0	0.0	38	83.5	24.6	518	4.2	95.0	522
3.0	0.4	38	91.6	23.0	588	4.1	99.5	817
3.0	0.6	40	92.4	22.8	676	3.8	100.4	1218
3.0	0.8	42	94.6	22.4	806	4.2	104.0	3770
3.0	1.2	40	103.5	21.0	825	4.6	105.2	3789
3.0	1.5	40	106.0	20.5	878	4.8	110.0	5808

^a Oxalic acid catalyst was added in two batches: part A was added in the liquefaction stage and part B was added together with formalin just before the cocondensation reaction. The value "0.0" in column A means that the liquefied mixture was completely neutralized before the addition of part B.

^b The amount of combined phenol in the phenolated wood.

^c PW content means the phenolated wood content in the cocondensed resin.

Table VI Number Average Molecular Weights (M_n), Polydispersities (M_w/M_n), and Thermofluidities of the Cocondensed Resins Prepared at a Fixed Oxalic Acid Concentration of 2.5%

PW Content ^a (%)	Combined Phenol ^b (%)	M_n	M_w/M_n	Flow Temperature (°C)	Melt Viscosity (Poise)
Novolac, HP-700	—	872	5.2	89.9	270
PW resin ^c	43	505	3.5	105.0	3789
26.3	38	502	4.3	85.0	285
20.8	39	518	4.1	89.0	414
19.6	45	585	4.0	90.5	522
17.9	42	519	4.3	89.8	455

^a PW content means the phenolated wood content in the cocondensed resin.

^b The amount of combined phenol in the phenolated wood.

^c A pure phenolated wood resin prepared by the oxalic acid catalyzed method.

phenolated wood components and PF resin fragments can markedly interact with each other and their ratio is not critical to obtain the excellent properties within our experimental range.

In addition, from Table I, it can be found that in the case of the oxalic acid catalyzed method, the percent residue is relatively high compared with that of the phosphoric acid catalyzed method. Therefore, an attempt was made to use the residues as fillers for molded products. The results (shown in Table VII) indicate that the flexural strength and toughness of such molded products are close to those of the molded products filled with wood powder, while the flexural modulus of the former is much higher than that of the latter. This result could be attributed to the fact that oxalic acid is too weak for the rapid as well as complete destruction of cellulose during liquefaction; as a result, the cellulose fibers remain in the residues, and can be used again as

fillers without sacrificing the properties of the resulting molded products.

CONCLUSION

The cocondensation reaction occurring among phenolated wood, phenol, and formaldehyde after the liquefaction stage has been found to be a novel technique not only for converting the nonreacted phenol into resin, but also for obtaining an excellent wood-based novolac resin. When phosphoric acid was used as catalyst, the acidity in the liquefied mixtures after liquefaction reaction was strong enough for the following cocondensation reaction. The conversion rate of the phenol to resin was comparable to that of the industrial yield of the novolac resin regardless of the nature of the catalysts and the presence of phenolated wood components. The

Table VII Flexural Properties of the Molded Specimens Made from the Cocondensed Resins Prepared Using Oxalic Acid as a Catalyst

PW Content ^a (%)	Combined Phenol ^b (%)	Flexural Strength (MPa)	Flexural Modulus (MPa)	Flexural Toughness (MPa × 10 ²)
Novolac, HP-700	—	96.0	8012	58.0
PW resin ^c	43	49.7	8471	14.5
26.3	38	103.6	8382	64.5
20.8	39	99.9 ^d	10142 ^d	55 ^d
19.6	45	104.0	7965	68.2
17.9	42	103.5	8135	65.4
		103.9	8043	67.0

^a PW stands for phenolated wood.

^b The amount of combined phenol in the phenolated wood.

^c A pure phenolated wood prepared by the oxalic acid catalyzed method.

^d Residues from the liquefaction reaction were used as the fillers in the molded specimens.

resulting cocondensed resins showed thermofluidities as good as those of the commercial novolac resin. The mechanical properties of the molded products prepared from these cocondensed resins were not only much better than those of the phenolated wood resins, but also somewhat superior to those of the commercial novolac resin. Although oxalic acid is a weak catalyst compared with phosphoric acid, the remaining residues could be used as the fillers for molded products without sacrificing their mechanical properties.

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