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# Characterization of phenol–formaldehyde resins derived from liquefied lodgepole pine barks

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## ABSTRACT

In this study, lodgepole pine (*Pinus contorta* Dougl.) barks with and without infestation by mountain pine beetle (MPB, *Dendroctonus ponderosae* Hopkins) were liquefied in phenol with sulfuric acid. The liquefied portions of the bark were used to synthesize bark-derived phenol–formaldehyde (BPF) adhesive resins under alkaline conditions. In comparison to a commercial phenol–formaldehyde (PF) resin and a lab PF resin, the BPF resins were found to have larger average molecular weights, higher polydispersity indices and shorter gel times. The viscosities of the BPF resins were higher than the viscosity of the lab PF resin but lower than the viscosity of the commercial PF resin. Isothermal DSC tests indicated that all resins exhibited both *n*th-order and autocatalytic cure mechanisms. The post-curing thermal stability of the BPF resins was similar to that of the lab PF resin at higher temperatures but differed significantly from that of the commercial PF resin. All these resins had similar dry bonding strengths; the BPF resins showed the highest wet bonding strengths. Beetle infestation was shown to have no negative effect on the bonding properties of the BPF resins.

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## 1. Introduction

Bark is generally available in large quantities as waste residues from conversion of wood logs to various forest products. In mills, bark is usually mixed with other woody residues and used as hog fuel<sup>1</sup> for heat recovery. However, bark has a rather low heating value and its heating value drops sharply particularly when wet. Therefore, exploring other value-added, more cost- and energy-efficient uses for bark would be highly advantageous for the forest mills.

Bark has a similar chemical composition to wood except that it contains more extractives and phenolic compounds [1]. Previous research has shown that lignin and bark extractives, such as tannin, could partially replace 30–50% of petroleum derived phenol for synthesizing PF resins [2–7]. However, wood composites made using these types of adhesives have previously shown inconsistent and unsatisfactory performance due to the highly variable chemical structure of the lignin obtained through different origins and methods, as well as the low reactivity of lignin and flavonoids B-ring units within tannins. Chemical modification of lignin or tannin, such as liquefaction or phenolation,

was found to be able to effectively improve the reactivity and produce resins with more satisfactory performance [2–4,7].

Previous studies [4,8–11] have shown that bark can be successfully liquefied in the presence of phenol using an acid catalyst. The liquefied products can be subsequently converted to bark-derived phenol–formaldehyde (BPF) resins to be used for manufacturing plywood and particleboard. It was found that the mechanical properties of the wood composite products bonded with the BPF adhesives were comparable to those bonded with commercial PF resins. However, no studies have reported on the curing kinetics and curing behavior of BPF resins.

Recently, due to rampant mountain pine beetle (*D. ponderosae* Hopkins) infestation outbreaks in the western provinces of Canada, there is a large amount of beetle infested lodgepole pine (*P. contorta* Dougl.) resources which is available for utilization. Liquefaction of bark from the beetle-infested lodgepole pine and conversion of the liquefied bark to BPF resins as wood adhesives could be one of the attractive possibilities. However, the impact of beetle infestation on the suitability of bark as a raw material for resin synthesis is unknown.

In this study, lodgepole pine barks with and without the mountain pine beetle infestation were first liquefied in phenol using sulfuric acid as the catalyst. Without the need to remove any excess phenol, the liquefied bark mixtures were reacted with formaldehyde under alkaline conditions to give BPF resins, which were then tested and compared with a lab PF resin and a commercial PF resin.

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<sup>1</sup> Note: hog fuel: wood chips or shavings, residue from sawmills, etc., which is used for fuel, landfill, animal feed and surfacing paths and running tracks (<http://dictionary.reference.com/browse/hog+fuel>).

## 2. Experimental

### 2.1. Resin synthesis

Mountain pine beetle-infested lodgepole pine bark and non-infested lodgepole pine bark were first liquefied in phenol with the bark to phenol ratio of 1:3 using sulfuric acid as the catalyst (3% of phenol weight). The liquefaction reaction was conducted at 150 °C for 120 min. A calculated amount of the liquefied bark, 37% formaldehyde, and 40% sodium hydroxide (1/3 of total NaOH weight) were mixed in a three-neck flask. The reaction temperature was increased to 65 °C within 30 min and was kept at 65 °C for about 10 min, followed by the addition of the remaining 2/3 of NaOH. The reaction mixture was then heated to 85 °C and kept at 85 °C for 60 min. After the reaction, the system was cooled down to room temperature. The resulting resins were viscous liquid with dark color. The resins were subjected to various tests without further dehydration.

A lab PF resin without liquefied bark was prepared following exactly the same reaction steps used for the synthesis of BPF resins. All the chemicals were purchased from Caledon laboratory chemicals, Canada, and used without further purification. A commercial PF resin for the face layers of oriented strand board production was provided by FP-Innovations-Forintek Division for comparison.

### 2.2. Resin characterization

#### 2.2.1. pH, viscosity, solids content, gel time, $M_w$ and $M_w/M_n$ of the BPF resins

pH values of the resins were measured at 25 °C. The viscosity of the bark-derived resins was measured using a Brookfield rotary viscometer with spindle 3 at 25 °C. Solids content measurement was according to ASTM D 3529. Gel time was measured by charging 1 g of resin into a 16 mm wide test tube and heating the test tube in an oil bath at  $120 \pm 1$  °C. Gel time was defined as the time period from the immersion of the test tube into the oil bath to the beginning of the resin gelation (resin forming a string when a glass rod was lifted from the resin). An average value of three replicate measurements was reported.

Weight-average molecular weight ( $M_w$ ), number-average molecular weight ( $M_n$ ) and polydispersity ( $M_w/M_n$ ) were measured using the Matrix Assisted Laser Desorption/Ionization-Time of Flight/Time of Flight (MALDI-TOF/TOF, Applied Biosystems, Framingham, MA, USA) instrument. The mass spectra were acquired in low linear mode over a mass range from 60 to 2000 Da at 6000 laser intensity. The samples were prepared with DHB (2,5-dihydroxy benzoic acid) and 3,5-dimethoxy-4-hydroxycinnamic acid as the matrix. The matrix solution was obtained by mixing the matrix material in 50% aqueous acetonitrile and 0.1% trifluoroacetic acid to give a 10 mg/ml concentration. The matrix was premixed with the resin sample at a ratio of 4:1 (v/v). 1  $\mu$ L of the mixture was added on the MALDI target and air-dried. Each spectrum was the total number of ions from 500 laser pulses. The average molecular weight and polydispersity were calculated using Mané et al.'s [12] methods.

#### 2.2.2. Differential scanning calorimetry (DSC) analysis of the resins

High pressure pans (TA DSC-Q100, TA Instruments, USA) were used for investigating the resin curing behavior. Dynamic scans were carried out at heating rates of 5, 10, 15 and 20 °C/min, starting from room temperature and increasing to 250 °C.

Kissinger method was used to calculate the activation energy:

$$\ln\left(\frac{\phi}{T_p^2}\right) = -\frac{E}{R} \frac{1}{T_p} + \ln\left(\frac{RA}{E}\right)$$

where  $\phi$  is the heating rate (K/s),  $T_p$  is the peak temperature (in Kelvin) at the given heating rate,  $A$  is the pre-exponential factor,  $R$  is the ideal gas constant and  $E$  is the activation energy.

For isothermal scans, a steady isothermal baseline was first established at a cure temperature using two empty sample pans. Five cure temperatures (110, 120, 130, 140 and 150 °C) were used in the isothermal DSC experiments. Three replicates were run for a number of reaction conditions to check for reproducibility and the maximum variations of the onset and peak temperature were less than 1 °C for these replicates.

#### 2.2.3. Thermal gravimetric analysis (TGA) of the cured resins

The BPF, lab and commercial PF resins were cured in an oven at 80 °C for 48 h. The cured resins were ground into fine powders that were able to pass through a 100-mesh screen. About 10 mg of each cured resin sample was added to a platinum pan and heated from the room temperature to 700 °C at the rate of 10 °C/min under  $N_2$  atmosphere using a thermal gravimetric analyzer (TGA, TA TGA-Q500, TA Instruments, USA).

#### 2.2.4. Evaluation of bonding strength

Poplar veneer was cut into strips (3 mm thick, 25.4 mm wide and 108 mm long) with the length direction parallel to wood grain. The veneers were conditioned at 20 °C and 50% relative humidity for at least one week before usage. The two-layered poplar wood veneer specimens were bonded using the four different types of resins, i.e., liquefied mountain pine beetle-infested lodgepole pine bark-PF resin (LBI-PF) and liquefied non-infested lodgepole pine bark-PF resin (LGP-PF), lab PF resin and commercial PF resin. The adhesives were applied on one side of the poplar strip in an area of 25.4 mm  $\times$  25.4 mm (Fig. 1). The spread rate of the adhesives was 0.025–0.035 g/cm<sup>2</sup> on a solids basis. The adhesive-coated area of the poplar strip was then overlapped with an uncoated poplar strip. The resulting two-layered lap shear specimen was hot pressed at 160 °C under the thickness control of 4.5 mm for 3 min. After cooling and conditioning, the specimen was tested for shear strength on a Zwick universal test machine (Zwick/Z100, Zwick Roell group, Germany) following the standard lap shear test methods as described in ASTM D5868. The crosshead speed was 1.3 mm/min. The average values based on a minimum of 10 replicates were reported.

#### 2.2.5. Water resistant test

The lap shear specimens were subjected to both a water-soaking-and-drying (WSAD) test and a boiling water test (BWT), according to voluntary standard PSI-95 published by the US Department of Commerce through the Engineered Wood Association (APA), Tacoma, WA. For the WSAD test, the specimens were soaked in water at room temperature for 24 h, and then were dried in a fume hood at room temperature for 24 h, followed by the shear strength measurements. For the BWT test, the specimens were first boiled in water for 4 h, and then dried for 20 h at  $63 \pm 2$  °C. After the drying, the specimens were boiled in water again for 4 h, and then cooled down with tap water, followed by the shear strength measurements when they were still wet. The shear strength obtained using this method was defined as BWT/wet strength.

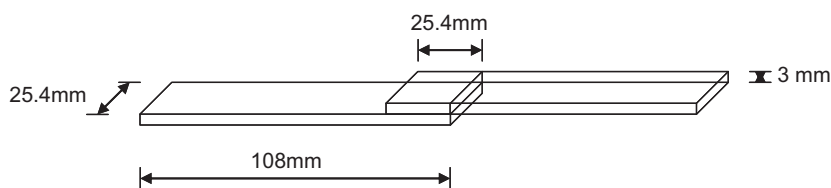


Fig. 1. Lap shear specimen dimensions.

Table 1  
Resin properties.

	pH	Solids' content (%)	Viscosity (cps)	Gel time at 120 °C (s)	$M_n$ (Da)	$M_w$ (Da)	$M_w/M_n$
Commercial PF	11.16	64.37	200	172	212.09	386.48	1.82
LBI-PF	12.07	52.97	125	152	325.57	619.49	1.89
LGP-PF	11.96	52.35	150	161	437.17	849.24	1.95
Lab PF	11.93	48.87	25	173	258.95	327.27	1.25

LBI-PF: liquefied mountain pine beetle infested pine bark-PF resin; LGP-PF: liquefied non-infested pine bark-PF resin.

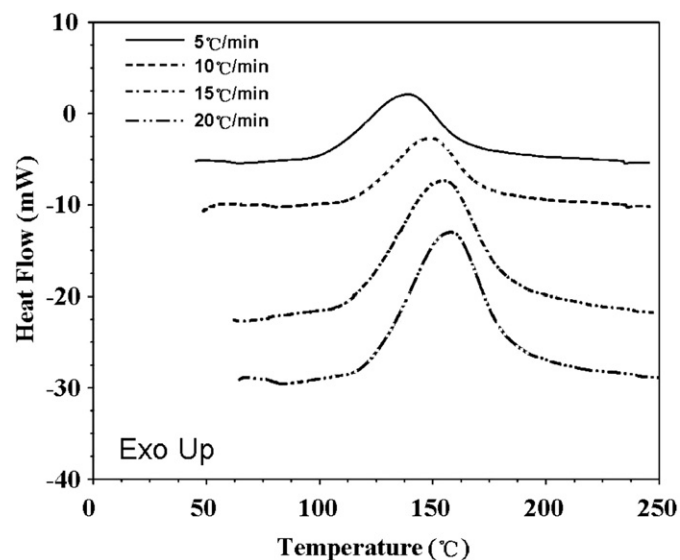


Fig. 2. Dynamic DSC curves of the liquefied non-infested lodgepole pine bark-PF resin (LGP-PF).

### 3. Results and discussion

#### 3.1. Basic properties of the adhesives

The properties of the synthesized resins are shown in Table 1. The pH values for the BPF resins and the lab PF resin were similar. The solids content of liquefied mountain pine beetle infested pine bark-PF (LBI-PF) and liquefied non-infested pine bark-PF (LGP-PF) resins were 52.97% and 52.35%, respectively. The solids content of the bark-derived resins was lower than the solids content of the commercial PF resin (64.37%) but was higher than the solids content of the lab PF resin (48.87%). The higher solids content associated with the commercial PF resin is attributed to the existence of urea and the elemental analysis of the resin confirmed the existence of urea in the formulation (N: 11.52%).

Even though the same synthesis procedure was followed, the BPF resins had higher viscosities, higher molecular weights ( $M_w$  and  $M_n$ ) and higher polydispersity indices than the lab PF resin. This could be the result of the presence of some larger molecular compounds, i.e., degraded bark components in the liquefied bark fraction. The low viscosity, low  $M_w$  and low polydispersity index of the lab PF resin

(25 cps) indicated that this resin had a lower degree of polymerization, which also explained why its solids content was lower than those of the BPF resins. The BPF resins had the shortest gel time when compared to the lab and commercial PF resins.

#### 3.2. Adhesives curing behavior

The DSC curves of the liquefied non-infested lodgepole pine bark-PF resins at different heating rates had a single exothermic peak (Fig. 2). The same was true for all other types of resins (curves not shown). These curves were consistent with what were typically observed for PF resins [13]. The DSC curves also seemed to suggest that the curing process of the resins was mainly dominated by condensation reactions. The addition reactions for the formations of methylol compounds might have largely completed during the resin synthesis stage.

The onset and peak temperatures of the resins are listed in Table 2. With an increase in heating rate, both the onset temperature and peak temperature shifted to higher temperatures. Since the actual cure temperatures should be independent of the heating rate, peak and onset temperatures were extrapolated to the heating rate of zero for comparison [14]. The extrapolated onset temperatures for the liquefied mountain pine beetle infested lodgepole pine bark-PF resin and liquefied non-infested lodgepole pine bark-PF resin were found to be 98.86 and 99.34 °C, respectively. The extrapolated onset temperatures for the bark-derived resins were similar to the commercial PF resin but slightly higher than the lab PF resin. It indicated that the lab PF resin was more reactive at the low temperatures.

The extrapolated peak temperatures for the liquefied mountain pine beetle infested pine bark-PF resin and liquefied non-infested pine bark-PF were 133.93 and 133.29 °C, respectively. The extrapolated peak temperatures for the commercial PF resin and lab PF resin were 127.76 and 136.00 °C, respectively. It implied that the commercial PF resin had a higher reactivity than the BPF resins and lab PF resin at higher temperatures. The lab PF resin was more reactive at lower temperature while the BPF resins were more reactive at higher temperature, and the commercial PF was the most reactive resin at higher temperatures. The degraded bark components might have contributed to the different reactivities among different types of resins at different temperatures. Since the detailed composition of the commercial PF resin is unknown, it is difficult to speculate the mechanism associated with the behavior of the commercial PF resin.

**Table 2**  
Resin curing temperatures.

Heating rate (°C/min)	LBI-PF		LGPB-PF		Commercial PF		PF (lab made)	
	Onset temp. (°C)	Peak temp. (°C)	Onset temp. (°C)	Peak temp. (°C)	Onset temp. (°C)	Peak temp. (°C)	Onset temp. (°C)	Peak temp. (°C)
0 <sup>a</sup>	98.86	133.93	99.34	133.29	98.11	127.76	95.86	136.00
5	103.66	140.57	104.90	139.81	105.54	134.35	103.89	143.74
10	113.43	151.45	113.66	151.47	113.94	143.66	112.53	155.74
15	117.97	159.89	119.38	158.67	122.21	151.35	120.66	164.79
20	123.03	164.73	124.78	164.51	128.81	156.85	128.60	171.23

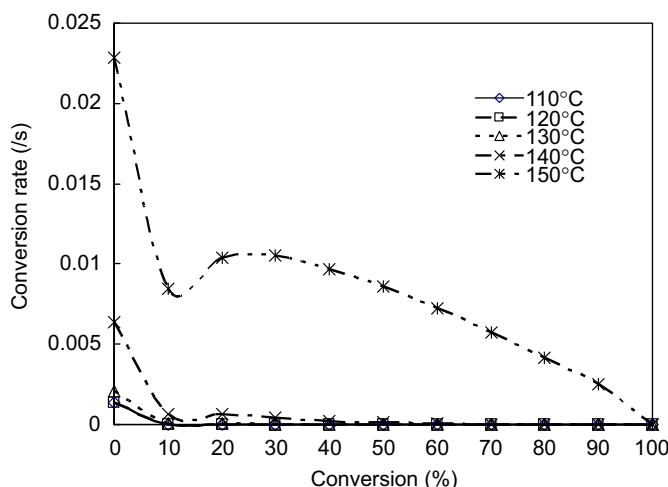
LBI-PF: liquefied mountain pine beetle infested pine bark-PF resin; LGP-PF: liquefied non-infested pine bark-PF resin.

<sup>a</sup> Extrapolated values from the intercept of the plots of the onset temperatures and peak temperatures versus the heating rate.

**Table 3**  
Dynamic cure kinetic parameters for different resins.

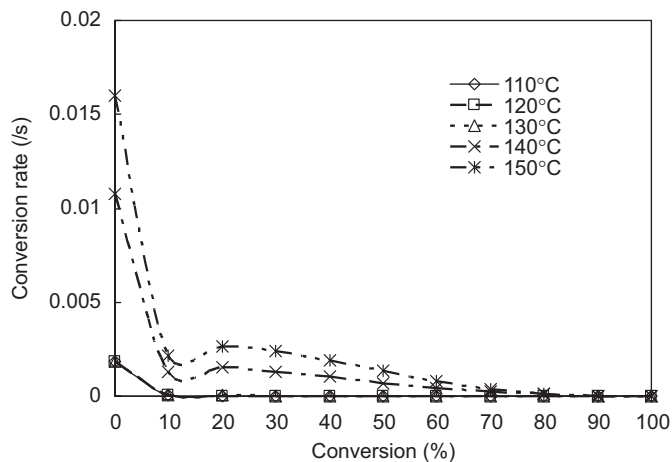
	$E$ (kJ/mol)	$A$ (s <sup>-1</sup> )	Kinetic equation	$r$
LBI-PF	78.12	$2.08 \times 10^9$	$\frac{dz}{dt} = 2.08 \times 10^9 \exp(-\frac{9400}{T})(1-\alpha)^{0.84}$	0.99
LGP-PF	77.60	$1.85 \times 10^9$	$\frac{dz}{dt} = 1.85 \times 10^9 \exp(-\frac{9338}{T})(1-\alpha)^{0.75}$	0.99
PF (Lab)	70.22	$1.59 \times 10^8$	$\frac{dz}{dt} = 1.59 \times 10^8 \exp(-\frac{8450}{T})(1-\alpha)^{0.64}$	0.99
COM PF	82.23	$1.18 \times 10^{10}$	$\frac{dz}{dt} = 1.18 \times 10^{10} \exp(-\frac{9895}{T})(1-\alpha)^{0.56}$	0.99

$r$ : correlation coefficient.

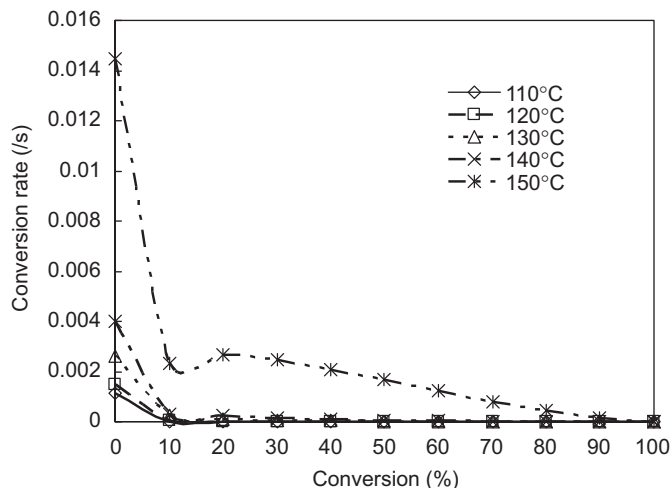


**Fig. 3.** Conversion rate as a function of the degree of conversion at various isothermal temperatures for the liquefied mountain pine beetle infested lodgepole pine bark-PF resin (LBI-PF).

The activation energy was calculated using the Kissinger equation and is given in Table 3. Other dynamic parameters, including the kinetic equations derived from the dynamic DSC analysis, are also shown in Table 3. Compared with the lab PF resin, the BPF resins had higher activation energies, which seemed to suggest that the degraded bark components in the liquefied bark fraction might have made the resin more difficult to cure. One possible mechanism could be related to the lower molecular mobility of these components to form crosslinking. Even though the cure activation energy was higher for the BPF resins, the reactive sites on the bark components might have shortened the gel time and accelerated the curing process of the resins at higher curing temperatures where cure reaction was mainly controlled by diffusion. The commercial PF resin had the highest activation energy while its value of the pre-exponential factor was the highest among the different types of resins. And the latter indicated that the commercial PF resin had the fastest curing rate.



**Fig. 4.** Conversion rate as a function of the degree of conversion at various isothermal temperatures for the liquefied non-infested lodgepole pine bark-PF resin (LGP-PF).



**Fig. 5.** Conversion rate as a function of the degree of conversion at various isothermal temperatures for the lab PF resin.

Figs. 3–6 show the resin conversion rate versus the degree of conversion under different isothermal temperatures. It was evident from Figs. 3–6 that the curing reactions for all resins followed an  $n$ th-order kinetic mechanism when the conversion rate was below 10%. When the conversion rate reached above 20%, the cure reactions became autocatalytic. The autocatalytic cure mechanism dominated at higher curing temperatures. The change in the curing mechanism as a function of temperature was also observed for some commercial PF resins before [14,15].

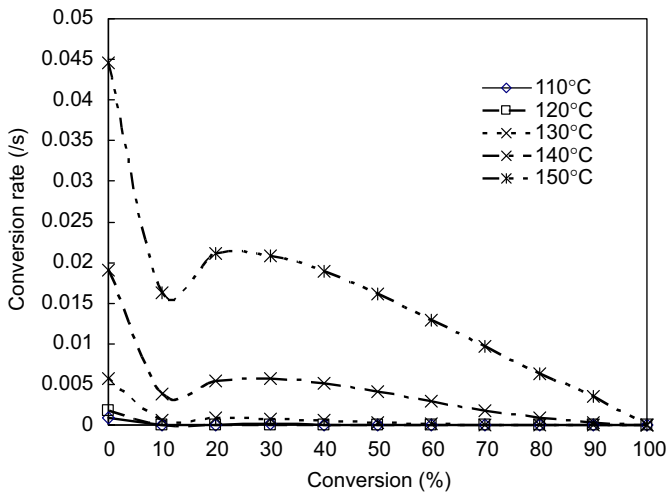


Fig. 6. Conversion rate as a function of the degree of conversion at various isothermal temperatures for the commercial PF resin.

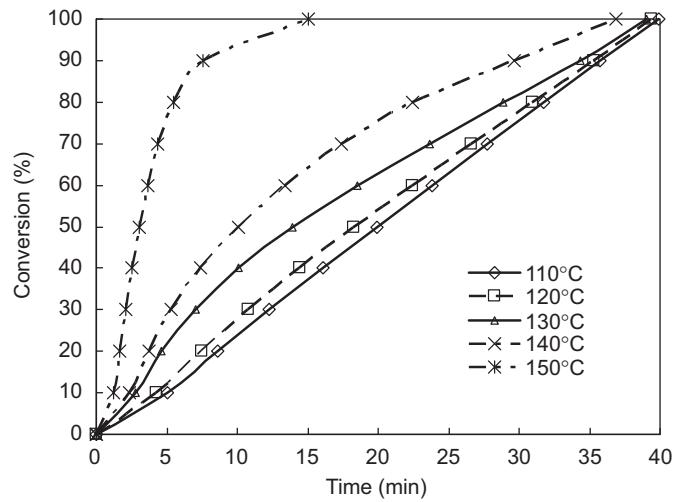


Fig. 9. Conversion as a function of cure time at various isothermal temperatures for the lab PF resin.

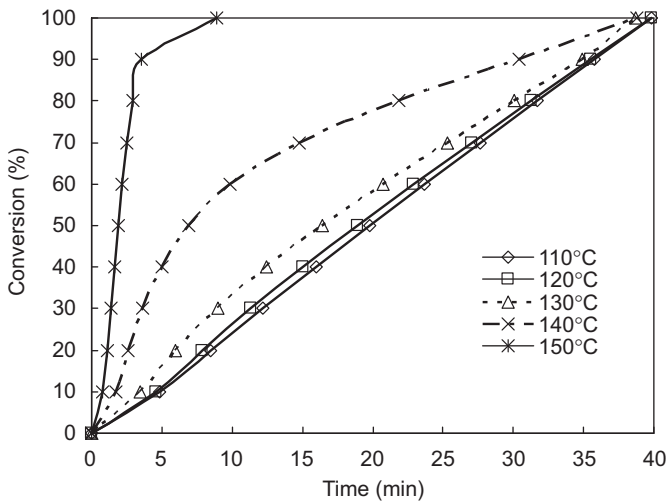


Fig. 7. Conversion as a function of cure time at various isothermal temperatures for the liquefied mountain pine beetle infested lodgepole pine bark-PF resin (LBI-PF).

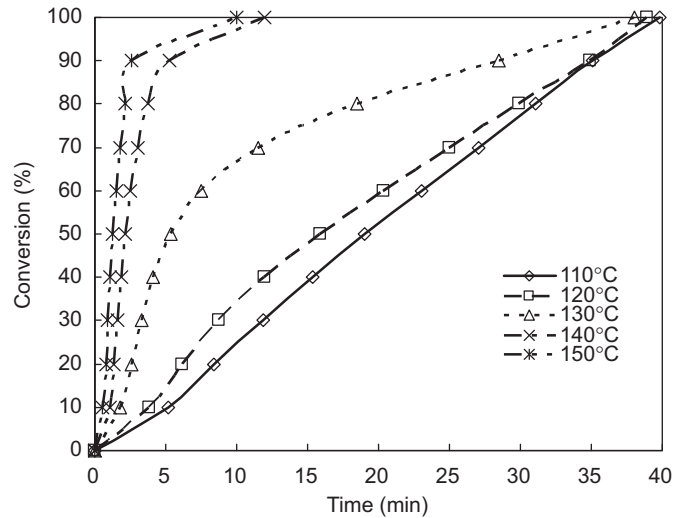


Fig. 10. Conversion as a function of cure time at various isothermal temperatures for the commercial PF resin.

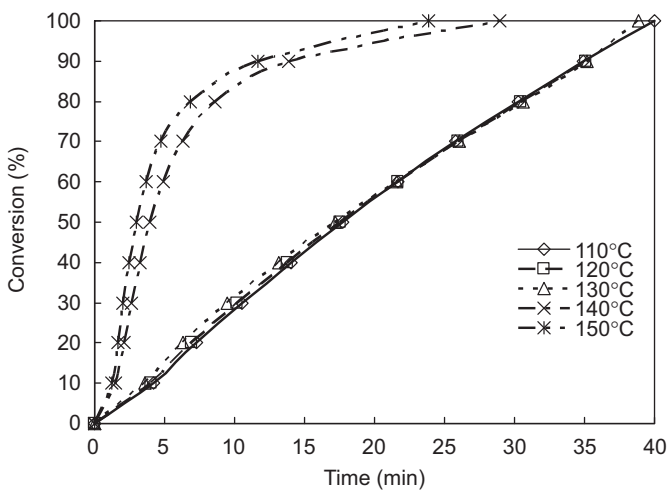


Fig. 8. Conversion as a function of cure time at various isothermal temperatures for the liquefied non-infested lodgepole pine bark-PF resin (LGP-PF).

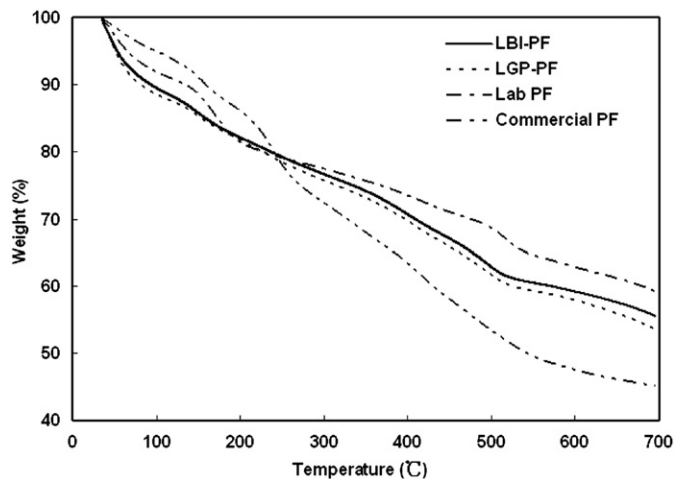
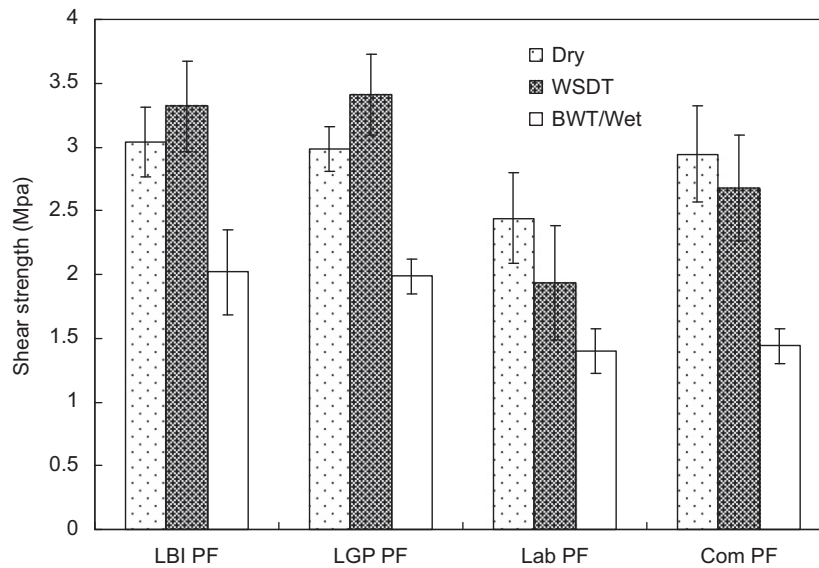


Fig. 11. Thermal stability of different cured resins as measured by TGA.



**Fig. 12.** Shear strength of lap shear specimens bonded with different types of adhesives (LBI-PF: liquefied mountain pine beetle infested pine bark-PF resin; LGP-PF: liquefied non-infested pine bark-PF resin; Com PF: commercial PF resin).

Conversion rates of different resins as a function of time at various isothermal temperatures are shown in Figs. 7–10. All the resins reached about 60% of conversion within 25 min at the five isothermal temperatures. With the increase in isothermal cure temperature, the cure reaction reached the same level of conversion at a shorter time. The shape of the curves changed with different isothermal cure temperatures. The shape change of the curves for LBI-PF resin was similar to the lab PF resin but different from the change of LGP-PF and commercial PF resins. These changes were probably due to the change in the cure mechanism. At high cure temperature, the autocatalytic mechanism might have dominated the cure reaction.

### 3.3. Thermal stability of the cured resins

The thermal degradation process of the commercial PF resin differed significantly from those of the lab PF and BPF resins, especially when the temperature was higher than 200 °C (Fig. 11). This could be due to the fact that commercial PF resin contained a significant amount of urea, which is known to decompose more easily at high temperatures. The lab PF resin and BPF resins had more similar thermal degradation processes. The lab PF resin had a slightly higher amount of weight retained after thermal degradation compared with the BPF resins.

### 3.4. Lap shear test results

Results of the lap shear tests of two-layered specimens bonded with four different types of resins are shown in (Fig. 12). The specimens bonded with BPF resins had similar dry shear strength values as the specimens glued by the commercial and lab PF resins. After the water-soaking-and-drying (WSAD) treatment and the boiling water treatment (BWT), all samples showed no delamination. The BPF resins gave higher lap shear strength than the commercial and lab PF resins after both the WSAD and BWT/wet tests. Some previous studies on condensed tannins-polyethylenimine resins and bark extractives-diisocyanate mixtures also showed good wet bonding strength in resulting wood composites [6,16]. The researchers attributed the good bonding properties to the extractives and to the effects from the catechol moiety of the tannins in the bark, serving as the wet strength

agent in wood composites, which is consistent with the findings in this study. Furthermore, the bonding properties of the bark-derived resins did not seem to be negatively affected by the beetle infestation of the lodgepole pine bark.

## 4. Conclusions

The bark-phenol-formaldehyde resins synthesized with liquefied barks of beetle-infested lodgepole pine bark and lodgepole pine bark without infestation were found to have higher average molecular weights, higher polydispersity indices and shorter gel times than lab PF and commercial PF resins. The cure activation energy for the BPF resins was lower than that of the commercial PF resin but higher than the cure activation energy of the lab PF resin. The curing behavior of all these resins followed both *n*th-order and autocatalytic mechanisms. The cured BPF resins had a more similar thermal stability as the cured lab PF resin, which was different from the commercial PF resin. BPF resins showed similar dry bonding strength and better wet bonding strength than those of commercial and lab PF resins. Beetle infestation was shown to have no negative effect on the bonding properties of the BPF resins.

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