Investigation of Bio-Composites using Novolac Type Liquefied Wood Resin: Effects of Liquefaction and Fabrication Conditions

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Abstract

Wood liquefaction using an organic solvent and an acid catalyst has long been studied as a novel technique to utilize biomass as an alternative to petroleum-based products. Oxalic acid is a weaker organic acid than a mineral acid and wood liquefaction with oxalic acid as a catalyst will result in a higher amount of wood residue than that with a mineral acid. Yet the wood residue can be used as a filler in the bio-composite fabrication. In this study, bio-composites were fabricated from wood flour and novolac type liquefied wood resins with wood residue. The effects of liquefaction temperature, reactor type, hot press temperature, and press time on the mechanical and physical properties of the composites were investigated. 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. Both hot press temperature and press time had significant effects on the mechanical and physical properties of the composites. The results of dimensional stability tests implied that the matrix resin didn't cure well at the hot press temperature 155°C.

Introduction

The rapidly changing economic and environmental needs of society are putting increasing pressure on the forest products industry to increase the conversion and efficient use of wood resources. Competition in high volume markets has focused attention on low priced materials that offer a more favorable strength to weight ratio. Wood fiber composites have the lowest material cost compared to other polymeric industries (Rowell et al., 1993). Wood liquefaction using an organic solvent and an acid catalyst has long been studied as a novel technique to utilize biomass as an alternative to petroleum-based products. Liquefied wood can be applied as a precursor in preparing various products, such as phenolic resins (Lin et al., 1995) and polyurethane foams (Yao et al., 1996), depending on the reagent solvent used in the liquefaction. Novolac type liquefied wood resin (LWR)

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can be prepared from the condensation reaction of formaldehyde and liquefied wood using phenol as the reagent solvent. Several studies have been done to make molding composites using liquefied wood resin as the matrix resin. The effects of combined phenol and phenol to formaldehyde ratio on the flexural properties of the composites have been investigated (Alma et al., 1995; Lin et al., 1995). It was reported that the mechanical properties of the molding composites using novolac type liquefied wood resin were much higher than those using the phenolated wood and also somewhat superior to those using the conventional novolac resin (Lin et al., 1995).

Oxalic acid is a weaker organic acid than a mineral acid such as sulfuric acid. Wood liquefaction with oxalic acid as a catalyst will result in a higher amount of wood residue than that with a mineral acid (Alma et al., 1995; Pan et al., 2005), which is not ideal for a liquefaction reaction. However the wood residue contains higher cellulose portion than the original wood does since the lignin has been partially removed during the liquefaction reaction (Pan et al., 2007). Therefore, it could be used as a filler in the bio-composite fabrication. Thus, the objectives of this chapter were to 1) investigate the effects of selected liquefaction variables (i.e., liquefaction temperature and reactor type) on the mechanical and physical properties of the composites, and 2) investigate the effects of hot press temperature and time on the mechanical and physical properties of the composites.

Experimental

Materials

Chinese tallow (*Triadica sebifera* syn. *Sapium sebiferum)* tree wood was sawn on a laboratory table saw and the saw dust was collected. The particles were oven dried at 105ºC to a moisture content of 3-5% and then reduced in a Wiley mill to fine powder of 20-200 mesh. Liquid industrial grade phenol (90% concentration) was used as the liquefaction reagent. Hexamethyleneteramine (HMTA) and calcium hydroxide were used as a hardener and an accelerator, respectively, in the cure reaction. All other chemicals were reagent grade.

Preparation of liquefied wood and novolac type liquefied wood resin

Wood powder, phenol, and oxalic acid were mixed in a container until a uniform mixture was obtained. The mixture was then transferred to a 1L three-neck glass reactor equipped with a condenser and a stirring system. The liquefaction procedure was also conducted in a 1L Parr reactor. Two liquefaction temperatures were chosen (150 and 180ºC). Phenol to wood (P/W) ratios was 2/1 in the liquefaction. Oxalic acid was used as a catalyst and its content was 5% based on the amount of phenol. After the liquefaction reactions, the liquefied mixture was mixed with formaldehyde (36%) at a phenol/formaldehyde molar ratio of 1/0.8 (phenol was based on the initially charged amount) and additional oxalic acid (7% of phenol, w%), and then refluxed under continued stirring at 105°C for 80 min. The resin mixture (i.e., resin and wood residue) were used as they are after resin synthesis without further filtration.

Preparation of bio-composite

The bio-composite consisted of 30% novolac type liquefied wood resin, 8% Hexamin, 1% calcium hydroxide, 1% zinc stearate, and 60% wood filler. Liquefied wood resin was first mixed with hexamine, calcium hydroxide, and zinc stearate. Sufficient acetone was then added to the mixture and stirred to thoroughly dissolve the resin. Wood filler was then added to the acetone mixture to make a homogeneous mixture. After thoroughly mixing, the acetone was removed from the mixture under reduced-pressure at 50ºC. The mixture was then freeze-dried overnight to remove water and any remaining acetone. The dried material was sieved again to pass through a 20 mesh sieve and aggregated materials remaining on the 20 mesh sieve were ground into powder. The resulting material was subjected to compression molding to fabricate 5×5×1/8 in. panels using a 6×6 in. single-opening laboratory hot-press.   The panels were first compressed under a selected temperature and time and then cooled under the same pressure for 10 min.   Three compressing temperatures (155, 175, and 195˚C) and two compressing times (2 and 4 min.) were used for the molding process. Two panels were produced for each compressing temperature and time combination.

Test of mechanical properties

Flexural and tensile test were performed on an Instron-4465 test machine in accordance with ASTM D-1037-96 (American Society for Testing and Materials (ASTM), 1996). Each panel was cut to yield two static-bending specimens (0.5×5 in.) and two dimensional stability test specimens (0.5×5 in.). The span for flexural test was 4 in. and the crosshead speed if 0.107 in/min. according to the standard.[5] 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.

Test of dimensional stabilities

Two specimens from each composite were chosen for the 24 to 96 h soaking and 2 to 8 h boiling test. The thickness of the specimens before and after the tests was measured. The percent of thickness swelling was calculated by Equation 1:

$$TS(\%) = \frac{T_1 - T_0}{T_0} \times 100 \qquad (1)$$

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.

Results and discussion

Effects of liquefaction temperature and reactor type

As discussed in our previous paper (Pan et al., 2007; Pan et al., 2008), liquefaction temperature and reactor type caused some variations between the liquefied wood and

liquefied wood resins. Consequently, the physical and mechanical properties of the composites using the liquefied wood resin as a matrix resin also varied as shown in Table 1.

Table 1. Flexural and tensile strength of the composites using different liquefied wood resin.

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

Table 2. ANOVA results of the effects of reactor type and temperature during the liquefaction process on the flexural properties of the panels.

Source	df	Type III SS	Mean Square	F Value	Pr > F
1. dependent variable: modulus of rupture (MOR)					
M[a]	1	110556	110556	1.12	0.3109
T[b]	1	4395312	4395312	44.50	<.0001
M*T	1	6237506	6237506	63.15	<.0001
2. dependent variable: modulus of elasticity (MOE)					
M[a]	1	19157466510	19157466510	25.68	0.0003
T[b]	1	65446174800	65446174800	87.71	<.0001
M*T	1	144490834280	144490834280	193.65	<.0001

[a]Reactor type.
[b]Liquefaction temperature.

Table 2 presents the effects of two liquefaction factors on the flexural properties of the composites. It can be seen that liquefaction temperature had a significant effect on the modulus of rupture (MOR) of the composites. Both reactor type and liquefaction temperature had significant effects on the modulus of elasticity (MOE) of the composites. And these two factors had significant interactions for both MOR and MOE as shown in Fig. 1. It is interesting to note that although two types of reactors showed opposite trends to each other for 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 effects of liquefaction factors on the tensile strength of the composites were also analyzed by ANOVA and the results were summarized in Table 3. Reactor type had a significant effect on the MOR of the composites while both factors had significant effects on the MOE. Moreover, the interactions between these two factors were significant in both MOR and MOE. As shown in Fig. 2, the interaction between reactor type and liquefaction temperature exhibits similar trends in tensile strength as 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°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.
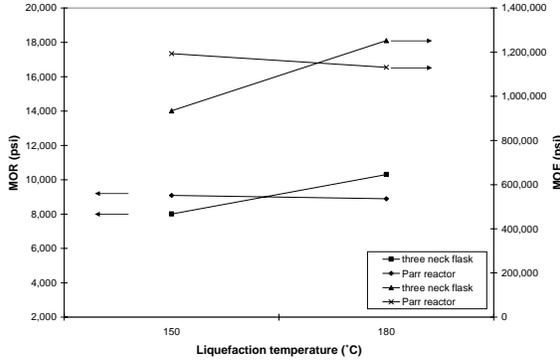

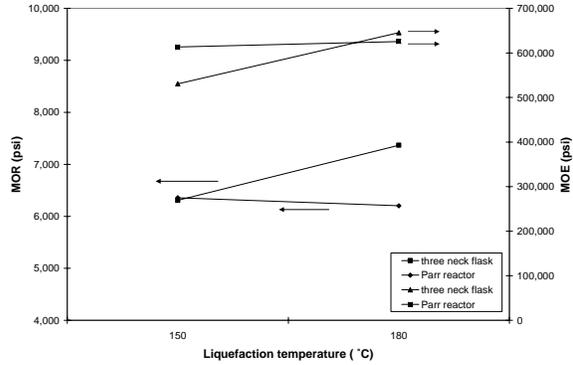Fig. 1. Interaction plot of reactor type and liquefaction temperature on flexural properties of the panels.

Fig. 2. Interaction plot of reactor type and liquefaction temperature on tensile properties of the panels

Table 3. ANOVA results of the effects of reactor type and temperature during the liquefaction process on the tensile properties of the panels.

Source	df	Type III SS	Mean Square	F Value	Pr > F
1. dependent variable: modulus of rupture (MOR)					
M[a]	1	1244675	1244675	4.50	0.0553
T[b]	1	821869	821869	2.97	0.1103
M*T	1	1476043	1476043	5.34	0.0394
2. dependent variable: modulus of elasticity (MOE)					
M[a]	1	3950091075	3950091075	8.83	0.0117
T[b]	1	16122968064	16122968064	36.03	<.0001
M*T	1	10516041030	10516041030	23.50	0.0004

[a]Reactor type
[b]Liquefaction temperature
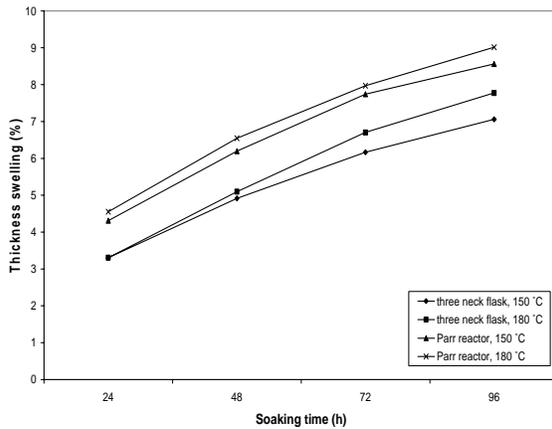
(a)
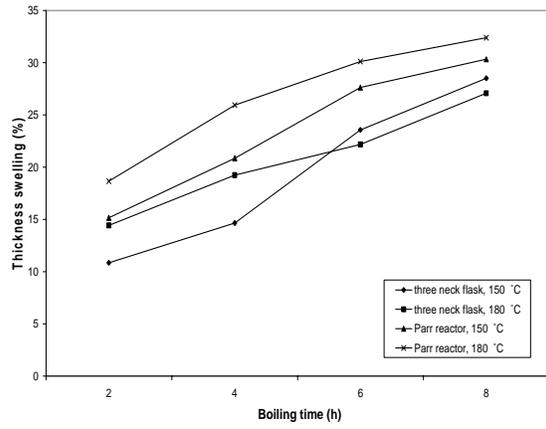
(b)

Fig. 3. Thickness swelling of the composites as a function of (a) soaking and (b) boiling time.

Fig. 3 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 very 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 contained 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., 1995). Besides 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 our previous study (Pan et al., 2008), 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. 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 molecular weight would yield less cross-link during the resin cure process due to less reaction cites compared with the liquefied wood resin with a lower wood component content and higher average molecular weight.

Effects of hot press temperature and time
Hot press temperature and time are two factors highly related to the economic cost of the panel products. Table 4 summarizes the flexural and tensile strength of the composites fabricated under different temperatures and time.

Table 4. Flexural and tensile strength of composites under different hot press temperature and time.

	2 min. Hot Press Time				4 min. Hot Press Time			
	Flexural		Tensile		Flexural		Tensile	
	MOR	MOE	MOR	MOE	MOR	MOE	MOR	MOE
	(psi)		(psi)		(psi)		(psi)	
155 °C	4596	676870	2769	326068	8488	1134845	4725	483873
175 °C	8430	1111775	5273	482262	8512	1096622	5927	467720
195 °C	8598	1091481	5707	484342	9356	1068845	5991	473841

The ANOVA results show that both hot press temperature and time had significant effects on the flexural and tensile strength of the composites (Table 5 and 6). Generally, the composites made under higher hot press temperatures and longer press time yielded higher flexural and tensile strength. However, they changed at different rates with different

press time as the hot press temperature changed from 155 to 195˚C. As shown in Fig. 4 and 5, both the flexural and tensile strength of the composites with a press time of 2 min. increased dramatically when the hot press temperature was increased from 155 to 175˚C. The slope of the curves then decreased as the hot press temperature increased to 195˚C. When the press time increased to 4 min., only a slightly increase can be observed in the tensile MOR of the composites as the temperature changed for 155 to 175˚C. All other values did not change much while the hot press temperature changed. This result infers that certain amount energy is needed to cure the matrix resin. When the hot press temperature is not high enough to give the needed energy, a prolonged press time will be necessary.

Table 5. ANOVA results of the effects of hot press temperature and time on the flexural properties of the panels.

Source	df	Type III SS	Mean Square	F Value	Pr > F
1. dependent variable: modulus of rupture (MOR)					
Te[a]	2	26423444	13211722	44.72	<.0001
Ti[b]	1	14936540	14936540	39.55	<.0001
Te*Ti	2	16516622	8258311	24.72	<.0001
2. dependent variable: modulus of elasticity (MOE)					
Te[a]	2	187465325483	93732662742	55.77	<.0001
Ti[b]	1	117704743453	117704743453	44.41	<.0001
Te*Ti	2	303261494936	151630747468	71.84	<.0001

[a]Temperature of hot press process.　　[b]Time of hot press process.

Table 6. ANOVA results of the effects of hot press temperature and time on the tensile properties of the panels.

Source	df	Type III SS	Mean Square	F Value	Pr > F
1. dependent variable: modulus of rupture (MOR)					
Te[a]	2	21100164	10550082	36.00	<.0001
Ti[b]	1	5582084	5582084	68.05	<.0001
Te*Ti	2	3083221	1541611	9.94	0.0012
2. dependent variable: modulus of elasticity (MOE)					
Te[a]	2	27769937362	13884968681	11.57	0.0032
Ti[b]	1	11750327657	11750327657	13.67	0.0002
Te*Ti	2	38698139756	19349069878	19.04	<.0001

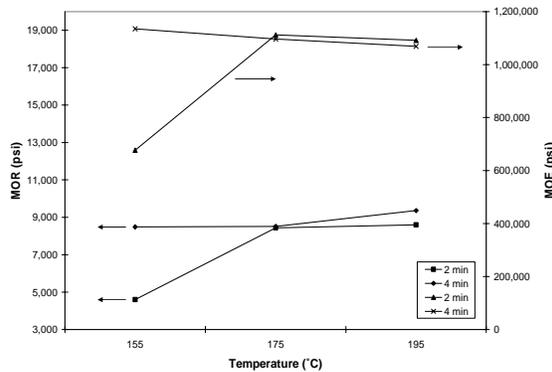[a]Temperature of hot press process.　　[b]Time of hot press process.

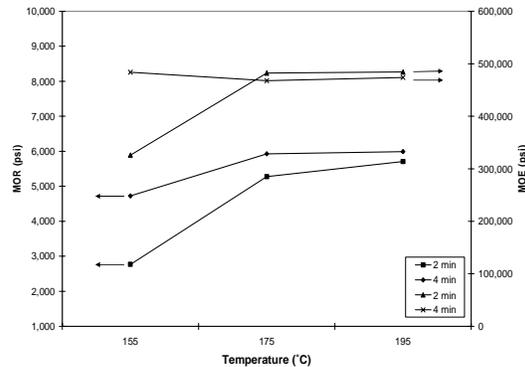Fig. 4. Interaction plot of hot press temperature and timeon flexural properties of the panels

Fig. 5. Interaction plot of hot press temperature and time on tensile properties of the panels

The results of the soaking and boiling tests of the composites under different hot press temperatures and time are shown in Fig. 6. No test specimen from the composite made with 155°C and 2 min. could withstand for the entire soaking and boiling tests. Moreover, the composites compressed for 4 min. at 155°C had much higher thickness swelling than any other composites in both soaking and boiling tests. Therefore, it can be concluded that the matrix resin did not cure well at the hot press temperature of 155°C even with prolonged press time. It is also worthwhile to note that the order of the thickness swelling decreased as 155°C, 4 min. >175°C, 2 min. >195°C, 2 min. >175°C, 4 min >195°C, 4 min. in the boiling test, indicating that the enough curing time takes precedence over temperature during the molding process.
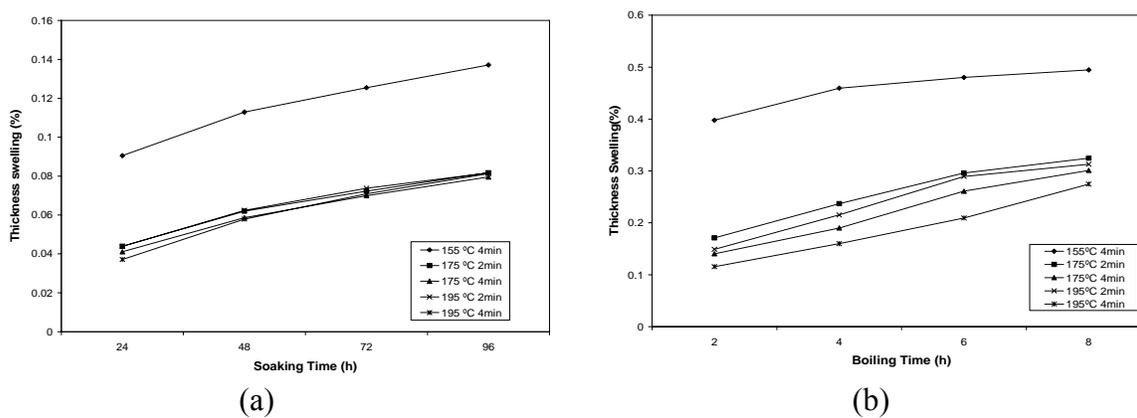

Fig. 6. Thickness swelling of the composites as a function of (a) soaking and (b) boiling time

Conclusions

Bio-composites were fabricated from wood flour and novolac type liquefied wood resins. The effects of liquefaction temperature, reactor type, hot press temperature, and press time on the mechanical and physical properties of the composites were investigated. The composites with the liquefied wood resin from the atmospheric three neck flask showed increased flexural and tensile strength when liquefaction temperature increased from 150 to 180°C. 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.

Both hot press temperature and press time had significant effects on the mechanical and physical properties of the composites. The flexural and tensile strength of the composites with a press time of 2 min. increased dramatically when the hot press temperature increased from 155 to 175°C. But the rate of increase decreased as the temperature changed from 175 to 195°C and with the press time of 4 min. The results of dimensional stability tests implied that the matrix resin didn't cure well at the hot press temperature 155°C.

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