Synthesis of Biobased Phenolic Resins/Adhesives with Methylolated Wood-Derived Bio-Oil

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ABSTRACT: Bio-oil from the hydrothermal liquefaction of Eastern White Pine (*Pinus strobus L.*) sawdust was methylolated with formaldehyde in the presence of sodium hydroxide. The obtained methylolated bio-oil (MB) was used to synthesize methylolated bio-oil–phenol formaldehyde (MBPF) resol resins with a phenol substitution ratio of up to 75 wt %. All of the resins were used as wood adhesives for the production of a three-layered plywood. The MBPF resol resins were comprehensively characterized for their physical, chemical, thermal, and mechanical properties (e.g., viscosity, nonvolatile content, shelf life, free formaldehyde level, molecular weight and distribution, curing temperature, bonding strength) when used as plywood adhesives. All of the MBPF resins contained similar nonvolatile contents as the reference pure phenol formaldehyde (PF) resin but had higher viscosities and shorter shelf lives, depending on the amount of MB in the MBPF. All of the MBPF resins displayed a lower curing temperature than the reference PF resin, with the main curing peak around 140°C, which was similar to that of the pure PF resin. According to thermogravimetric analysis, the methylolation treatment of bio-oil improved the thermal stability of the MBPF resins compared to the bio-oil–PF resol resins, which used untreated bio-oil. The dry/wet bonding strengths of the plywood specimens glued with the MBPF resol resins with up to 60 wt % phenol substitution exceeded or were comparable to those of the conventional PF resol resin. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: adhesives; curing of polymers; differential scanning calorimetry (DSC); gel permeation chromatography (GPC); resins

INTRODUCTION

Lignin and bio-oil derived from lignocellulosic biomass have been employed as potential sources of biophenols to replace phenol in the production of phenol formaldehyde (PF) resins. However, substituting phenol with lignin or bio-oil at a high substitution ratio (e.g., >50%) without affecting the final product quality is very challenging[1–5] because of the much lower reactivity of these biofeedstocks in the reaction with formaldehyde. As shown in Scheme 1, monolignols are less reactive than phenol because of the presence of steric hindrance in the large molecules and fewer reactive sites for reacting with formaldehyde.[6–8]

To improve the reactivity of lignin in the production of lignin–PF resins, many researchers have attempted to modify lignin by methylolation,[7,9] phenolation,[10,11] and demethylation.[12–15] For example, Cetin and Ozmen[10,11] demonstrated that the level of phenolated lignin for phenol in phenolated lignin–PF resol resins had to be controlled at less than 30 wt % to achieve a comparable strength to that of a traditional PF resole resin. Methylolation treatment of lignin proved to be effective for increasing the lignin substitution level while maintaining the strength of the resins. This was due to the introduction of methylol groups at a C_5 position of the guaiacyl units (via the Lederer Manasse's reaction), and the methylol groups could condense with phenols (including biophenol) molecules, or the prepolymer of PF resin could be introduced. Olivares et al.[12] reported that methylolated lignin–PF resin with a phenol substitution level of 40 wt % demonstrated a higher bonding strength than traditional PF resins and lignin–PF resins with 40 wt % unmodified lignin and demethylolated lignin.

As an exciting achievement, our group demonstrated that a low-molecular-weight biocrude produced from the hydrothermal liquefaction of sawdust could replace phenol up to 75 wt % in the synthesis of bio-oil phenol formaldehyde (BPF) resol
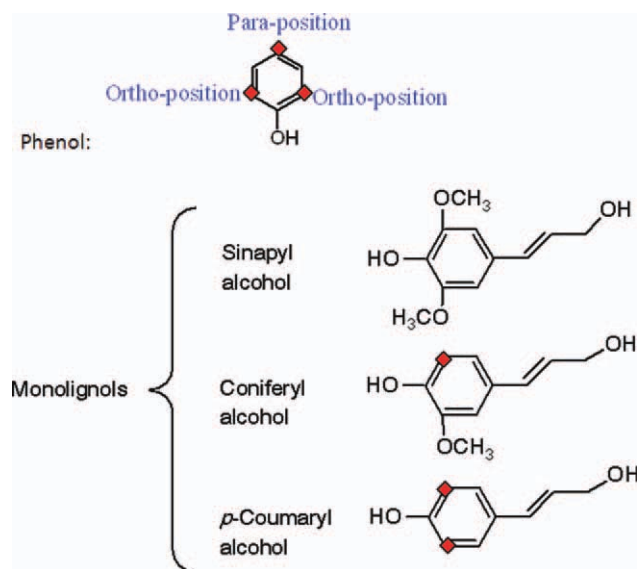
Scheme 1 Reactive sites in the phenol and three monolignols for the PF resin synthesis reactions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

resins.[5] The obtained BPF resol resins were found to be comparable to the conventional pure PF resin with respect to the physical, chemical, and mechanical (bonding strength) properties, whereas the BPF resol resins had slightly deteriorated thermal properties (carbon residue at elevated temperatures).[5] Moreover, the BPF resol resins at a high substitution ratio (>50 wt %) did exhibit slightly inferior properties in terms of their wet strength and wood failure in plywood bonding.[5] As described previously, the methylolation treatment of lignin proved to be effective for increasing the lignin substitution level while maintaining the strength of the resins. Accordingly, the reactivity of bio-oil would also be improved through methylolation to introduce methylol groups. So far, no research on the methylolation treatment of bio-oil has been reported in this regard. As shown in Scheme 1, the main monolignol component of pine (softwood) lignin is coniferyl alcohol, with one reactive site where one methylol group can be introduced, as illustrated in Scheme 2.

In this study, to obtain high-quality BPF resol resins with a high phenol substitution level, pinewood-derived bio-oil was first treated with formaldehyde to introduce methylol groups and then copolymerized with phenol and formaldehyde in the presence of sodium hydroxide as the catalyst to prepare methylolated bio-oil–phenol formaldehyde (MBPF) resol resins. The degree of the methylolation reaction of bio-oil with formaldehyde was analyzed with ^{1}H-NMR spectroscopy. The methylolated bio-oil (MB) was also analyzed with gel permeation chromatography (GPC), and the amount of unreacted formaldehyde in MB was also determined. The physico-

chemical properties of the experimental MBPF resins were characterized with respect to their viscosities, nonvolatile content, shelf life, free formaldehyde level, molecular weight and distribution, curing temperature, and thermal stability. The MBPF resol resins were also employed as plywood adhesives, whose dry and wet tensile strengths were evaluated.

EXPERIMENTAL

Materials

The bio-oil used in this study as a phenol substitute was derived from Eastern White Pine sawdust by hydrothermal liquefaction at 300°C in a 50 wt% ethanol–water medium. The main compositions of the pine sawdust were cellulose (40.2 wt %), hemicellulose (21.9 wt %), and lignin (28.4 wt %), determined in accordance with TAPPI test method T249cm-85 (for cellulose and hemicellulose) and TAPPI test method T222 om-88 (for acid-soluble and acid-insoluble lignins). The detailed procedure for the production of the hydrothermal bio-oil can be found in our previous work.[16] Other raw materials used in the synthesis of the BPF resol resins included American Chemical Society (ACS) reagent-grade chemicals, that is, ethanol (Fisher Scientific, Batesville, IN), acetone (Fisher Scientific, Fair Lawn, NJ), solid phenol crystal (99%, J. T. Baker, Phillipsburg, NJ), sodium hydroxide solution (ca. 50%, Ricca Chemical Co., Arlington, TX), and formaldehyde (ca 37%, Anachemia, Montreal, QC).

For GPC analysis, the HPLC (High-performance liquid chromatography)-grade solvent tetrahydrofuran containing 0.03 wt % 2,6-di-t-butyl-4-methyl phenol stabilizer and ACS reagent-grade pyridine and acetic anhydride (Sigma-Aldrich, Louis, MO) were used. In the ^{1}H-NMR analysis for MB, ACS reagent-grade chloroform-d (99.8 atom % D), containing 0.1% tetramethylsilane, was used as the solvent.

Preparation of the MB

The methylol groups were introduced to the bio-oil according to the reaction mechanism shown in Scheme 2, whose procedure is described briefly as follows. In a typical run, the bio-oil was first mixed in a three-necked flask with formaldehyde at a
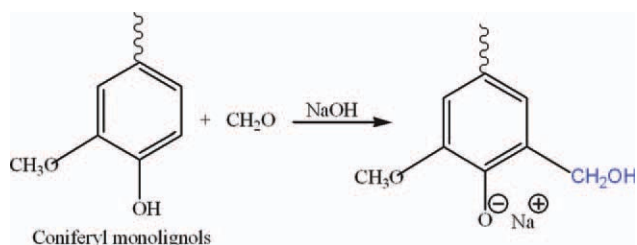
Scheme 2 Methylolation reaction mechanism of bio-oil with formaldehyde. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
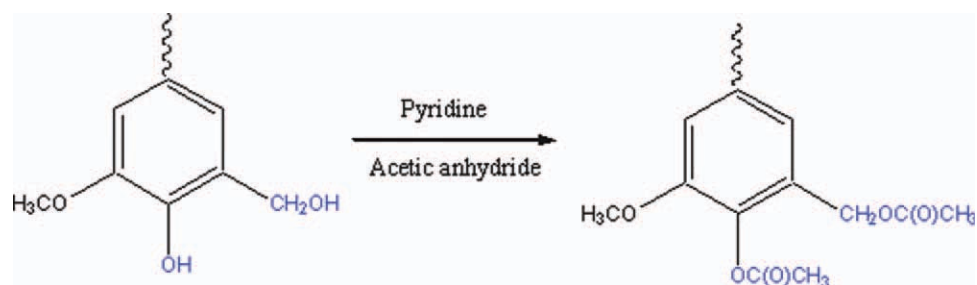
Scheme 3 Acetylation reaction of MB. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

formaldehyde/bio-oil weight ratio of 0.37, sodium hydroxide at a NaOH/bio-oil weight ratio of 0.1, and ethanol at an ethanol/bio-oil weight ratio of 1.0.[17] Distilled water was also added to obtain a solid content of the reaction mixture of 29.4 wt %. All of the materials were then reacted in the three-necked flask in a water bath at 50°C under continuous stirring for 1.0 h to get a homogeneous solution. Then, the temperature of the water bath was raised to 80°C, and the reaction was continued for another 2.0 h before the reactor was cooled down to room temperature.

Preparation of the MBPF resol resins

Various MBPF resol resins with different phenol substitution ratios were synthesized in a 250-mL, three-necked flask equipped with a pressure-equalizing addition funnel, a thermometer, a water-cooled condenser, and a water bath with a magnetic stirrer. The MBPF resol resin pH value was controlled at around 10 with an NaOH solution. In a typical run, with the synthesis of 50% MBPF resol resin used as an example, 10.0 g of phenol was added to 10.0 g of MB with 2.0 g of a 50 wt % aqueous solution of sodium hydroxide (10 wt % of the phenolic feed). The mixture was mixed at 80°C for 2.0 h under magnetic stirring to ensure a homogeneous solution. Then, 11.2 g of an aqueous solution of formaldehyde [ca. 37 wt %, formaldehyde/phenol = 1.3 (molar ratio)] was added dropwise into the flask through a cylindrical separatory funnel. After the addition of formaldehyde, the flask was held at 80°C for 3.0 h of a resinification reaction. The mixture was then cooled down to 40–50°C. Some of the resin product was sampled for viscosity measurement with a Brookfield viscometer (Brookfield Engineering Laboratories, Middleboro, MA). The resin was collected in a sealed plastic bottle and stored at 4°C. By varying the amount of MB in the reaction mixture, we prepared a series of MBPF resins with phenol substitutions ranging from 0 to 75 wt % (i.e., 0, 25, 50, 60, and 75 wt %). The as-synthesized MBPF resol resins were designated as PF, 25% MBPF, 50% MBPF, 60% MBPF, and 75% MBPF, respectively.

Characterizations of the MB and MBPF resins

Free formaldehyde levels

The free formaldehyde levels in the MB and MBPF resins were determined with a modified Walker's hydroxylamine hydrochloric method.[18] Approximately 2.0 g of MB or MBPF sample was diluted with 25 mL of water, and the pH was adjusted to 4.0 with 0.1M HCl; this was followed by the addition of 30 mL of hydroxylamine hydrochloride (0.5M, pH = 4.0). The mixture was stirred for 10 min at room temperature with a magnetic stirrer. The unreacted formaldehyde was determined by back titration to pH 4.0 with 0.1M aqueous sodium hydroxide.

^{1}H-NMR and GPC

Before the ^{1}H-NMR and GPC analyses, the bio-oil samples were subjected to acetylation to improve their solubility in organic solvents. The acetylation pretreatment was to substitute all of the hydroxylic functions with acetyl groups, as illustrated in Scheme 3. The bio-oils (with and without methylolation) were acetylated with pyridine and acetic anhydride. The bio-oil or MB (0.5 g) was treated at room temperature for 48.0 h with a 1 : 1 (v/v) mixture of pyridine (10 mL) and acetic anhydride (10 mL). The mixture was added to 100 mL of ice cold 1% HCl, and the precipitated solid product was separated by filtration with a Whatman No. 5 filter paper (Whatman Inc. Clifton, NJ) and rinsed with deionized water until the filtrate attained a neutral pH. The acetylated bio-oils were vacuum-dried at room temperature overnight before they were subject to ^{1}H-NMR and GPC analyses.

The degree of methylolation of the bio-oil was determined by ^{1}H-NMR. ^{1}H-NMR spectra were obtained on a 500-MHz Unity Inova NMR instrument at room temperature where CDCl$_3$ containing 0.1 wt% tetramethylsilane as an internal standard was used as the solvent to dissolve the acetylated bio-oil samples. For the preparation of the samples, 25.0 mg of acetylated raw bio-oil or MB was dissolved in 1.0 mL of CDCl$_3$. The number of phenolic

acetate and aliphatic acetate (A-acetate) protons were detected relative to the number of methoxyl protons by integration of the corresponding ^{1}H-NMR signals. The relative molecular weights and their distribution of acetylated bio-oil and MB were analyzed through a tetrahydrofuran-eluted Waters Breeze GPC instrument (Waters, Milford, MA, 1525 binary HPLC (High-performance liquid chromatography) pump, UV detector at 270 nm, Waters Styragel HR1 column at 40°C) at a flow rate of 1 mL/min, and polystyrene standards were used for calibration.

Characterizations of the MBPF resins

The viscosity of the as-synthesized resins was measured at 50°C with a Brookfield CAP 2000+ viscometer (Brookfield Engineering Laboratories, Middleboro, MA) according to ASTM D 1084–97. The nonvolatile content of the resins was determined at 125°C for 105 min in accordance with ASTM D 4426-01(2006). The thermal behavior of the resins was evaluated by differential scanning calorimetry (DSC; DSC 1, Mettler-Toledo, Switzerland), where the sample was heated at 10°C/min from 40 to 250°C in a sealed aluminum crucible under a 50 mL/min N_2 flow. GPC analyses were performed to evaluate the average relative molecular weights of the resins. The thermal stability of the resins was determined on a thermogravimetric analysis (TGA) instrument (TGA 1000i, Instrument Specialists, Inc.) from 25 to 700°C with about 10 mg of nonvolatile resin sample heated at a 10°C/min under 30 mL/min N_2.

Dry/wet bonding strengths of the plywood specimens glued with MBPF resol resins

The detailed procedure can be seen elsewhere.[5] Simply, three-ply laboratory plywood panels with rough dimensions of 11 × 11 × 3/16 in.[3] were prepared from 11/6-in. yellow birch veneers with the conventional PF resol resin or the MBPF resol resins as the adhesives. The resin was mixed with wheat flour (15 wt % of the resin) and uniformly applied with a brush to the two surfaces of the center veneer at a spread rate of 250 g/m² per single glueline. The hot pressing was carried out at 140°C under 2500 psi of pressure for 4 min on the three-ply plywood panels with two face veneers and a center veneer aligned in a perpendicular direction. According to ASTM D 906–98(2004), 40 specimens were prepared for tensile strength testing, and 20 specimens were used to test the dry tensile strength after conditioning. The other 20 specimens were boiled in water for 3.0 h before we tested the wet tensile strength to evaluate the water resistance of all of the resins. The specimens were tested for shear stress by tension loading until failure with a benchtop universal testing machine

(model H10K-T UTM, Tinius Olsen Material Testing Machine Co., Horsham, PA) at a loading rate of 10 mm/min. The percentage wood failure in the bonding area for each specimen was assessed visually.

RESULTS AND DISCUSSION

Characterizations of the raw bio-oil and the MB

^{1}H-NMR spectra

Scheme 3 shows the acetylation reaction scheme of MB. As shown in the scheme, the groups ─CH_2OH and ─OH in the bio-oil molecules formed the ester groups ─$CH_2OC(O)CH_3$ and ─$OC(O)CH_3$, respectively, after acetylation. Figure 1 shows the ^{1}H-NMR spectra of the acetylated raw bio-oil and the acetylated MB. Table I lists the integrals of the ^{1}H-NMR signals of the A-acetate groups [─$CH_2OC(O)CH_3$] and ─OCH_3 groups in the acetylated bio-oils at 1.85–2.25 and 3.4–4.2 ppm, respectively. The values were normalized relative to the integrals of the ─OCH_3 group. The signals of the A-acetate became stronger after methylolation, as expected, from 0.760 to 0.943. This suggested that a certain amount of ─CH_2OH groups was introduced to the bio-oil through the methylolation reaction.

GPC analysis

The average relative molecular weights and their distribution of the raw bio-oil and MB after acetylation were determined with GPC, and the obtained GPC spectra are displayed in Figure 2. Both samples displayed a wide molecular weight distribution. The peaks of the acetylated bio-oil shifted to a higher molecular weight position [number-average molecular weight (M_n) from 490 to 592 g/mol, and weight-average molecular weight (M_w) from 1120 to 1563 g/mol] after the methylolation treatment. The value of M_w increased more than M_n did; this suggested a wider molecular weight distribution for MB. As shown in the curve of MB, there were two split peaks. The small peak at a lower retention time was possibly derived from the oligomerization reactions of MB during the methylolation treatment; this could have been due to the presence of NaOH catalyst in the process. The increases in M_n and M_w may also imply the introduction of the methylol groups during the methylolation treatment. The increase in the polydispersity (PD) value of MB suggested a broader distribution.

Free-formaldehyde levels

The free-formaldehyde levels of MBs collected at various reaction stages during the methylolation treatment were measured and are shown in Figure 3. The samples were collected at various reaction
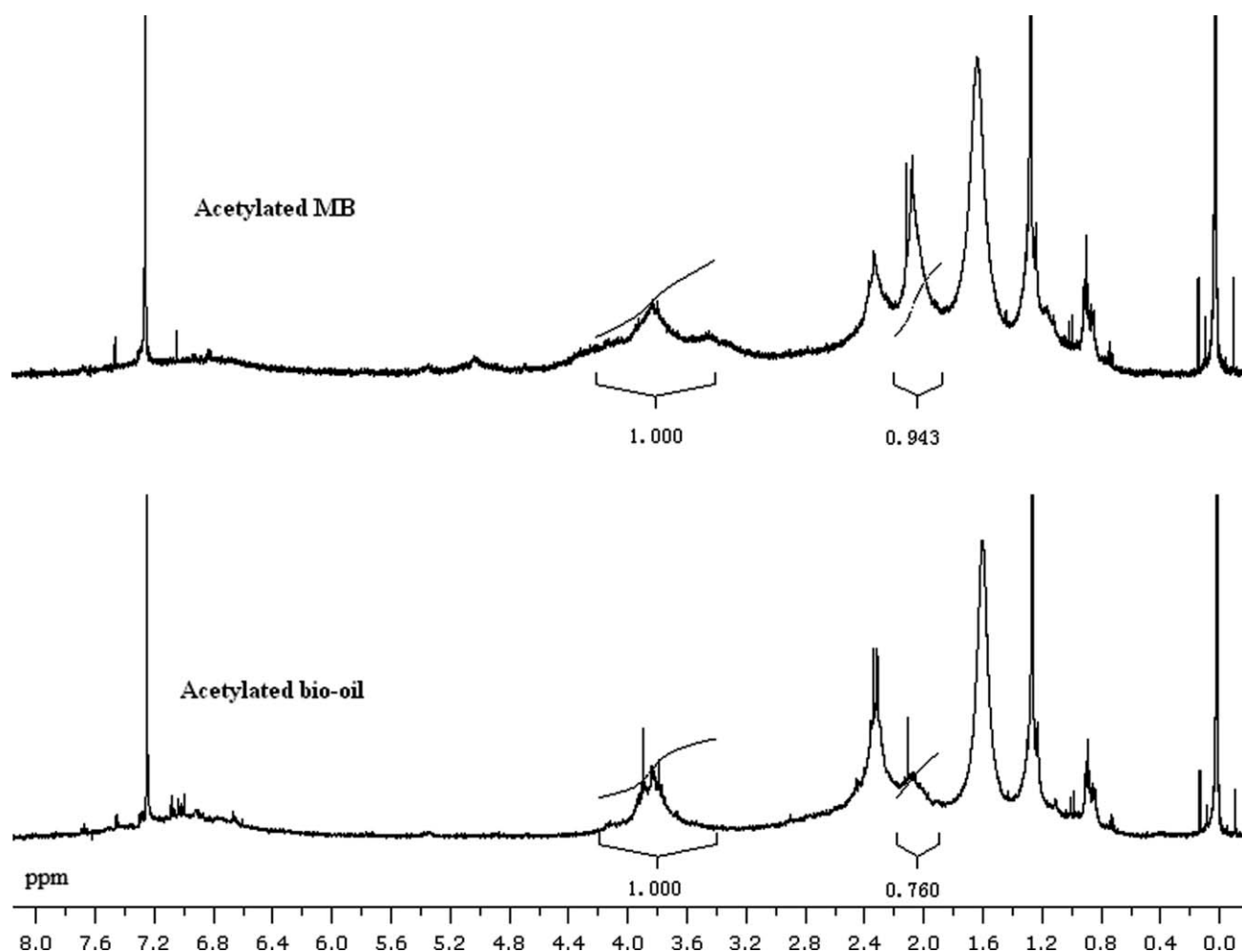
Figure 1 ^{1}H-NMR spectra of the acetylated raw bio-oil and the acetylated MB. The peaks at 7.26 and 1.6 ppm are the solvent and water, respectively.

stages: that is, sample b at 50°C for 1.0 h, sample c after 50°C for 1.0 h and further at 80°C for 1.0 h, and sample d after 50°C for 1.0 h and at 80°C for 2.0 h. Before the methylolation reaction, 10.5% of the initial formaldehyde (sample a) was present in the reactor. As shown in Figure 3, the majority of the formaldehyde was consumed after the reaction at 50°C for 1.0 h. The percentage of free formaldehyde was further reduced to levels as low as 0.57% (sample c) from 2.14% (sample b) when the temperature was further increased to 80°C for 1.0 h. After the methylolation reaction at 80°C for 2.0 h, only 0.35% of unreacted formaldehyde content was detected. It appeared that the free-formaldehyde level would become relatively stable with the continuing reaction. The almost complete consumption of the formaldehyde may evidence that the raw bio-oil was successfully methylolated during the methylolation treatment and the possible resinification reaction between formaldehyde and phenolic compounds in the bio-oil.

Characterizations of the MBPF resol resins

Physical properties

All of the MBPF resins had a dark color with the odor of bio-oil. The measured viscosity, nonvolatile content, and shelf life values of the various MBPF resins, compared with MB, the reference PF resol resin, and various BPF resins are summarized in Table II. As shown in Table II, all of the MBPF and BPF resins exhibited higher viscosities than the

TABLE I
Integrals of the ^{1}H-NMR Signals in the Acetylated Raw Bio-Oil and the MB

Acetylated bio-oils	—OCH$_3$ (3.4–4.2 ppm)	A-Acetate (1.85–2.25 ppm)
Raw bio-oil	1.00	0.760
MB	1.00	0.943

The values are normalized relative to the integrals of the —OCH$_3$ signal, A-Acetate: Aliphatic acetate.
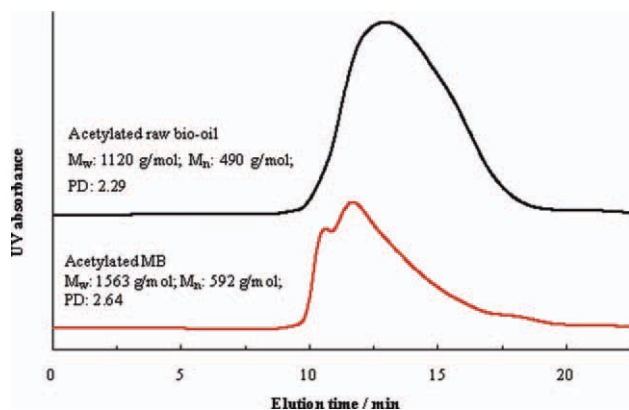
Figure 2 GPC chromatograms of the raw bio-oil and the MB after acetylation (PD $= M_w/M_n$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
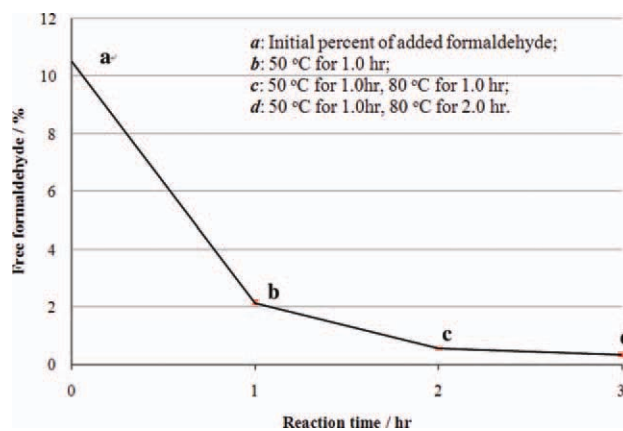

Figure 3 Free formaldehyde levels during the process of the methylolation treatment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reference PF resin. Similar observations were reported previously by our group[5] and by Ferreira et al.[19] The GC–MS analysis of the bio-oil in our previous work[5] demonstrated that the bio-oil was a highly complex mixture of aldehyde, phenolic compounds, long-chain ketones and alcohols, esters, carboxylic acids, and ether compounds. These compounds might have participated in the polymerization or condensation reactions with formaldehyde to form complicated large molecules, which increased the viscosities of the final products. Meanwhile, it was clearly shown that the viscosity values of the MBPF resins increased with increasing MB value in the resin. Particularly for the 75% MBPF, the viscosity drastically increased to 124.2 cp. Thus, the properties of the MBPF at a high phenol substitution with MB were governed by those of the MB, as similarly reported for our previous study.[20] The amount of MB also had a significant effect on the shelf life of the MBPF resin at low temperatures

(4°C). Interestingly, from Table II, the MBPF resin at a 25% MB ratio had a similar shelf life as the reference PF resol resin. After 3 months of storage at 4°C, the resin was still in a fluid form. The MBPF resins containing MB at higher than 25%, however, precipitated in about a week. This shorter shelf life could have been due to the lower solubility of bio-oil products in water at low temperature. The precipitated MBPF resins could become a uniform liquid again with heating, and their shelf life could also be improved by the addition of more water before storage. Therefore, such appearing-to-be shorter shelf lives for the MBPF resins due to precipitation would not affect the applications of the MBPF resins. Our group[20] also reported that a lignin phenolic resin with 60% phenol substitution precipitated in about a week. In contrast, all of the BPF resins exhibited shelf lives of longer than 3 months. This implied that the methylolation treatment of bio-oil caused a reduced shelf life of the MBPF resins due to the enhanced precipitation effects at low temperatures. The free formaldehyde could not be detected in the

TABLE II
Physical Properties of the MB, PF, MBPF, and BPF Resol Resins

MB and resins	Viscosity (cps)[a]	Shelf life (days)[b]	Free formaldehyde (wt %)[d]	Nonvolatile content (wt %)[a]
MB	38.2 (±0.03)	∼ 7	0.35 (±0.06)	29.4 (±0.1)
PF	16.4 (±0.03)	>90[c]	ND[e]	34.4 (±0.1)
25% MBPF	18.2 (±0.02)	>90[c]	—	35.4 (±0.1)
50% MBPF	26.2 (±0.02)	∼ 7	0.37 (±0.03)	36.8 (±0.1)
60% MBPF	35.7 (±0.06)	∼ 7	—	35.2 (±0.1)
75% MBPF	124.2 (±0.13)	∼ 1	—	32.9 (±0.1)
25% BPF	19.5 (±0.01)	>90[c]	0.19 (±0.003)	37.7 (±0.2)
50% BPF	21.0 (±0.01)	>90[c]	0.51 (±0.01)	38.3 (±0.3)
75% BPF	29.5 (±0.01)	>90[c]	0.67 (± 0.01)	38.1 (±0.2)

[a] Each value represents an average from three samples.
[b] At 4°C.
[c] The sample was still fluid after 3 months.
[d] The value represents an average from two samples.
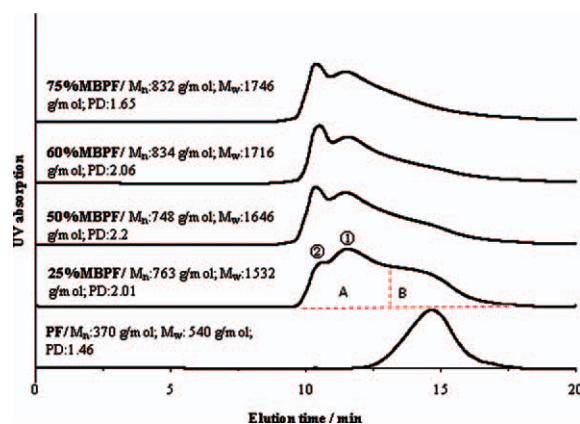[e] ND, not detectable.

Figure 4 GPC chromatograms of the MB and MBPF resins. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reference PF resol. Negligible or very low levels of free formaldehyde (<1 wt %) were detected in all of the MBPF and BPF resins. The nonvolatile contents of all of the MBPF resins were very similar to those of the PF or BPF resins, in the range of 34–38 wt %.

GPC analysis

Figure 4 illustrates the gel permeation chromatograms of the PF and MBPF resins. As shown in Figure 4, all of the MBPF resins presented much higher values of M_n and M_w and wider distributions than the PF resin because of the high molecular weights of MB (M_w = 1563 g/mol and M_n = 592 g/mol) versus that of phenol. This suggested that the MBPF resins, particularly those with high fractions of MB, such as 75% MB, were mainly governed by the properties of the bio-oil; this caused the peak of the GPC chromatogram for the MBPF resin to shift to a higher position. Furthermore, the GPC curve of 25% MBPF (Fig. 4) could be separated into two parts, A and B. The first part, part A, showed that the shorter retention time was caused by the MB-based resin. Part B, at a longer retention time, resulted from the pure phenol-based resin. With increasing MB ratio, the peak of the PF resin polymer gradually decreased; this led to the molecular weights shifting to higher values, as expected. Most of the reported literature demonstrated similar results.[5,20] Furthermore, another phenomenon observed was two split peaks in part A, shown in all of the MBPFs. Peak 1 was likely due to the menthyolated bio-oil reacted with formaldehyde. Peak 2 might have been derived from the oligomerization of peak 1 components through the menthylolation reaction between bio-oil molecules. The higher the level of bio-oil substitution was, the higher the chance of oligomerization was, as shown in the GPC curves.

Thermal curing behaviors

DSC analysis, as a popular technique for examining the curing process of thermosetting resins,[4,21,22] was employed to determine the thermal behavior of the MBPF resins. Figure 5 shows the DSC curves obtained at a heating rate of 5°C/min for different resins from 40 to 250°C in a nitrogen atmosphere. Table III summarizes the characteristic curing temperatures of these resins. Again, to examine the effects of the methylolation treatment of the bio-oil on the thermal behavior of the bioresins, the DSC results for BPF resins are also listed in Table III. As shown in Figure 5, more than one exothermic peak was detected for resins containing less than 60% bio-oil. All of the DSC curves showed distinct exothermic signals (peak 2) at a temperature around 140°C; this could have been due to the main exothermic peak of the phenolic resol resin. All of the MBPF and BPF resins (containing <75 wt % bio-oil) displayed peak 2 at a lower temperature than PF; this suggested a reduced curing temperature, as similarly reported in many previous studies[4,23,24] on the synthesis of biobased PF resins with phenol substitutes, such as tannin and lignin. It was an interesting finding that, as shown in Table III, the curing temperature of 75% MBPF (139.6°C) was lower than that of 75% BPF (146.2°C). The main curing peak (peak 2) could be attributed to the condensation of phenol or bio-oil with methylol groups ($-CH_2OH$) to form a methylene bridge and the condensation of methylol groups with phenolic compounds to form dibenzyl ether bridges.[20,21,23,25] The curve of PF produced a large and well-split peak at a lower temperature of 133.3°C. The DSC curves for 25% MBPF, 50% MBPF, and 60% MBPF showed shoulder exothermic signals (peak 1) at a lower temperature of around 133°C, which could have been due to the additional reactions of unreacted free formaldehyde with bio-oil
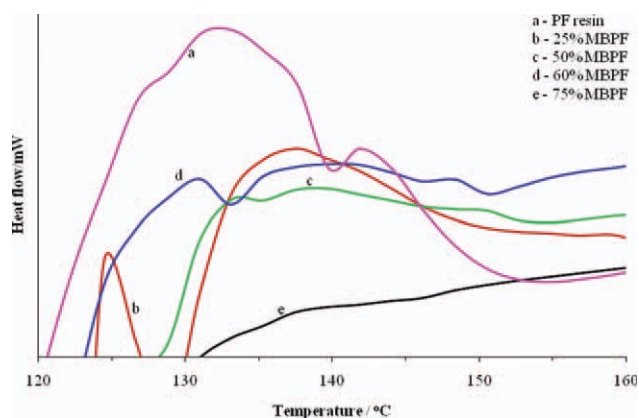

Figure 5 DSC curves for the different resin systems obtained at a heating rate of 5°C/min from 40 to 250°C with 50 mL/min of N_2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III
Characteristic Curing Temperatures of the PF, MBPF,
and BPF Resins

Type of resin	Characteristic curing temperatures (°C)		
	Peak 1	Peak 2	Peak 3
PF	133.3	141.9	—
25% MBPF	135.3	137.5	—
50% MBPF	133.1	139.6	150.5
60% MBPF	135.3	139.6	148.3
75% MBPF	—	139.6	—
25% BPF	133.2	135.4	—
50% BPF	131.0	137.5	—
75% BPF	—	146.2	—

and phenol and the methylolated phenolic components.[26] It can be observed from Figure 5 that 50% MBPF and 60% MBPF showed small signals (peak 3) around 150°C; these might have been due to the subsequent radical coupling reactions, for example, the condensation reaction between side chains and bio-oil to form ether bridges[27] and the breakage of dimethylene ether linkages and recondensation through the methylene bridges.[20,21,23] Interestingly, only one very weak exothermic peak was observed for 75% MBPF. As discussed previously, the properties of MBPF resins with high phenol substitution with bio-oil were governed by MB, whereas the MB contained many fewer active sites for crosslinking.

Thermal stability

The thermal stability of the MBPF resins was investigated with TGA by the heating of the sample from 25 to 700°C in an N_2 atmosphere. The corresponding thermogravimetry (TG) and derivative thermogravimetry (DTG) results are shown in Figures 6(a,b). The decomposition temperatures for various thermal events and the mass residue at 700°C are summarized in Table IV. As shown in Figure 6(a), the DTG curves for all of the resins similarly showed three thermal decomposition events, which reflected the three-step degradation of the phenolic resins: postcuring, thermal reforming, and ring stripping.[23,28] In this regard, for the pure PF resin, the first maximum thermal event at 214°C could be attributed to the postcuring reactions of the resin, which involved the removal of moisture and terminal groups and further crosslinking or condensation reactions, the transformation of ether bridges to methylene bridges with the simultaneous release of formaldehyde.[24] The second event, in the range from 300 to 460°C, could be ascribed to the thermal reforming to break the bridged methylene linkage; and the third event, in the range 460–650°C, was the main mass loss event due to the breakdown of the ring network. MBPF resins with a phenol substitution of 50% or lower exhibited very similar DTG profiles to those

of the pure PF resin, as reported previously for BPF resins with untreated bio-oil[5] with three thermal decomposition events at 70–300, 300–450, and 450–650°C. However, with an MB amount of greater than 50%, the MBPF resins exhibited similar DTG profiles as MB, especially for 75% MBPF. As displayed in Figure 6(b), the first of thermal event of MB occurred approximately between 160 and 330°C; this was larger than others, mostly because of the loss of free formaldehyde and the release of formaldehyde from the breakage of ether bridges to methylene and the second event, which was due to the breakdown of the side chains of bio-oil and the bridged methylene linkage in the bio-oils. Similarly, the third event at the higher temperature could have been caused by the breakdown of the ring network of the MB.

As for the carbon residues of these resins, the 25% MBPF resin had a slightly higher carbon residue (71%) at 700°C than the pure PF (66%). These results suggest that the addition of a small amount of MB could improve the thermal stability of the resol-type
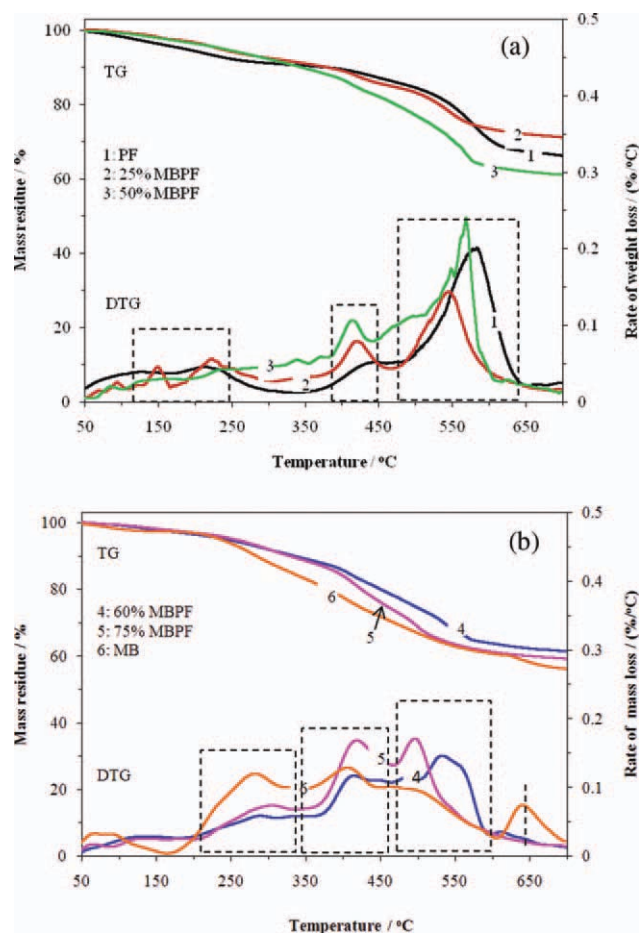

Figure 6 TG and DTG profiles of various MBPF resins obtained by heating from 25 to 700°C in 30 mL/min of N_2 atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE IV
TG and DTG Results of the MBPF Resins and MB Observed from Figures 6

Resin	DTG results			TG results
	First thermal event: T_p (°C)	Second thermal event: T_p (°C)	Third thermal event: T_p (°C)	Carbon residue at 700°C (%)
PF	214	432	585	66
25% MBPF	222	422	541	71
50% MBPF	224	414	548	61
60% MBPF	289	414	532	61
75% MBPF	304	418	496	59
25% BPF	236	418	548	72
50% BPF	240	393	535	61
75% BPF	240	466	616	48
MB	281	405	461	56

T_p, peak temperature.

phenolic resin. Even for the MBPF resins with a higher phenol substitution of greater than 25%, the carbon residues (59–61%) were still comparable with that of the pure PF resin. The BPF resins with a lower bio-oil content (≤50%) had similar carbon residues as the MBPF resins, as shown in Table III, but interestingly, the 75% MBPF had a higher carbon residue at 700°C (59%) than the 75% BPF (48%). This suggested that the thermal stability of the bio-oil phenolic resins could be improved by the methylolation treatment of the bio-oil before resinification.

Evaluation of the bond strength of the plywood samples glued with MBPF resins

Various MBPF resins and the reference PF resin were used as adhesives for plywood. The dry and wet tensile strengths of the plywood specimens were measured and are compared in Figure 7. The dry and wet wood failure percentages (WFPs) of all of the plywood specimens were also observed after tensile strength testing and are reported in Table V. As shown in Figure 7, both the dry and wet strengths for the MBPF resins (with ≤60% bio-oil) were comparable to those of PF. Under dry conditions, all of the plywood specimens with MBPF adhesives possessed better or very similar tensile strengths compared to those with the reference PF adhesive. All of the MBPF adhesives surpassed the minimum requirement of dry tension shear strength (i.e., 1.2 MPa) in accordance with JIS K-6852 for resol-type plywood adhesives. The wet tensile strengths of all of the MBPF resins also exceeded the minimum requirement of wet strength (i.e., 1.0 MPa). These results suggest that it is practically feasible for one to produce MBPF resins as plywood adhesives with 60% phenol replacement with MB without compromising the bond strength of the PF adhesives.

Table V lists the WFPs from these bond strength tests. Under the dry conditions, it was found that only the specimen with the adhesive of 25% MBPF performed comparably with that of the PF adhesive, which met the minimum requirement of WFP (>85%) for exterior-grade plywood products in accordance to U. S. Plywood Product Standard PS 1–83. However, for the adhesives of MBPF containing MB contents of 50 or 60%, the corresponding WFP dropped drastically to lower than 10%. In contrast, the specimens glued with adhesives of BPF resins showed much better WFP than the adhesives of MBPF resins under either dry or wet conditions. These results reveal that the MBPF adhesives were more sensitive to water than the PF and BPF adhesives. They could be used as adhesives for the production of interior wood products.

The plywood glued with an adhesive of 75% MBPF suffered from blowouts immediately after hot pressing, as displayed in Figure 8. In Figure 8, the wide, dark area represents a blowout of the upper glueline. As reported in our previous work,[5] plywood specimens bonded with BPF adhesives with
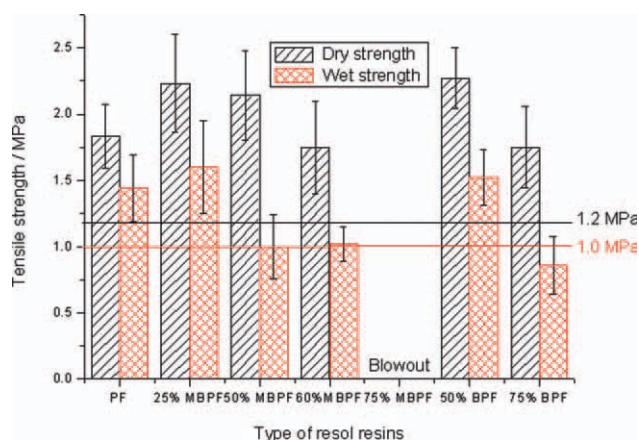

Figure 7 Tensile strength (dry and wet) of the plywood specimens bonded with MBPF and PF adhesives. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE V
WFPs of Plywood Glued with Various Resol Type (PF, MBPF, and BPF) Adhesives under Dry and Wet Conditions

Test condition	WFP[a]						
	Pure PF	25% MBPF	50% MBPF	60% MBPF	25% BPF	50% BPF	75% BPF
Dry[b]	89 (±19)	86 (±24)	8 (±12)	2 (±5)	97 (±13)	87 (±36)	22 (±33)
Wet[c]	65 (±43)	8 (±12)	0 (0)	0 (0)	33 (±42)	35 (±41)	15 (±31)

[a] Each value represents an average from 20 specimens. Standard deviations are given in parentheses.
[b] Testing after conditioning.
[c] Testing after boiling in water for 3.0 h.

up to 75 wt % phenol substitution had comparable dry and wet tensile strengths to those bonded with the PF adhesive. Thus, the results indicate that the methylolation treatment of bio-oil reduced the bonding strength of the BPF adhesives, especially for resins with a high phenol substitution. This could be explained by the recondensation of bio-oil via the methylol group in the process of the methylolation, which resulted in fewer linking sites, as evidenced by the higher average molecular weight of MB (Fig. 2), the high viscosity (Table II), and the small thermal curing peak (Fig. 5) for the 75% MBPF.

As shown, the bio-oil- and MB-based phenolic resins with high substitutions of phenol of up to 75 and 60% demonstrated similar or comparable properties to the pure PF resin. The phenol substitution ratio was higher than that in others' work with lignin. This can be explained from the effect of the thermal conversion processes. Lots of studies[29–31] on the production bio-phenolic resin with pyrolysis oil have shown that it is only feasible if the phenol substitution level is below 50% in the resin synthesis; otherwise, the properties of the resin will be significantly affected. To our knowledge, pyrolysis oils are highly complex mixtures, which have been reported to contain hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids, and phenolics. The molecular weights of pyrolysis oil reside in the range of several hundreds to 5000 or more, depending on the conditions.[32] This may cause the low reactivity and the low substitution. In contrast, solvolytic liquefaction processes performed in an organic solvent, such as water, alcohol, acetone, or cosolvent, produced a uniform and high-quality bio-oil with more phenolic compounds of lower molecular weights. In this study, bio-oil was derived from a solvolytic liquefaction process, which was carried out in 50/50 (v/v) water–ethanol at 300°C. A high yield of bio-oil (68%) with low molecular weights ($M_n = 342$ g/mol and $M_w = 1072$ g/mol) was produced. Therefore, the high reactivity of the bio-oil used in this study may have contributed to the higher phenol substitution ratio.

CONCLUSIONS

^{1}H-NMR analysis of the bio-oil before and after methylolation demonstrated that the methylolation

treatment increased the methylol groups. The GPC analysis of the bio-oil and MB suggested that condensation reactions occurred to the bio-oil during the methylolation treatment. All of the MBPF resins showed similar nonvolatile contents as the pure PF. Although the MBPF resins containing MB at contents greater than 25% precipitated in about a week at 4°C, the resins could become liquid again by reheating.

The experimental MBPF resol resins could be cured in the range from 128 to 155°C. All of the MBPF resol resins exhibited a lower curing temperature and better or comparable thermal stability than the PF resin. Interestingly, the 75% MBPF showed a higher carbon residue at 700°C (59%) than the 75% BPF (48%). This suggested that the methylolation treatment of bio-oil could improve the thermal stability of bio-phenolic resins. When used as plywood adhesives, the MBPF resins with 60% substitution for phenol proved to be effective without compromising the bond strength (dry and wet tensile strengths) of the plywood specimens. However, the MBPF adhesives were more sensitive to water than the PF and BPF adhesives.

Figure 8 Blowout of plywood glued with the adhesive of 75% MBPF after hot pressing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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