

Characterization of novolac type liquefied wood/phenol/formaldehyde (LWPF) resin

Hui Pan · Todd F. Shupe · Chung-Yun Hse

Received: 4 July 2008 / Published online: 5 May 2009
© Springer-Verlag 2009

Abstract Novolac type liquefied wood/phenol/formaldehyde (LWPF) resins were synthesized from liquefied wood and formaldehyde. The average molecular weight of the LWPF resin made from the liquefied wood reacted in an atmospheric three neck flask increased with increasing P/W ratio. However, it decreased with increasing phenol/wood ratio when using a sealed Parr reactor. On average, the LWPF resin made from the liquefied wood reacted in the Parr reactor had lower molecular weight than those from the atmospheric three neck flask. The infrared spectra of the LWPF resins were similar to that of the conventional novolac resin but showed a major difference at the 1800–1600 cm⁻¹ region. These results indicate that liquefied wood could partially substitute phenol in the novolac resin synthesis. The composites with the liquefied wood resin from the sealed Parr reactor yielded higher thickness swelling than those with the liquefied wood resin from the three neck flask likely due to the hydrophilic wood components incorporated in it and the lower cross-link density than the liquefied wood resin from the three neck flask during the resin cure process.

H. Pan (✉)
Calhoun Research Station, Louisiana State University
Agriculture Center,
321 Highway 80 E,
Calhoun, LA 71225, USA
e-mail: Hpan@agcenter.lsu.edu

T. F. Shupe
School of Renewable Natural Resources, Louisiana State
University Agriculture Center,
Baton Rouge, LA 70803, USA

C.-Y. Hse
Southern Research Station, USDA Forest Service,
Pineville, LA 71360, USA

Beschreibung von novolakartigem verflüssigtem Holz/Phenol/Formaldehyd-Harz (LWPF)

Zusammenfassung Novolakartige LWPF-Harze wurden aus verflüssigtem Holz und Formaldehyd synthetisch hergestellt. Das mittlere Molekulgewicht des LWPF-Harzes, das aus verflüssigtem Holz in einem atmosphärischen Dreihals-Kolben hergestellt worden war, nahm mit steigendem Phenol/Holz-Verhältnis (P/W) zu, wohingegen es bei der Herstellung in einem versiegelten Parr Reaktor mit steigendem P/W-Verhältnis abnahm. LWPF-Harz, das aus verflüssigtem Holz in einem Parr Reaktor hergestellt worden war, hatte durchschnittlich ein niedrigeres Molekulgewicht als LWPF-Harz, das in einem atmosphärischen Dreihals-Kolben hergestellt worden war. Die Infrarot-Spektren der LWPF-Harze ähnelten denjenigen von konventionellem Novolak Harz, unterschieden sich jedoch im 1800–1600 cm⁻¹ Bereich deutlich. Diese Ergebnisse zeigen, dass das Phenol bei der Synthese von Novolak-Harz teilweise durch verflüssigtes Holz ersetzt werden kann. Verbundwerkstoffe mit LWPF-Harz, das aus verflüssigtem Holz im versiegelten Parr Reaktor hergestellt worden war, wiesen eine höhere Dickenquellung auf als diejenigen mit LWPF-Harz, das im Dreihals-Kolben hergestellt worden war. Der Grund besteht wahrscheinlich in den im Vergleich zu LWPF-Harz aus dem Dreihals-Kolben eingebundenen hydrophilen Holzbestandteilen und der niedrigeren Vernetzungsdichte während der Aushärtung.

1 Introduction

With the diminishing supply of crude oil and environmental concerns, biomass has been studied and considered a renewable source for fuels and chemicals to substitute for petroleum-based products. Biomass can be converted

to liquid and gaseous products that can then be used directly in internal-combustion engines or for organic synthesis (Rustamov et al. 1998). The technique of wood liquefaction in the presence of an organic solvent is one of the thermochemical conversion processes of biomass and has been studied by many researchers for several decades (Pu and Shiraishi 1993, Alma et al. 1998, Lin et al. 2001). Compared to other thermochemical biomass conversion processes like pyrolysis and gasification, liquefaction of biomass dissolves biomass in an organic solvent at moderate temperature from 120 to 250 °C (Rezzoug and Capart 2002). Partial liquefaction of biomass provides valuable chemicals, mainly pure cellulose and phenolic compounds, and complete liquefaction provides fuels (Rezzoug and Capart 1996).

Liquefied wood can be applied as a precursor in preparing various products, such as phenolic resins and polyurethane foams, depending on the reagent solvent used in the liquefaction. Novolac type liquefied wood resin can be prepared from the condensation reaction of formaldehyde and liquefied wood using phenol as the reagent solvent. Some studies have been done to investigate the effects of several variables, such as phenol to formaldehyde molar ratio, and catalyst concentration on the physical properties of liquefied wood/phenol/formaldehyde (LWPF) resin and mechanical properties of the molded products from LWPF resin (Alma et al. 1995, Lin et al. 1995a, Lee et al. 2000). It has been reported that the further condensation reaction of liquefied wood and formaldehyde is an effective method to convert the unreacted phenol (i.e., free phenol) remaining from the liquefaction stage and therefore, greatly improve the thermal flow properties and the mechanical properties of the original liquefied wood (Lin et al. 1995a).

Despite many advances in LWPF resin, some fundamental aspects of this new resin system are still lacking. The objective of this study was to characterize the LWPF resins by gel permeation chromatography (GPC) and Fourier trans-

form infrared (FT-IR) and investigate the effects of different reaction conditions during liquefaction stage on the above characteristics of the LWPF resins. The physical and mechanical properties of the composite using LWPF resin were also investigated in this study.

2 Materials and methods

2.1 Materials

Chinese tallow (*Triadica sebifera* syn. *Sapium sebiferum*) tree wood was sawn on a table saw and the sawdust was collected. The particles were oven-dried at 105 °C to a moisture content of 3–5% and then reduced in a Wiley mill to fine powder of 20–200 mesh and used for both wood liquefaction and filler of the composites. Liquid industrial grade phenol (90% concentration) was used as the liquefaction reagent. Formaldehyde used in the resin synthesis was 37% aqueous solution. All other chemicals were of reagent grade.

2.2 Wood liquefaction and synthesis

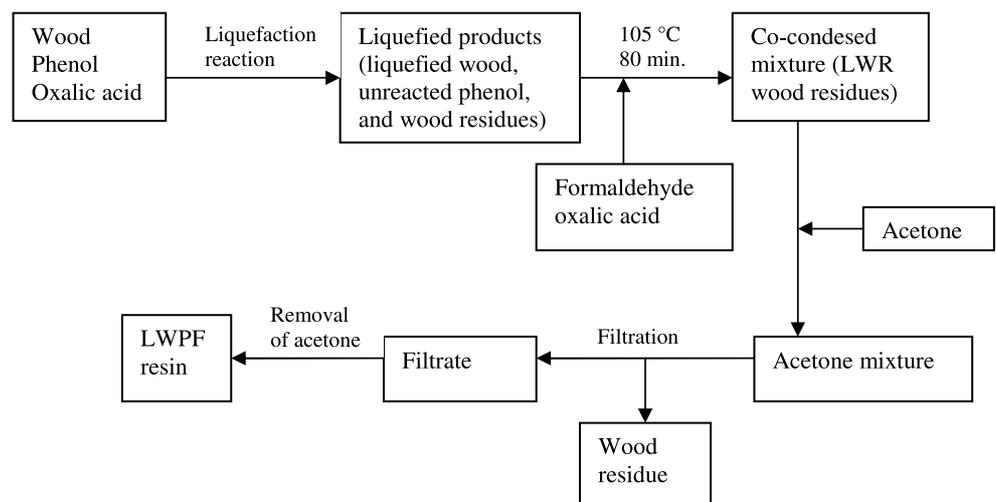
of liquefied wood/phenol/formaldehyde (LWPF) resins

The procedures of wood liquefaction and LWPF resin synthesis are shown in Fig. 1. The detailed procedures were described in our previous papers (Pan et al. 2007, 2008). Two liquefaction temperatures (150 and 180 °C), two type of reactors (1 l atmospheric three-neck flask and 1 l sealed Parr reactor), and three phenol to wood ratios (1/1, 2/1, and 3/1, w/w) were investigated during the liquefaction stage.

2.3 High performance liquid chromatography (HPLC)

The amount of free phenol (i.e., unreacted phenol) in the liquefied wood mixture was measured on a Perkin Elmer series

Fig. 1 Flowchart of LWPF resin preparation
Abb. 1 Ablaufdiagramm der Herstellung von LWPF-Harz



200 HPLC with an Alltima HP C18 ODS column (250 × 4.6 mm). Methanol/water (2/1, v/v) mixture was used as the mobile phase with the flow rate of 1.0 ml/min. The wavelength of the UV-Vis detector in the HPLC series was set at 272 nm. A series of phenol solutions of known concentration (0.06, 0.1, 0.15, 0.3, 0.5, and 0.7%) were used as the standard to calculate the amount of free phenol. The percentage of free phenol in liquefied wood mixture was calculated with the following equation:

$$\text{Free Phenol Percent (\%)} = \frac{W_{\text{ph}}}{W_{\text{lw}}} \times 100$$

where W_{ph} is the weight of free phenol measured by HPLC and W_{lw} is the weight of liquefied wood mixture.

2.4 Gel permeation chromatography (GPC)

The molecular weight and molecular weight distribution of the LWPF resins were measured on a Waters-Wyatt GPC system equipped with a differential refraction index detector. Two Jordi Flash Gel Mixed Bed columns (250 mm × 10 mm) were used in series. Tests were conducted at ambient temperature using tetrahydrofuran (THF)/methanol (90/10) mixture as the mobile phase at a flow rate of 1.0 ml/min. LWPF resin samples were dissolved in the same solvent as the mobile phase at a concentration of 5 mg/ml in solution. The amount of each sample injection was 100 µl. Polystyrene standards with a concentration of 1 mg/ml were used for calibration (molecular weight as follows: 393.4 k, 223.2 k, 111.4 k, 44.1 k, 31.6 k, 13.2 k, 3.68 k, 2.33 k, and 820).

2.5 Fourier transform infrared spectroscopy (FT-IR)

The FT-IR analysis of the LWPF resin was performed by a Nicolet Nexus 670 spectrometer equipped with a Thermo Nicolet Golden Gate MKII Single Reflection ATR accessory. A small amount of resin was applied directly on the diamond crystal.

2.6 Preparation of bio-composite and test of physical and mechanical properties

The preparation of bio-composite using LWPF resin was the same as in our previous study (Pan et al. 2005). LWPF

resin made from phenol/wood ratio of 2/1 was chosen to prepare the bio-composite considering the performance/cost value of the products. Flexural and tensile test were performed using an Instron-4465 test machine in accordance with ASTM D 1037-96 (1996). Each panel was cut to yield two static-bending specimens (1/2 × 5 in.) and two tensile test specimens (1/2 × 5 in.). Data for modulus of rupture (MOR) and modulus of elasticity (MOE) were automatically collected and computed by the Instron Series IX Automated Materials Tester program. Two specimens (1/2 × 5 in.) from each panel were chosen for dimensional stability test (i.e., 24 h soaking and 2 h boiling). The thickness of the specimens before and after the tests was measured. The percent of thickness swelling was calculated by the following equation.

$$TS(\%) = \frac{T_1 - T_0}{T_0} \times 100$$

where TS is the percent of thickness swelling and T_0 and T_1 are the thickness of the specimen before and after the test, respectively.

3 Results and discussion

3.1 Amount of free phenol in liquefied wood

The percentage of free phenol in the liquefied wood mixture is listed in Table 1. It can be seen that phenol to wood ratio (P/W) had significant effects on the amount of free phenol in the liquefied wood. In general, the average amount of free phenol increased as the P/W ratio increased except for the liquefied wood from Parr reactor at P/W ratio 2/1 under 150 °C and from three neck flask at P/W ratio 2/1 under 180 °C. This result was expected since the absolute amount of phenol used in the liquefaction increased with increasing P/W ratio and an excessive amount of phenol was necessary in the liquefaction in order to achieve a satisfied liquefaction (Lin et al. 1995a). It was also expected that the extent of liquefaction reaction (i.e., amount of solid wood converted to liquid) would increase as the P/W ratio increased (Pan et al. 2007). The amount of free phenol had a significant effect on the polymerization reaction of liquefied wood mixture with formaldehyde during the LWPF resin synthesis process.

Table 1 Average percentage of free phenol in liquefied wood mixture

Tabelle 1 Durchschnittlicher Anteil an freiem Phenol (in Prozent) in verflüssigten Holzmischungen

	150 °C			180 °C		
	1/1	2/1	3/1	1/1	2/1	3/1
A ^a Free phenol (%)	56.21	63.02	69.47	55.50	54.73	70.12
P ^b Free phenol (%)	54.79	51.12	62.80	50.94	64.61	68.28

^a Liquefaction in the atmospheric three neck flask

^b Liquefaction in the sealed Parr reactor

Table 2 Average molecular weight and polydispersity (Mw/Mn) of the LWPF resins
Tabelle 2 Durchschnittliches Molekulgewicht und Polydispersität (Mw/Mn) der LWPF Harze

	P/W ^b	Three neck flask ^c			Parr reactor ^c		
		Mn	Mw	Mw/Mn	Mn	Mw	Mw/Mn
150 °C ^a	1/1	1207.5	2378.3	1.97	1336.7	3822.5	2.86
	2/1	1454.3	3476.6	2.39	1284.5	2692.9	2.09
	3/1	1589.7	3920.8	2.46	1224.6	2644.8	2.13
180 °C ^a	1/1	1277.6	2794.8	2.19	1246.2	3052.1	2.44
	2/1	1458.1	3720.8	2.55	1270.0	3679.9	2.89
	3/1	1489.9	3831.5	2.56	1118.9	2249.7	2.00

^a Temperature of wood liquefaction reaction

^b Phenol to wood ratio in wood liquefaction reaction

^c Two types of reactors used in wood liquefaction reaction

3.2 Molecular weight and molecular weight distribution of LWPF resins

The number average (Mn), weight average (Mw) molecular weight, and the polydispersity (Mw/Mn) of the LWPF resins were calculated from the polystyrene calibration curve and the results are given in Table 2. It can be seen that the LWPF resin made from the liquefied wood using two types of reactors had opposite trends for Mn and Mw as the P/W ratio changed from 1/1 to 3/1. The Mn and Mw of the LWPF resin from the three neck flask increased while they slightly decreased with the liquefied wood from the Parr reactor as the P/W ratio increased with the only exception of the LWPF from liquefied wood in Parr reactor at P/W ratio 2/1 under 180 °C. Figure 2 illustrates the changes in GPC chromatograms of the LWPF from (a) three neck flask system and (b) Parr reactor system with the change of P/W ratio. Figure 3 shows the difference between the GPC chromatograms of the LWPF resins made from the liquefied wood conducted in two different reactors at a P/W ratio of (a) 1/1 and (b) 3/1. All of the GPC chromatograms of the LWPF resins present similar shapes of two board peaks and are partially overlaid on each other. This lack of separation between different species is a typical behavior of phenolic resin in conventional GPC and results from the multiplicity of phenolic resin species having similar hydrodynamic volumes (Myers et al. 1991).

It can be assumed that there were two different effective compositions in the liquefied wood mixture that may react with formaldehyde during the polymerization process: free phenol remaining from the liquefaction stage and the decomposed wood lignin that has similar structure to phenol but with C3 and/or C5 position blocked by methoxyl groups. Therefore, liquefied wood should be less active than phenol in the polymerization reaction because of fewer reaction sites and steric hindrance. Based on the results from our previous paper (Pan et al. 2007), wood liquefaction conducted in the Parr reactor has a greater extent of liquefaction. More wood components have been decomposed into liquid and consumed more phenol in this system than those in the three neck flask system. As a result, it is very likely that the poly-

merization reaction between free phenol and formaldehyde dominated the resin synthesis process of the LWPF resin made from liquefied wood using the three neck flask (i.e., with higher free phenol content), and therefore, the average molecular weight increased with the increased amount of free phenol as the P/W ratio increased. Similar result has also been reported by Lin et al. (1995a). Compared to the three neck flask, the polymerization reaction in the resin synthesis system with the liquefied wood from the Parr reactor was less effective because of the existence of large amounts of decomposed wood components. Consequently, it has lower average molecular weight than those of LWPF made from the liquefied wood using the atmospheric three neck flask.

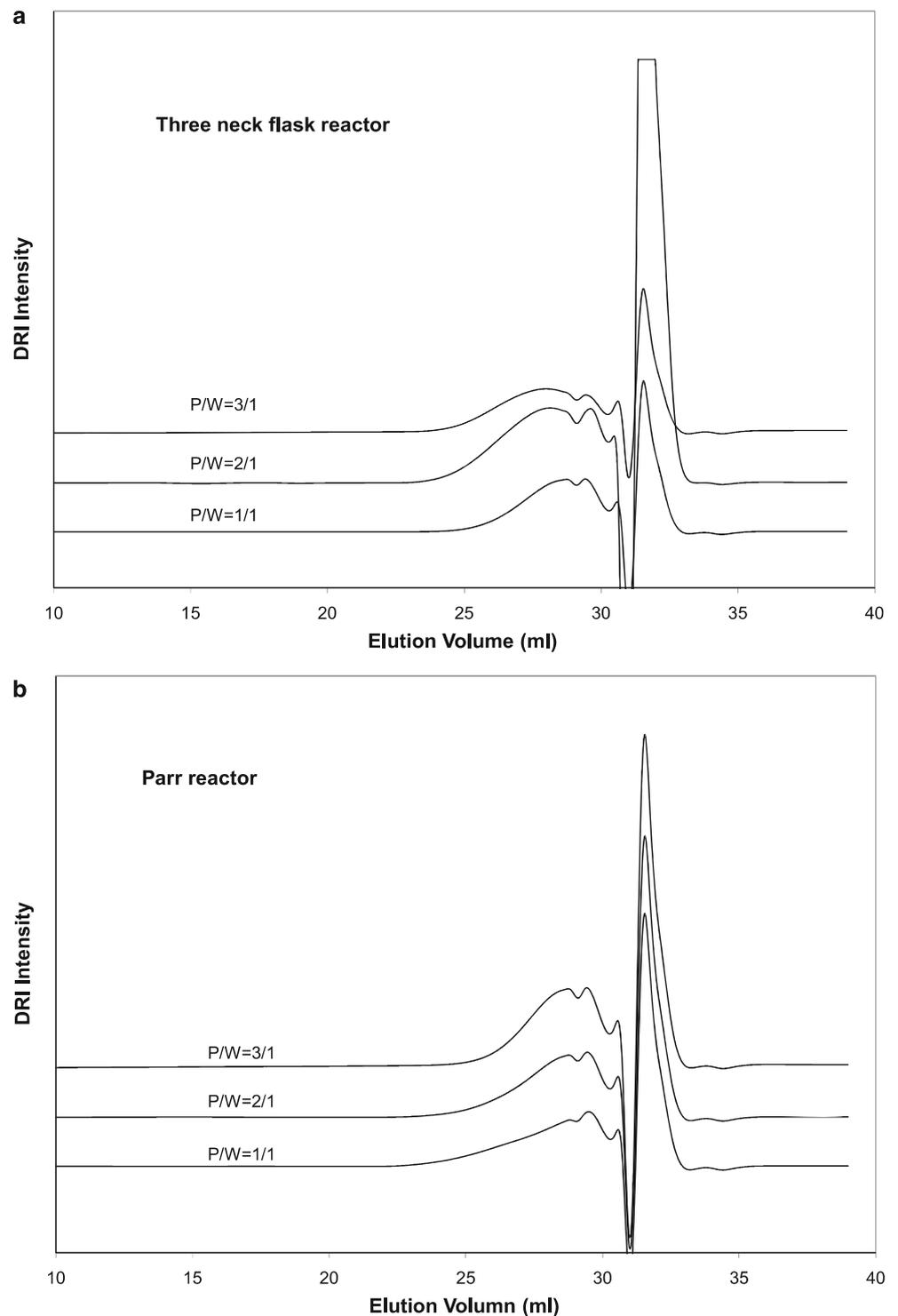
3.3 FTIR spectroscopy

The assignment of the main bands in the FT-IR spectra of the LWPF resins are summarized in Table 3 based on the literature.

In general, the novolac-type LWPF resin showed a similar FT-IR absorbance to that of a conventional novolac resin. However, with the incorporation of wood components, the FT-IR spectra of the LWPF resin contained some different bands compared with that of the conventional novolac resin. Figure 4 shows the FT-IR spectra of two typical LWPF resins compared with a conventional novolac resin. The major difference in the spectra between the LWPF resin and conventional novolac is the absorbance in the carbonyl region. Moreover, changes in the liquefaction conditions resulted in LWPF resin with a different absorbance pattern in this region. As shown in Fig. 4, the LWPF resin made from the liquefied wood reacted in the atmospheric three neck flask had three peaks at 1735, 1697, and 1654 cm⁻¹ due to the ester carbonyl stretch, aryl ketone or aldehyde carbonyl stretch, and the di-substituted alkene C=CH₂, respectively. The LWPF resin made from the liquefied wood reacted in the sealed Parr reactor showed one broad peak centered at 1708 cm⁻¹ mainly due to the aryl aldehyde C=O stretch. However, the conventional novolac resin showed no absorbance in this region as expected. The spectra of

Fig. 2 GPC chromatogram of LWPF resins made from the liquefied wood using **a** atmospheric three neck flask and **b** sealed Parr reactor at different P/W ratios

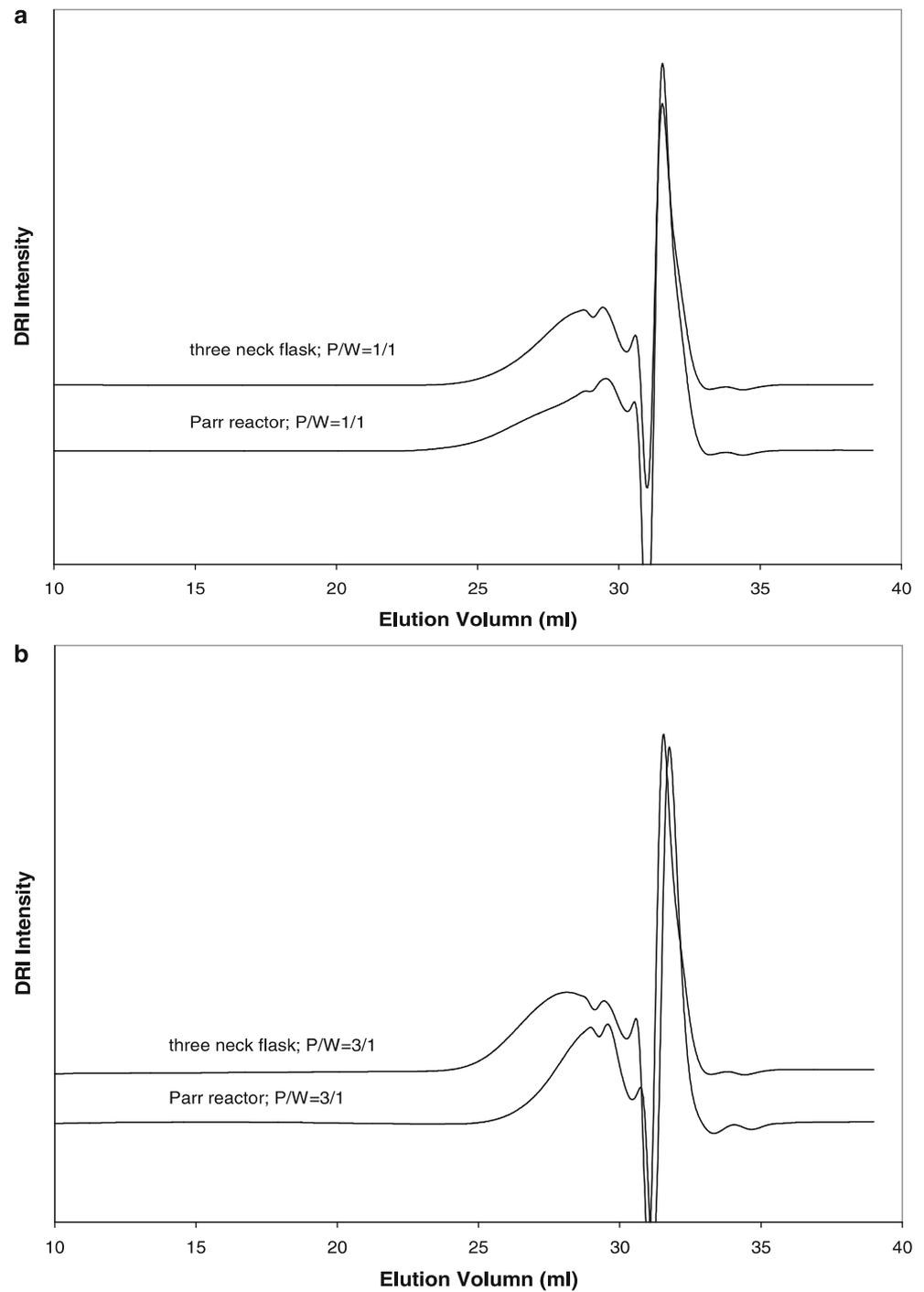
Abb. 2 GPC-Chromatogramme der LWPF-Harze, die aus verflüssigtem Holz im **a** atmosphärischen Dreihals-Kolben und **b** versiegelten Parr Reaktor mit unterschiedlichen Phenol/Holz-Verhältnissen (P/W) hergestellt worden waren



the LWPF resin also showed two weak bands at 1475 and 885 cm^{-1} caused by tetra substituted (1, 2, 4, and 6) ring which did not occur in the spectra of novolac resin. A possible explanation for this result could be the existence of some lignin fragments, most of which are tetra substituted aromatic rings in the LWPF resin. A sharp peak at 691 cm^{-1}

in the spectra of the LWPF resin represents the mono substituted aromatic ring (i.e., phenol). This peak diminished in the spectra of novolac resin, indicating that the LWPF resin synthesized in this study contained a higher amount of free phenol than the conventional novolac resin. Based on the above discussion, the absorbance at 1735 , 1708 , 1697 ,

Fig. 3 Comparison of GPC chromatograms of LWPF resins using two types of reactors at a P/W ratio of **a** 1/1 and **b** 3/1
Abb. 3 Vergleich der GPC-Chromatogramme von LWPF-Harzen, die nach den zwei verschiedenen Verfahren mit einem P/W Verhältnis von **a** 1/1 und **b** 3/1 hergestellt worden waren



1654, 1475, and 885 cm^{-1} are very likely associated with the wood components that reacted with phenol during the liquefaction reaction.

Figure 5 shows the spectra of the LWPF resin made from liquefied wood reacted at different phenol to wood (P/W) ratios during the liquefaction stage. As shown in Fig. 5a (three neck flask), the peaks at 2838 and 1436 cm^{-1} , which are associated with CH_2 stretch and bending, have a higher in-

tensity at P/W ratio 3/1 and 2/1 than P/W ratio 1/1. A sharp peak at 1697 cm^{-1} occurred in the spectra of the LWPF resin from P/W ratio 2/1, and the intensity of this peak increased dramatically when the P/W ratio increased to 3/1. Meanwhile, the peak at 1654 cm^{-1} diminished from P/W ratio 1/1 to 2/1 and almost disappeared in the spectra of LWPF resin from P/W ratio 3/1. The other two peaks that increased in intensity with an increase of P/W ratio are 1475

Table 3 FT-IR assignment of the LWPF resin**Tabelle 3** FT-IR-Banden des LWPF-Harzes

Wavenumber (cm ⁻¹)	Assignment	References
3350	Phenolic and methylol –OH stretch	Holopainen et al. 1998
3017	Aryl–H stretch	Crews et al. 1998
2916	Aliphatic –CH ₂ asymmetric stretch	Crews et al. 1998; Kristkova et al. 2004;
2838	Aliphatic –CH ₂ symmetric stretch	Costa et al. 1997
1735	Ester C=O stretch	Pecsok and Shield 1968
1708	Aryl aldehyde C=O stretch	
1697	Aryl aldehyde, ketone C=O stretch	
1654	di-substituted C=C (<i>gem</i>) stretch	
1610	Aromatic C=C stretch	Holopainen et al. 1998;
		Kristkova et al. 2004;
1510	Semicircle aromatic C=C stretch	Costa et al. 1997;
		Poljansek and Krajnc 2005
1475	Tetra substituted ring	Kristkova et al. 2004
1456	Semicircle ring stretch	
1436	Aliphatic –CH ₂ scissor bending	Costa et al. 1997
1350	Phenolic OH in plane deformation	Kristkova et al. 2004;
		Pecsok and Shield 1968
1328	CH ₃ attached to the aromatic ring	Kristkova et al. 2004
1215	Phenolic OH bending, C–O stretch	Pecsok and Shield 1968
1168	Alkyl-phenol C–O stretch	Costa et al. 1997
1099	Aromatic CH in plane deformation	Holopainen et al. 1998;
		Kristkova et al. 2004
1040	Single bond C–O stretch, –CH ₂ OH vibrations	Poljansek and Krajnc 2005
1013	Aliphatic ethers C–O–C stretch	Pecsok and Shield 1968
940	–CH=CH ₂	
908	Aliphatic CH ₂ wag	Kristkova et al. 2004
885	Tetra substituted ring	Holopainen et al. 1998;
		Poljansek and Krajnc 2005
811	Adjacent 2H, para-substituted	Holopainen et al. 1998;
753	Adjacent 4H, ortho-substituted	Haslam and Willis 1965
691	Adjacent 5H, phenol	Holopainen et al. 1998;
		Poljansek and Krajnc 2005

Fig. 4 Comparison of FTIR spectra of typical LWPF resins with conventional novolac resin
Abb. 4 Vergleich der FTIR-Spektren typischer LWPF-Harze mit konventionellem Novolak Harz

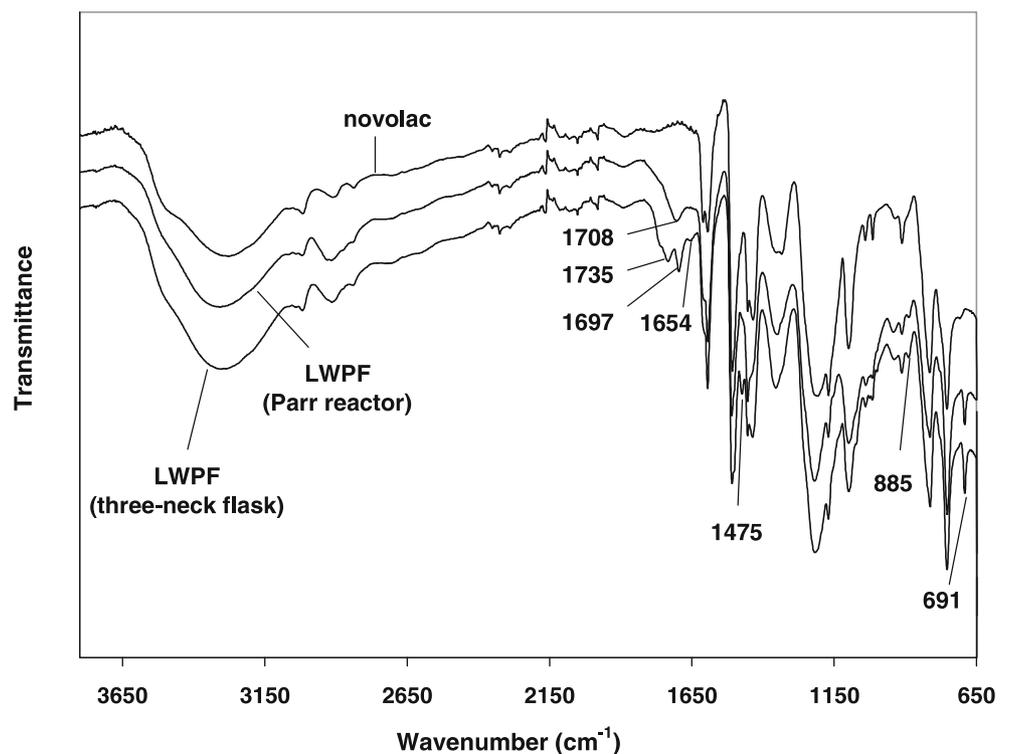
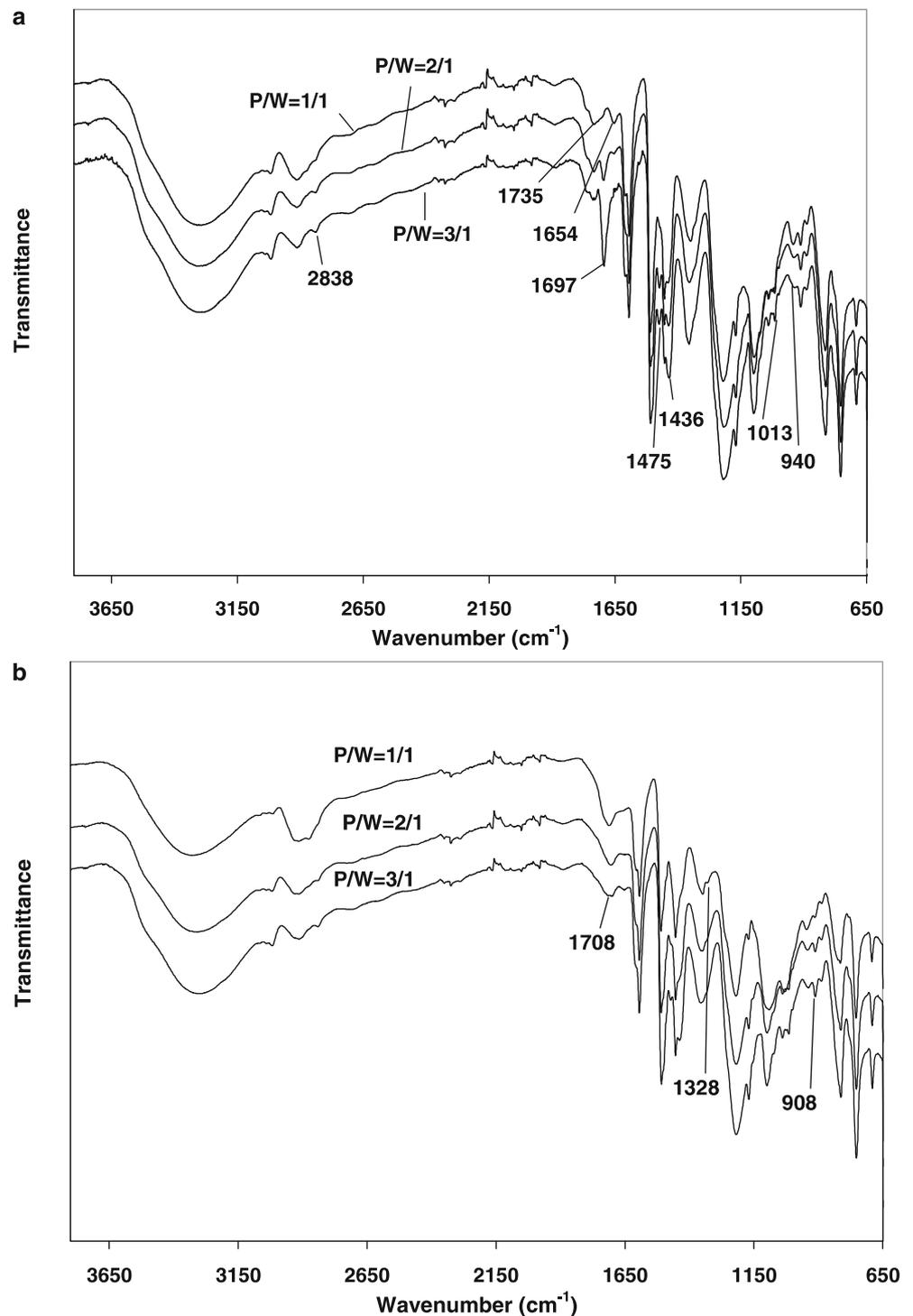


Fig. 5 FTIR spectra of LWPF resins at different P/W ratios: **a** three neck flask, 150 °C; **b** Parr reactor, 150 °C
Abb. 5 FTIR-Spektren von LWPF-Harzen mit unterschiedlichen P/W Verhältnissen **a** Dreihals-Kolben, 150 °C, **b** Parr Reaktor, 150 °C



and 1013 cm^{-1} , which were caused by a tetra substituted ring and an ether C-O-C stretch, respectively. On the contrary, peaks at 1654 and 940 cm^{-1} , due to the di-substituted alkene and $-\text{CH}=\text{CH}_2$ alkene, respectively, decreased in intensity as the P/W ratio increased.

The LWPF resin from the sealed Parr reactor did not exhibit significant differences in the FT-IR spectra among the

three P/W ratios (Fig. 5b). Similar to the LWPF resin from three neck flask, the absorbance at 2838 , 1475 , 1436 , and 1013 cm^{-1} showed a weak increasing trend as the P/W ratio increased. Unlike the spectra of the LWPF resin from the three neck flask system, a weak band at 1328 cm^{-1} occurred in the spectrum of the LWPF resin from the sealed Parr reactor at P/W ratio 1/1 while it disappeared in the spectra of

that from P/W ratios 2/1 and 3/1. On the other hand, the absorbance at 908 cm^{-1} due to the aliphatic CH_2 wag occurred as an intense peak in the spectra of the LWPF resin from P/W ratio 2/1 and 3/1, but decreased in intensity as the P/W ratio decreased to 1/1.

As described in our previous paper (Pan et al. 2007), liquefaction reaction conducted in an atmospheric three neck flask and a sealed Parr reactor underwent different liquefaction mechanisms. The FT-IR spectra of the LWPF resins made from the liquefied wood reacted in these two systems also implied different reactions in the liquefaction stage of the two systems (Fig. 5). The spectra of the LWPF resin from the three neck flask showed an absorbance at 1735 cm^{-1} due to the ester carbonyl groups in the carbohydrate components in wood, which does not occur in the spectra of the LWPF resin from the Parr reactor. This result is consistent with the FT-IR result of the liquefied wood residues in our previous study (Pan et al. 2007), indicating that the ester carbonyl groups have been broken down during the liquefaction reaction in the Parr reactor. It is also noted that the LWPF resin from the three neck flask exhibited three bands in the $1800\text{--}1600\text{ cm}^{-1}$ region (i.e., 1735 , 1697 , and 1654 cm^{-1}) while the LWPF resin from the Parr reactor only showed one peak at 1708 cm^{-1} in the same region, which might be due to the different liquefaction extent of the carbohydrate components of wood.

3.4 Physical and mechanical properties of the bio-composite

Table 4 presents the mechanical properties of the composites using LWPF resin as the matrix resin. No apparent trends were observed for the flexural and tensile strengths of the composites in this experiment. This lack of consistency could be attributed to the complicated compositions of the LWPF resins and/or the un-uniform panel density caused by manual preparation of the panel mats. It is interesting to note that although two types of reactors showed opposite trends to each other for flexural MOR or MOE, each individual reactor displayed consistent trends for both MOR and MOE. In other words, the composites with the liquefied wood resin from the atmospheric three neck flask showed higher MOR and MOE at higher liquefaction temperatures. On the contrary, the composites showed a slightly lower MOR and MOE with the liquefied wood resin from

the sealed Parr reactor at higher liquefaction temperatures. The tensile strength of the composites exhibited similar trends in flexural strength. The composites with the liquefied wood resin from the atmospheric three neck flask had increased MOR and MOE when the liquefaction temperature increased from 150 to $180\text{ }^\circ\text{C}$. However, the composites with the liquefied wood resin from the sealed Parr reactor had slightly decreased MOR and slightly increased MOE with the increasing liquefaction temperature.

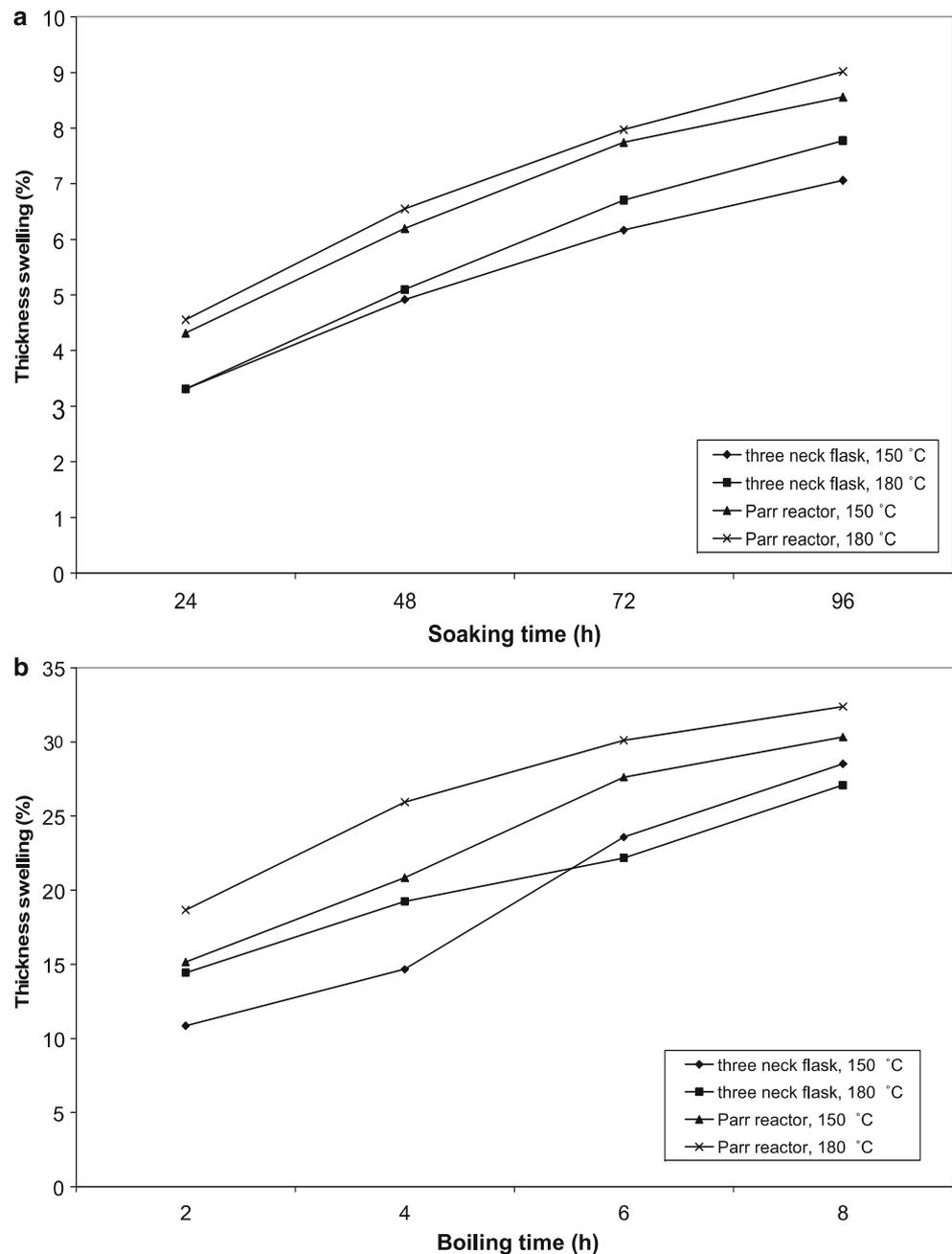
Figure 6 illustrates the dimensional stabilities of the composites in (a) soaking and (b) boiling tests. The composites with the liquefied wood resin from the sealed Parr reactor yielded higher thickness swelling than those with the liquefied wood from the three neck flask in both soaking and boiling test. On average, the composites with the liquefied wood resin under higher liquefaction temperature had higher thickness swelling. These results are understandable. Wood is a type of hydrophilic material due to the large amount of hydroxyl groups in the major wood components. It could be assumed that liquefied wood resin would retain the hydrophilic characteristic from wood. Based on the liquefaction results of our previous paper (Pan et al. 2007), the liquefaction reaction conducted in the sealed Parr reactor had a greater liquefaction extent than that in the three neck flask. Therefore, the composites with the liquefied wood resin containing more wood components would be more easily accessible to water and resulted in a higher thickness swelling. A similar result was also reported by another researcher (Lin et al. 1995b). In addition to the hydrophilic feature of the matrix resin, the cross-link density within the matrix resin and between the matrix resin and wood filler is also a critical factor for the dimensional stability of the composites.

As discussed in the GPC result of the LWPF resin, the condensation reaction between free phenol and formaldehyde could be the dominant reaction during the resin synthesis process of the liquefied wood from the three neck flask. In the meantime, there would be a large amount of wood components incorporated into the liquefied wood resin during the resin synthesis process of the liquefied wood from the Parr reactor, which was shown in the FT-IR results of the LWPF resins. In addition, the LWPF resins from the Parr reactor had lower average molecular weight than those from the three neck flask reactor. Therefore, the liquefied wood resin with more wood components and lower average mo-

Table 4 Flexural and tensile strength of the composites using different liquefied wood resin
Table 4 Biege- und Zugfestigkeit von Verbundwerkstoffen mit unterschiedlich hergestellten LWPF

	Three neck flask				Parr reactor			
	Flexural		Tensile		Flexural		Tensile	
	MOR	MOE	MOR	MOE	MOR	MOE	MOR	MOE
	(psi)		(psi)		(psi)		(psi)	
$150\text{ }^\circ\text{C}$	8,008	934,279	6,308	530,711	9,090	1,193,544	6,357	613,410
$180\text{ }^\circ\text{C}$	10,305	1,252,251	7,369	645,472	8,890	1,131,397	6,203	625,624

Fig. 6 Thickness swelling of the composites as a function of **a** soaking and **b** boiling time
Abb. 6 Dickenquellung der Verbundwerkstoffe in Abhängigkeit von **a** der Dauer der Wasserlagerung und **b** der Kochdauer



lecular weight would yield less cross-link density during the resin cure process due to less reaction sites compared with the liquefied wood resin with a lower wood component content and higher average molecular weight.

4 Conclusion

Different liquefaction conditions have significant effects on the characteristics of LWPF resin. The average molecular weight of the LWPF resin made from the liquefied wood

reacted in the atmospheric three neck flask increased with increasing P/W ratio. However, it decreased with increasing P/W ratio when using the sealed Parr reactor. On average, the LWPF resin made from the liquefied wood reacted in the Parr reactor had lower molecular weight than those from the atmospheric three neck flask. The FT-IR spectra of the LWPF resins are similar to that of the conventional novolac resin but also showed a major difference at the 1800–1600 cm^{-1} region. The LWPF resin made from the atmospheric three neck flask exhibited three peaks at 1735, 1697, and 1654 cm^{-1} in this region while the LWPF

resin from the sealed Parr reactor had only one broad peak centered at 1708 cm^{-1} . These results indicated the incorporation of wood components into the LWPF resin and different liquefaction species occurred in different reactor systems. It is also shown that liquefied wood could be used as a substitute of phenol in novolac resin synthesis. The composites with the liquefied wood resin from the sealed Parr reactor yielded higher thickness swelling than those with the liquefied wood resin from the three neck flask likely due to the hydrophilic wood components incorporated in it and the lower cross-link density than the liquefied wood resin from the three neck flask during the resin cure process.

Acknowledgement The authors are grateful for the assistants of Dr. Rafael Cueto at Louisiana State University Chemistry Department in the GPC work of this study.

References

- Alma MH, Yoshioka M, Yao Y, Shiraishi N (1995) Preparation of oxalic acid catalyzed resinified phenolated wood and its characterization. *Mokuzai Gakkaishi* 41(12):1122–31
- Alma MH, Yoshioka M, Yao Y, Shiraishi N (1998) Preparation of sulfuric acid catalyzed phenolated wood resin. *Wood Sci Technol* 32:297–308
- American Society for Testing and Materials (ASTM) (1996) Standard test method for evaluating properties of wood-base fiber and particle panel materials. ASTM D 1037-96
- Costa L, Montelera LR, Camino G, Weil ED, Pearce EM (1997) Structure-charring relationship in phenol-formaldehyde type resins. *Polym Degrad Stab* 56:23–35
- Crews P, Rodriguez J, Jaspars M (1998) Organic structure analysis. Oxford university press, New York
- Hasllam J, Willis HA (1965) Identification and analysis of plastics. D Van Nostrand company, Inc., Princeton, New Jersey
- Holopainen T, Alivila L, Rainio J, Pakkanen TT (1998) IR spectroscopy as a quantitative and predictive analysis method of phenol-formaldehyde resin resins. *J Appl Polym Sci* 69: 2175–2185
- Kristkova M, Filip P, Weiss Z, Peter R (2004) Influence of metals on the phenol-formaldehyde resin degradation in friction composites. *Polym Degrad Stab* 84:49–60
- Lee SH, Yoshioka M, Shiraishi N (2000) Preparation and properties of phenolated corn bran/phenol/formaldehyde co-condensed resin. *J Appl Polym Sci* 77:2901–2907
- Lin L, Yoshioka M, Yao Y, Shiraishi N (1995a) Preparation and properties of phenolated wood/phenol/formaldehyde cocondensed resin. *J Appl Polym Sci* 58:1297–1304
- Lin L, Yoshioka M, Yao Y, Shiraishi N (1995b) Physical properties of moldings from liquefied wood resins. *J Appl Polym Sci* 55:1563–1571
- Lin L, Yao Y, Yoshioka M, Shiraishi N (2001) Liquefaction mechanism of β -O-4 lignin model compound in the presence of phenol under acid catalysis. I. Structural characterization of the reaction products. *Holzforschung* 55:617–624
- Myers GE, Christiansen AW, Geimer RL, Follensbee RA, Koutsky JA (1991) Phenol-formaldehyde resin curing and bonding in steam-injection pressing. I. Resin synthesis, characterization, and cure behavior. *J Appl Polym Sci* 43:237–250
- Pan H, Shupe FT, Hse CY (2005) Preliminary investigation of biocomposites fabricated from liquefied wood/phenol/formaldehyde co-condensed resin. In: Frihart C (ed) *Wood adhesives 2005*. Forest Product Society, Madison, pp 257–262
- Pan H, Shupe FT, Hse CY (2007) Characterization of liquefied wood residues from different liquefaction conditions. *J Appl Polym Sci* 105:3739–3746
- Pan H, Shupe FT, Hse CY (2008) Synthesis and cure kinetics of liquefied wood/phenol/formaldehyde resins. *J Appl Polym Sci* 108:1837–1844
- Pecsok RL, Shield LD (1968) Modern methods of chemical analysis. John Wiley & sons, New York
- Poljansek I, Krajnc M (2005) Characterization of phenol-formaldehyde prepolymer resins by in line FT-IR spectroscopy. *Acta Chim Slov* 52:238–244
- Pu S, Shiraishi N (1993) Liquefaction of wood without a catalyst I. time course of wood liquefaction with phenols and effects of wood/phenol ratios. *Mokuzai Gakkaishi* 39(4):446–452
- Rezzoug SA, Capart R (1996) Solvolysis and hydrotreatment of wood to provide fuel. *Biomass Bioenerg* 11(4):343–352
- Rezzoug SA, Capart R (2002) Liquefaction of wood in two successive steps: solvolysis in ethylene-glycol and catalytic hydrotreatment. *Appl Energ* 72:631–644
- Rustamov VR, Abdullayev KM, Samedov EA (1998) Biomass conversion to liquid fuel by two-stage thermochemical cycle. *Energ Convers Manag* 39(9):869–875