

Water-Resistant Plywood Adhesives Prepared from Phenolated Larch Bark in the Presence of Various Combination Catalysts

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ABSTRACT: The properties of larch barks phenolated with various combinations of acidic catalysts and the properties of adhesives synthesized with these phenolated barks have been investigated. The results have indicated that the catalyst species used has great effects on bark phenolation and many properties of the resultant bark adhesives (BA). High-performance liquid chromatography (HPLC) and Gel permeation chromatography (GPC) analyses have indicated that the amount of phenol bound to the bark and recondensation of phenolated components decreased with decreasing acidity of the combination catalysts used, resulting in decreases in the extent of phenolation, bound phenol content, and molecular weight but an increase in the number of active

sites on the phenolated bark. Larch bark phenolated with combined catalysts can be used to prepare water-resistant wood adhesives with low formaldehyde emission. By judiciously decreasing the acidity of the catalyst used for bark phenolation, the properties of BA, such as storage life, bond strength, and formaldehyde emission, could be effectively improved. BA-C showed the acceptable wet bond strength and a sufficiently low formaldehyde emission, making it a good potential candidate for commercial applications. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: adhesives; synthesis; catalysts; curing of polymers; mechanical properties; biomaterials

INTRODUCTION

Ever-increasing attention is being given to obtaining chemical resources from bio-based materials due to the decrease in availability of nonrenewable fossil resources. Therefore, many countries have focused on R&D in bio-based industries to obtain biomass energy, chemical resources, and materials or to create substitutes for petroleum-based materials to the greatest possible extent.

The technology of phenol liquefaction (or phenolation) in the presence of an acidic catalyst has been developed for more than a decade.¹ By this approach, some infusible and insoluble bio-based materials can be converted into fusible and soluble products that can be used to prepare some bio-based

polymers, such as adhesives, plastics, and foams. A variety of liquefied bio-based materials, such as cellulose,^{1,2} lignin,^{3,4} tannin,^{5,6} wood,^{7–9} corn bran,¹⁰ starch,¹¹ barks,^{12–14} bamboo,¹⁵ and waste paper,¹⁶ have been characterized and investigated with regard to the preparation of phenolic resins or polyurethane foams by reactions of the liquefied derivatives with formaldehyde or isocyanate.

Bark is an abundant and renewable bio-based material and is estimated to make up 15–20% of a tree by volume and 10–15% by mass.^{17,18} However, bark is underutilized around the world because of its heterogeneous structure and diverse chemical composition. The properties and chemical components of bark are highly variable and depend on tree species, tree age, climatic growth conditions, and growth site. As a result, most bark is abandoned or disposed by burning, and only some types of bark containing abundant tannins have been utilized in the past, most commonly the bark from pine, spruce, and wattle.^{19,20}

The uses of the resource of whole bark have been studied in the past decade. Alma and Kelley⁷ converted the whole barks of six different tree species into bakelite-like thermosetting materials by phenolation in the presence of sulfuric acid as a catalyst. These authors found that the properties of phenolated bark-based moldings (excluding those made

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from one particular species, acacia bark) were similar to those of commercial novolak resin-based moldings. Santana et al.¹⁹ prepared a bark-phenol-formaldehyde (BPF) resin using the bark of black wattle liquefied in phenol and reported that the BPF resin was comparable to a commercial phenol-formaldehyde (PF) resin in terms of the bonding properties of southern pine plywood. Lee and Liu²¹ observed that the catalyst used for bark liquefaction had a significant effect on the properties of liquefied barks and BPF resins. Gao and Yuan^{13,14} reported some new synthetic technologies for preparing environmentally safe and water-resistant BPF adhesives using phenolated whole larch bark.

Compared to phenol liquefaction without an acidic catalyst, lignocellulosic phenolation in the presence of an acidic catalyst gives high conversion and high yields of liquefaction products under conditions of low liquefaction temperature (100–150°C) and atmospheric pressure and therefore at lower operational cost.¹ In the references regarding lignocellulosic phenolation cited above, the acidic catalysts were most commonly sulfuric acid, or else hydrochloric acid or phosphoric acid, with these being used alone. Combinations of acidic catalysts for lignocellulosic liquefaction, however, have seldom been examined. In addition, larch forests are particularly extensive in eastern Siberia and the mountains of northeastern Asia.²² Large quantity of larch bark is produced in sawing plants every year but most of them is abandoned or disposed of by burning, resulting in the waste of abundant biomass resources and the environmental pollution. Therefore, with the attempt to find an effective utilization of the abundant larch bark with good value added, the objectives of this study have been to investigate the effects of combinations of acidic catalysts on the phenolation of larch bark and the properties of wood adhesives synthesized with the phenolated larch barks.

METHODS

Experimental materials

Fresh bark from larch trees (*Larix gmelinii*), obtained from a local tree farm, was ground into particles with diameters ranging from 0.42 to 1.00 mm and dried to moisture content below 5%. The chemicals used in this study, such as phenol, sulfuric acid, phosphoric acid, hydrochloric acid, sodium hydroxide, formaldehyde solution (36.8 w/w %), etc., were purchased from local chemical companies and used without further treatments. Birch veneers of dimensions 420 × 420 mm² (1.6 mm in thickness) were obtained from a plywood plant. The veneers were dried to moisture contents of about 2.5%.

Phenolation of larch bark

Phenol (500 g) and acidic catalyst (20 g) were placed in a four-necked flask and heated under stirring. Once the temperature reached 130°C, larch bark (200 g in total) was gradually loaded into the flask. After all of the bark had been loaded, a further 5 g of acidic catalyst was added, and the mixture was kept at 135–145°C for 90 min. The phenolated bark was then cooled and sampled for characterization.

Extent of phenolation

According to the reported test procedures,¹⁹ the extent of bark phenolation was determined as follows. About 15 g of phenolated bark (W_1 , accurate to 0.0001 g) was dissolved by stirring in acetone (100 mL). The mixture was filtered through an oven-dried glass-fiber filter (Whatman GF/C, Whatman) that was oven dried in advance and had mass W_2 . The residue on the filter was rinsed with acetone (2 × 50 mL), dried at 85°C for 24 h, and weighed (W_3 , accurate to 0.0001 g). The extent of phenolation was calculated according to $100\% - (W_3 - W_2)/(W_1 \times 27.6\%) \times 100\%$, where 27.6% corresponds to the bark content of phenolated bark calculated from the amounts of bark, phenol, and acidic catalyst added before phenolation.

Bound phenol content of phenolated bark by HPLC

The free phenol content (P_f) of each phenolated bark was measured by HPLC on an Agilent 1100 apparatus equipped with a C18 alkaline column. Each phenolated bark sample for HPLC measurement was dissolved in 20% NaOH solution at room temperature by stirring for 10 min, diluted to a concentration of 0.5% using distilled water, and the pH of the solution was adjusted to 10.5. Water was used as the mobile phase at a flow rate of 1.0 mL min⁻¹. The wavelength of the UV detector was set at 270 nm. A series of phenol solutions of known concentrations (0.1, 0.2, 0.3, 0.4, 0.5, and 0.6%, pH also adjusted to 10.5) were used as standards to calculate the free phenol content. The bound phenol content was calculated according to $(P_t - P_f)/P_t \times 100\%$, where P_t refers to the total phenol content of the phenolated bark based on the amounts of bark, phenol, and acidic catalyst added before phenolation.

Formaldehyde reactivity of phenolated bark

A 500-mL reaction kettle equipped with a mechanical stirrer, a thermostat, and a condenser for reflux was charged with phenolated bark (18 g; W_4 , accurate to 0.0001 g), 50 w/w % NaOH solution (2 g), 36.86 w/w % formaldehyde solution (30 g), and

distilled water (150 g), and then kept at $60 \pm 2^\circ\text{C}$ for 120 min. Thereafter, the reaction mixture was allowed to cool to room temperature and filtered through a glass-fiber filter (rinsed with distilled water, 2×50 mL). The filtrate was diluted to 1000 mL in a volumetric flask. The free formaldehyde content in the diluted filtrate (F_1 , mg L^{-1}) was tested according to the method described in a technical bulletin "Test method for free formaldehyde" issued in April 1994 by the Structure Board Association (SBA) of Canada, as follows: (1) after weighed about 2 g diluted filtrate (W_5 , accurate to 0.001 g) into a 250-mL beaker, 100 mL of distilled water and a magnetic spin bar were added; (2) the beaker was put on magnetic stirrer and the stirrer started; (3) the pH value of mixture solution in beaker was adjusted to 4.0 with 0.1 and 1 mol L^{-1} hydrochloride solution; (4) 10 mL of 7 wt % hydroxylamine hydrochloride solution that was adjusted to a pH of 4.0 in advance was added into breaker and the mixture was stirred for 5 min; (5) the pH of the mixture was titrated to 4.0 with V mL of 0.05 mol L^{-1} NaOH solution; and (6) the free formaldehyde content was calculated according to $F_1 = 0.05 \times V \times 30.03 \times 1000 / (W_5 / 0.999)$ (mg L^{-1}), where the 0.999 refers to the density of diluted filtrate (g mL^{-1}) at the ambient temperature. Three replicate blank tests were conducted under the same conditions without phenolated bark, giving the total free formaldehyde content (F_0 , mg L^{-1}) before reaction. Formaldehyde reactivity (mg g^{-1}) of the liquefied bark was defined as the equivalent solid formaldehyde mass (mg) that can react with 1 g of phenolated bark and calculated according to $(F_0 - F_1) / W_4$.

Gel-permeation chromatography (GPC) characterization

The molecular weight (MW) distribution of each phenolated bark and adhesive were measured by GPC on an Agilent 1100 apparatus using two chromatographic columns in series, namely a 79911GF-083 (MW range: 100–30,000) and a 79911GF-084 (MW range: 10,000–200,000). Each GPC sample was diluted with water to a concentration of 0.5% by weight. The mobile phase was water with a flow rate of 1 mL min^{-1} . The pressure on the columns was 78 psi. A differential refractive index detector was used. The GPC was calibrated with 10 polyethylene glycols produced by Polymer Laboratories. The molecular weights of these polyethylene glycols were 106, 194, 400, 620, 1010, 1900, 4020, 6450, 11,840, and 22,450. The distribution indices of the standard polymers ranged from 1.0 to 1.05.

Adhesive synthesis

Five batches of bark adhesive (BA) were synthesized as follows: (1) the phenolated bark, formaldehyde,

and a first batch of NaOH were loaded into a four-necked flask equipped with a stirrer, a condenser, and a thermometer, and the mixture was heated at $65 \pm 2^\circ\text{C}$ for 80 min; (2) the mixture was then heated at $90 \pm 2^\circ\text{C}$ for 30 min; (3) a first batch of water and a second batch of NaOH were added, and the mixture was kept at $70\text{--}85^\circ\text{C}$ until its viscosity reached 3500–4500 mPa s ; and (4) a second batch of water was added, and the mixture was kept at $70\text{--}85^\circ\text{C}$ until the target viscosity (1000–1300 mPa s) was reached. The final BA could be fully dissolved in water without leaving a deposit. All of the BA were prepared with a formaldehyde/phenolated bark weight ratio of 0.53 (solid basis), and the amounts of NaOH added in the first and second charges were 4.5 and 20.5%, respectively, of the phenolated bark loaded by weight (solid basis). The first portion of NaOH was added not only to neutralize the remaining acidic catalysts in the liquefied bark but also to adjust the pH of the mixture to the range 9.0–10, as the addition reaction of formaldehyde to the phenolic components is favored under alkaline conditions.

To evaluate the properties of the BA, a commercial PF adhesive was selected as a control (denoted as PF). It was prepared in the same way as adhesive R1 in a previous study¹³ with a NaOH/phenol weight ratio of 0.29 (solid/solid) and a formaldehyde/phenol weight ratio of 0.67 (solid/solid).

pH, viscosity, solid content, and storage of the adhesives

After synthesis for 24 h, each adhesive was kept in a thermostatted bath at 25°C for half-an-hour before being tested for pH and for viscosity. About 250 mL of thermostatted adhesive sample (25°C) was put in a 300-mL beaker for testing viscosity using a Brookfield rotational viscometer (DV-II Pro) and No. 2 spindle at appropriate rotation rate (12, 30, or 60 rpm). The spindle was rotated in each adhesive sample for exact 60 s before reading the viscosity. The solid content was obtained by measuring the masses before and after oven drying of an adhesive sample of about 2 g (accurate to 0.0001 g) at 120°C for 3 h. After synthesis, each adhesive was kept under ambient conditions, with the temperature ranging from 22 to 30°C , for storage evaluation by monitoring the viscosity at different intervals.

Differential scanning calorimetry (DSC) characterization of the adhesives

About 15 mg of each BA sample or PF sample was placed in a 100- μL high-pressure chrome-nickel steel crucible with a gold-plated surface. The crucible was sealed with gold sealing disc capable of maintaining

TABLE I
Properties of Phenolated Larch Bark

ID	Catalyst (ratio by weight)	Extent of phenolation (%)	Bound phenol content (%)	Formaldehyde reactivity (mg g ⁻¹)	M _n
A	S only	97.3	27.3	642	3780
B	S : P = 4 : 1	95.4	24.8	664	3463
C	S : P = 1 : 1	90.4	20.0	705	3088
D	S : P = 1 : 2	86.9	16.2	689	3119

S denotes sulfuric acid, P is phosphoric acid, and M_n is number-averaged molecular weight.

a 100-bar internal pressure at the maximum temperature of 500°C during DSC scanning. The sealed crucible containing the sample was then scanned by means of a NETZSCH DSC242 apparatus from room temperature to 300°C at heating rates of 2.5, 5, 7.5, 10, and 15°C min⁻¹ (under air atmosphere). The activation energy and the pre-exponential factor were calculated according to the Kissinger equation [eq. (1)] by plotting $-\ln(\beta/T_p^2)$ against $1/T_p$.

$$-\ln\left(\frac{\beta}{T_p^2}\right) = \frac{E_a}{RT_p} - \ln\left(\frac{ZR}{E_a}\right) \quad (1)$$

where β denotes the heating rate (°C min⁻¹), E_a is the activation energy (kJ mol⁻¹), R is the gas constant (8.314 J mol⁻¹ K⁻¹), T_p is the peak temperature (absolute temperature, K), and Z is the pre-exponential factor (s⁻¹).

Plywood bond evaluation

Birch (*Betula platyphylla*) veneers were laminated into 3-ply plywood panels with dimensional size of 420 × 420 mm². The adhesive without additive was brushed by hand to the two face veneers at a spread rate of 360 g m⁻² in a double glue line. After spreading the adhesive, the veneers were immediately assembled into panels. Each panel was subjected to a prepressure of 0.8 MPa at room temperature for 5 min, and then hot-pressed at 130°C and 1.2 MPa for 4.5 min. Three replicate panels were manufactured with each adhesive, which were sealed in independent PE plastic bags after cooling.

After the panels had been stored at room temperature for 24 h, specimens were cut from them to determine the wet-state bond strength and formaldehyde emission. Ten specimens were cut from each panel for wet-state bond strength tests, according to JIS K6806-2004 standard, after subjecting them to boiling in water for 4 h, drying at 60°C for 20 h, and further steady boiling in water for 4 h. Ten specimens with dimensional size of 50 × 150 mm² were also cut from each panel to determine the formaldehyde emission according to JIS A1460-2003 standard

as follows: ten specimens were placed in a support in a sealed glass desiccator with diameter of 240 mm for 24 h at 20°C, during which the emitted formaldehyde would be absorbed in 300 mL of distilled water that was put on the bottom of desiccator; the concentration of formaldehyde absorbed in distilled water was determined by ultraviolet spectroscopy based on the Hantzsch reaction.

RESULTS AND DISCUSSION

Properties of phenolated bark obtained in the presence of various combined catalysts

Table I summarizes some properties of phenolated larch barks obtained in the presence of various acidic catalysts, the acidities of which decreased on going from A to D. The extent and efficiency of phenolation is indicated by the proportion of the bark dissolved in phenol after phenolation at 135–145°C for 90 min at atmospheric pressure. The products obtained with catalysts A to D had extents of phenolation ranging from 86.9 to 97.3%. Product A with sulfuric acid as the sole catalyst showed the highest extent, 97.3%. This indicated that sulfuric acid was most effective in catalyzing bark phenolation due to its highest acidity among all of the catalysts. Lee and Liu²¹ confirmed that phenolation with a strong acid can promote the degradation of lignocellulose and reduce its molecular weight, thus facilitating its combination with phenol and assisting bark liquefaction. This provides a rationale for the gradual decrease in the extent of phenolation for the products from catalysts A to D, considering the lower acidity of phosphoric acid and the decrease of sulfuric acid content in the catalyst.

The bound phenol contents of the phenolated barks obtained in the presence of the various catalysts were in the range 16.2–27.3%, which were well correlated with the extents of phenolation, as presented in Figure 1. The correlation indicated that phenol bound to the bark was the prerequisite for bark liquefaction. Ono and Inoue²³ concluded that during the phenolation of bark in the presence of an acidic catalyst, phenol was bound to the bark

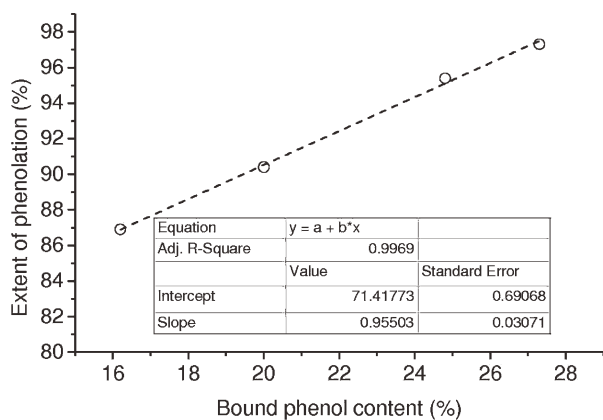


Figure 1 Correlation between extent of phenolation and bound phenol content.

material with concomitant degradation of the macromolecules, which led to dissolution of the bark in phenol and conversion into dark fusible and soluble products. The variations in bound phenol content with the catalyst species used, as indicated in Table I, also confirmed that the bark phenolation was highly dependent on the catalyst species, essentially the acidity of the catalyst that promoted the bonding of phenol to the bark materials. The binding modes of the bound phenol were derived from 1,2-substitution and/or 1,4-substitution reactions.¹

However, strong acid may also cause the recondensation of phenolated products and increase the molecular weight.²¹ The existence of such higher-molecular-weight components derived from recondensation was clearly evidenced by the GPC analysis in Figure 2. A total of six peaks could be detected in the GPC traces of the phenolated barks, with number-averaged molecular weights (M_n) around 11200, 3600, 1600, 930, 430, and 255, respectively (from left to right). Among them, the peak corresponding to M_n 3600 was the predominant feature, with a peak area accounting for 40.3–58.4% of the total. It is well known that the peak area ratio in a given GPC trace indicates the relative amounts of molecules having the molecular weights associated with the peaks. For the products obtained using catalysts A to D, the sulfuric acid contents of which were sequentially lower, the peak area ratios of the predominant peak decreased accordingly due to less recondensation under the less acidic conditions.

When a mixture of phenolated bark (18 g), 50 w/w % NaOH solution (2 g), 36.86 w/w % formaldehyde solution (30 g), and distilled water (150 g) was kept at $60 \pm 2^\circ\text{C}$ for 120 min during a formaldehyde reactivity test, the formaldehyde and phenolated bark mainly underwent an addition reaction, without condensation polymerization. This was because of the very weakly alkaline conditions (pH 9.4–9.7) and the low reaction temperature. Therefore, the

formaldehyde reactivity represented the number of active sites on the phenolated bark capable of addition reaction with formaldehyde. This was confirmed by carrying out a control test in which a mixture of phenol (12.7 g), 50 w/w % NaOH solution (1.2 g), 36.86 w/w % formaldehyde solution (30 g), and distilled water (150 g) was kept at $60 \pm 2^\circ\text{C}$ for 120 min (pH 9.5), which indicated a formaldehyde reactivity of 951 mg g^{-1} , i.e., 1 g of phenol consumed 951 mg of solid formaldehyde (equivalent to 2.98 active sites per phenol molecule).

The formaldehyde reactivities of phenolated barks obtained in the presence of various catalysts ranged from 642 to 705 mg g^{-1} , implying an effect of the catalyst species on the reactivity of the phenolated products. If the formaldehyde reactivity stems only from the phenol, and phenol is not bound to the bark at all during phenolation, the ideal value of formaldehyde reactivity would be 661 mg g^{-1} according to the charges of phenol, bark, and catalyst before phenolation. The test results in Table I indicate that the all products obtained with combination catalysts had formaldehyde reactivities higher than 661 mg g^{-1} , implying that the phenolation with these lower-acidic combination catalysts could add active sites. This might be attributed to recondensations of phenolated components and the bonding of phenol to bark via 1,2-substitution and/or 1,4-substitution reactions, which would consume many active sites. Recondensation would increase the number-averaged molecular weight (M_n) of phenolated bark products. Product A, obtained using sulfuric acid with the strongest acidity as catalyst, showed the highest extent of phenolation and M_n but the lowest formaldehyde reactivity. However, product D, obtained using S : P = 1 : 2 as the catalyst with the lowest acidity, did not show the highest formaldehyde reactivity or the lowest molecular weight. This indicated that the acidity of the catalyst had an

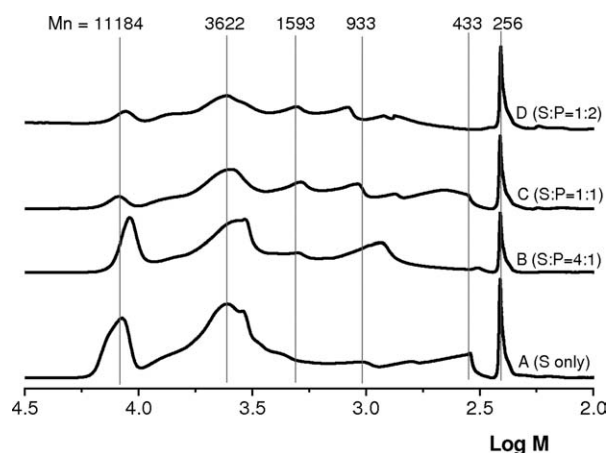


Figure 2 GPC traces of phenolated barks obtained with various catalysts.

TABLE II
Basic Properties of Bark Adhesives

ID	Catalyst species	Solid content (%)	pH Value	Viscosity, (mPa s)	Storage life (day)
PF	–	40.3	12.0	1250	>60
BA-A	S only	37.4	11.7	2525	7
BA-B	S : P = 4 : 1	38.4	11.6	1950	16
BA-C	S : P = 1 : 1	38.8	11.6	1050	22
BA-D	S : P = 1 : 2	38.1	11.4	1020	29

important but not an overriding effect on the formaldehyde reactivity and molecular weight of the phenolated products, due to very complicated phenolating mechanisms involving competing degradation reactions of bark, substitution reactions of phenol, and recondensation of phenolated components.

Basic properties of bark adhesives

Some basic properties, namely the solid content, initial viscosity, pH, and storage life of BA and PF adhesive are presented in Table II. The solid contents of all of the BA adhesives ranged from 37.4 to 38.9%, which were similar to but slightly lower than the solid contents of the control, PF adhesive (40.3%). The pH values of the adhesives were quite similar, in the range 11.4–12.0, because they had the same formulations apart from the catalyst species used for bark phenolation. Specifically, the pH values of the BA (11.4–11.7) were a little lower than that of the PF adhesive (12.0), which could be attributed to the neutralization of NaOH by the acidic catalysts in the phenolated barks during synthesis of the adhesives. The (initial) viscosities of adhesives tested within 24 h of synthesis should range from 1000 to 1300 mPa s because of the same target viscosity at the end of each adhesive synthesis. However, the adhesives BA-A and BA-B, prepared with

barks phenolated with catalysts A and B, respectively, as indicated in Table I, had much higher viscosities (2525 and 1950 mPa s) because they were very active, as evidenced by the viscosity traces in Figure 3, and had lower peak curing temperatures at the same heating rate, as indicated by the DSC results in Table III.

The storage life is essentially related to the period of time during which an adhesive increases its molecular weight from the initial to an infinite level (loss of fluidity) by building up chain lengths and forming crosslinks between the chains. The activity and molecular weight of an adhesive determines its storage life; in general, the greater the activity and the higher the molecular weight of an adhesive, the shorter its storage life will be. Commercial PF adhesive has a storage life of more than 60 days, while the present BA exhibited storage lives ranging from 7 to 29 days, as shown in Table II. The viscosity of the BA increased more rapidly than that of PF, as shown in Figure 3; the order of increase was the same as that of the acidity of the catalysts. The results indicated that the catalyst species used for bark phenolation, or more specifically the acidity of the catalyst, had great effects on the storage life and activity of the resultant BA. It has been confirmed that bark phenolated in the presence of catalysts with stronger acidity resulted in fewer active sites (i.e., lower formaldehyde reactivity in Table I) and more higher-molecular-weight components (as shown by the GPC spectra in Fig. 2). During synthesis of the adhesive, the higher-molecular-weight components led to the formation of adhesive molecules with much higher molecular weight, as confirmed by the GPC spectra of BA in Figure 4. The fewer active sites of the phenolate bark resulted in a higher reaction ratio of formaldehyde/phenolated bark, and therefore, the BA had more crosslinks as formaldehyde acted as a crosslinker during the synthesis. These features led to shorter storage and higher activity of the adhesive owing to the quicker increase of molecular weight and crosslinking density. For example, adhesive BA-A had the shortest storage life (7 days) because of the fewest active sites and the greatest amount of higher-molecular-weight

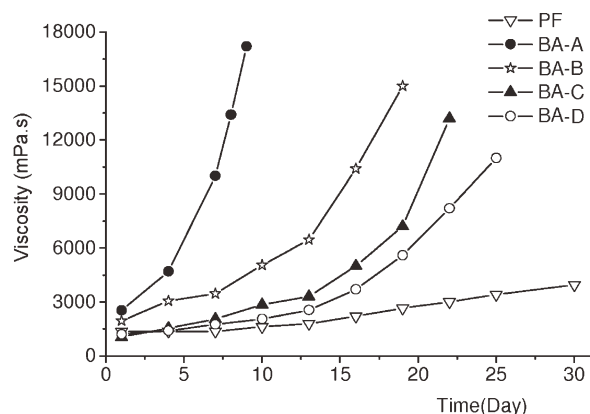


Figure 3 Viscosity tracing of bark adhesives and PF adhesive.

TABLE III
DSC Results for Bark Adhesives and PF Adhesive

Resin ID	T_p at various heating rates ($^{\circ}\text{C}$)					E_a (kJ mol^{-1})	Z (s^{-1})	Fitting coefficient, R^2
	2.5 ($^{\circ}\text{C min}^{-1}$)	5 ($^{\circ}\text{C min}^{-1}$)	7.5 ($^{\circ}\text{C min}^{-1}$)	10 ($^{\circ}\text{C min}^{-1}$)	15 ($^{\circ}\text{C min}^{-1}$)			
PF	135.2	143.2	150.8	154.5	163.5	86.40	1.91×10^{10}	0.9945
BA-A	106.0	114.0	118.4	122.1	130.1	89.77	4.66×10^{11}	0.9925
BA-B	126.8	135.6	140.8	148.8	155.3	80.17	4.91×10^9	0.9902
BA-C	128.5	137.8	144.0	149.1	160.3	75.31	9.66×10^8	0.9875
BA-D	129.2	139.7	145.1	147.9	158.1	85.26	1.92×10^{10}	0.9914

components in the phenolated bark. Conversely, adhesive BA-D had a much longer storage life (29 days) owing to more active sites and a smaller amount of higher-molecular-weight components.

Curing properties of the bark adhesives

DSC results obtained for the various BA and their kinetic analyses are summarized in Table III. The curing peak of each DSC curve illustrated in Figure 5 was correlated to the crosslinking reaction of BA because there was only one peak detected by the DSC when the liquid adhesive was cured and turned into rigid and insoluble solid. A higher peak temperature at the same heating rate means a lower curing rate as more heat or energy is needed to crosslink the adhesive. At the same heating rate, the peak temperature for PF adhesive curing was higher than those for all of the BA (as shown in Table III), indicating that the BA were cured more rapidly because the molecular weights of BA were higher than that of PF adhesive as indicated by the GPC spectra in Figure 4. In general, the peak temperatures of the BA increased with increasing acidity of

the catalyst for bark phenolation because stronger acidity of the catalysts resulted in fewer active sites and more higher-molecular-weight components of the phenolated barks that were confirmed by the formaldehyde reactivities in Table I and the GPC spectra in Figure 2, respectively.

Activation energy is frequently used as a reference in evaluating adhesive curing behavior because activation energy is the energy barrier that the reactants must overcome in order for a chemical reaction to occur. However, activation energy alone does not reveal the whole picture of the curing characteristics of BA. For example, the peak temperatures of adhesive BA-A were $12.5\text{--}30.5^{\circ}\text{C}$ lower than those of adhesive BA-C, but the activation energy of BA-A ($89.77 \text{ kJ mol}^{-1}$) was larger than that of BA-C ($75.31 \text{ kJ mol}^{-1}$). According to the well-known Arrhenius equation, shown as eq. (2), the rate constant of BA curing is determined by both the activation energy and the pre-exponential factor. According to collision theory, the pre-exponential factor is equivalent to the total number of successful collisions that result in a reaction; these successful collisions occur because of reactant particles coming sufficiently into contact with each other. Collision theory also indicates that the number of successful collisions is defined by both temperature and the characteristics of the reactant particles. The DSC results in Table III indicate that each BA had different rates of successful collisions due to differences in the nature and amount of chemical components of the phenolated barks in the presence of the various catalysts, thus leading to distinct peak temperatures and activation energies.

$$k = Z \cdot \exp(-E_a/RT) \quad (2)$$

where k denotes the rate constant of a chemical reaction, Z is the pre-exponential factor or Arrhenius frequency factor, E_a is the activation energy, R is the gas constant, and T is the absolute temperature at which the reaction is taking place.

In this case, the pre-exponential factor (Z) should be taken into consideration. The line for BA-D shows

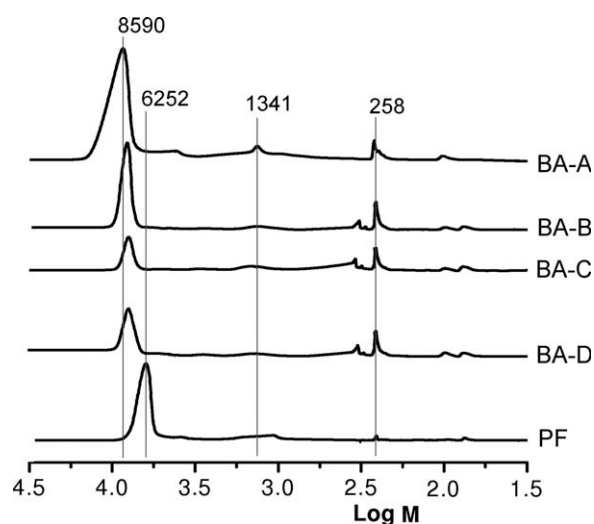


Figure 4 GPC spectra of bark adhesives and PF adhesive.

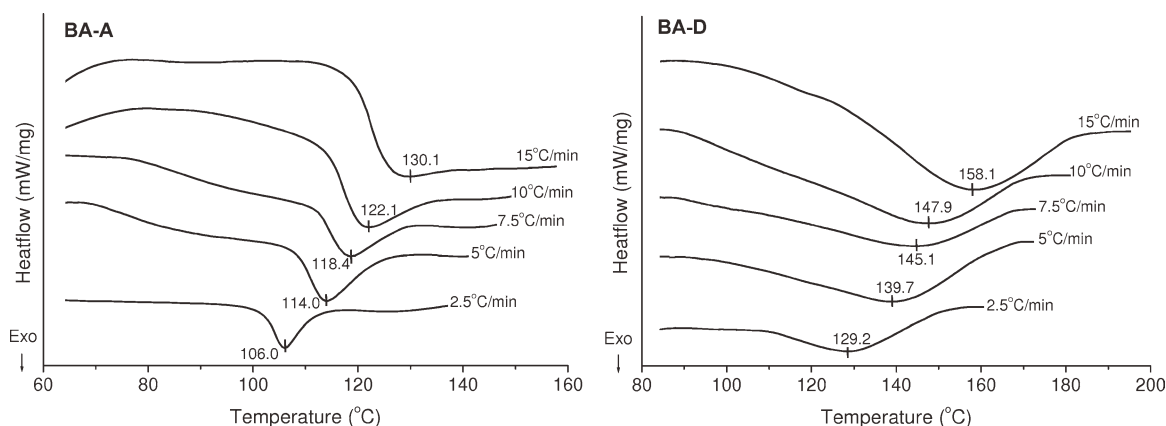


Figure 5 DSC curves of bark adhesives BA-A and BA-D.

a smaller intercept than the line for BA-A (14.44 versus 17.58) as shown in Figure 6, resulting in a lower Z value (1.92×10^{10} versus $4.66 \times 10^{11} \text{ s}^{-1}$), based on eq. (1). According to collision theory, the lower Z value of BA-D indicated that it had greater collision hindrance for curing. As a result, a higher temperature was needed to ensure enough successful collisions.

Bond properties and safety of bark adhesives

Wet bond strength and free-formaldehyde release were evaluated for plywood panels bonded with the four BA and the PF control. The test results are presented in Table IV. The wet bond strengths, as well as the bond durabilities, were evaluated after the plywood specimens had been subjected to a 28-h boiling–drying–boiling cycle. The control PF adhesive yielded the highest wet bond strength (1.58 MPa) among all of the prepared plywood panels. The BA yielded plywood panels with wet bond strengths ranging from 1.37 to 0.97 MPa. BA-C showed the highest wet bond strength (1.37 MPa), which could be attributed to the higher formalde-

hyde reactivity (705 mg g^{-1}), or more active sites on the phenolated bark using a combined catalyst of sulfuric acid : phosphoric acid = 1 : 1. More active sites could react with more formaldehyde, thereby resulting in a higher crosslinking density of the adhesive after curing. The lower formaldehyde emission indirectly confirmed this. Similarly, the plywood panel bonded with BA-A had the lowest wet bond strength (0.97 MPa) and the highest formaldehyde emission (0.717 mg L^{-1}) because of the lowest formaldehyde reactivity (642 mg g^{-1}). The percentage of wood failure also followed a similar trend to that observed for wet bond strength. The bond strength and wood failure are believed to correlate to the penetration of adhesives in the porous network of wood.^{24–26} The sufficient penetration of adhesives can repair the damaged cracks and cell cavities of wood that are considered as defects, and therefore, stresses can be more effectively distributed within a larger interphase region, resulting in improved bond strength and durability and higher wood failure.^{26,27} Both the bond strength and wood failures of BA-bonded plywood panels were lower than that of panels bonded by PF adhesive. This should be attributed to the larger molecular weights of BA, as shown by GPC spectra in Figure 4, which prevented the BA from effectively penetrating in the porous network of wood. However, BA-B, BA-C, and BA-D produced plywood panels with good bond strengths and bond durability that exceeded the required value (0.98 MPa) for structural uses according to JIS K6806-2003 standard. Their formaldehyde emissions were very low, ranging from 0.239 to 0.441 mg L^{-1} , which were smaller than the value required (0.5 mg L^{-1}) for Grade FC_0 plywood according to JAS JPIC-EW.SE00-01 standard. In other words, BA-B, BA-C, and BA-D were water-resistant and low formaldehyde-released. BA-C had the best wet bond strength and a sufficiently low formaldehyde emission, making it a good potential candidate for commercial applications.

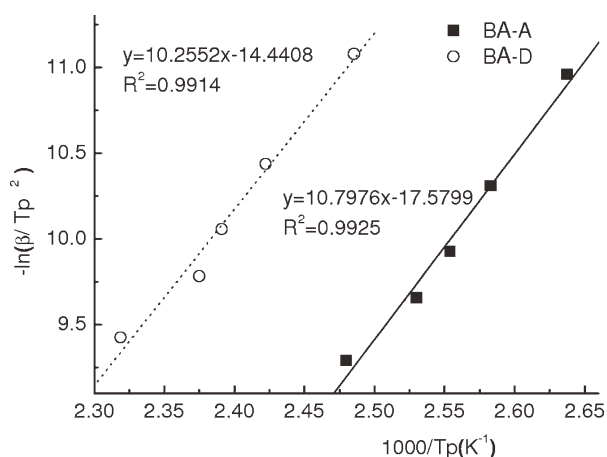


Figure 6 Kissinger plots for bark adhesives BA-A and BA-D.

TABLE IV
Properties of Plywood Panels Manufactured with PF and Bark Adhesives

Resin ID	PF	BA-A	BA-B	BA-C	BA-D	Required value
Wet bond strength (MPa)	1.58 (0.11)	0.97 (0.13)	1.25 (0.28)	1.37 (0.21)	1.20 (0.14)	>0.98
Wood failure (%)	90	45	60	85	50	>50
Formaldehyde emission (mg L ⁻¹)	0.104	0.717	0.441	0.256	0.239	<0.5

The numbers in parentheses are standard deviations; standard values of wet bond strength and wood failure are specified in JIS K6806-2003 standard; standard value of formaldehyde emission is specified in JAS JPIC-EW. SE00-01 standard.

CONCLUSIONS

Catalyst species have been shown to have great effects on the properties of phenolated larch barks and many properties of wood adhesives prepared with these phenolated barks. With decreasing sulfuric acid content of the combined catalysts, the extent of phenolation, the bound phenol content, and the molecular weight of the phenolated larch bark decreased, but formaldehyde reactivity increased. With decreasing acidity of the catalyst, the storage life of the BA apparently increased, and the formaldehyde emission of BA-bonded plywood panels gradually decreased while the wet bond strength initially increased and then decreased. Though the BA exhibit the desirable wood binder properties, further works are expected in order to develop a commercially viable wood adhesive.

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