Physical and Mechanical Properties of Bio-Composites from Wood Particles and Liquefied Wood Resin

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Abstract

Compression molded composites were made from wood particles and a liquefied wood/phenol/formaldehyde co-condensed resin. Based on our previous research, a phenol to wood (P/W) ratio of 2/1 was chosen for this study. The two experimental variables selected were: 1) liquefaction temperature (150° and 180°C) and 2) cooking method (atmospheric and sealed). Panels were tested in static bending for modulus of rupture (MOR) and modulus of elasticity (MOE). Dimensional stability properties were also measured by 24-hour soaking and 2-hour boiling test. On average, the composite from the atmospheric cooked liquefied wood yielded higher MOR and MOE than that from the sealed cooked liquefied wood at 150°C. But, the results were the opposite at the 180°C temperature. Composites from atmospheric cooked liquefied wood gave better dimensional stabilities than those from the sealed cooking both in 24-hour soaking and 2-hour boiling tests.

Introduction

Interest has been directed toward biomass liquefaction to obtain liquid fuels and potential feedstocks for industrial chemicals for more than 30 years and some encouraging results have been achieved. Shiraishi et al. reported that lignocellulosic biomass such as wood can be liquefied in the presence of phenol or polyhydric alcohols with an acid catalyst at a temperature of 120° to 180°C or without a catalyst at approximately 250°C (Pu and Shiraishi 1993a, 1993b; Alma et al. 1998; Shiraishi and Hse 2000). The effects of various factors such as liquefaction time, temperature, catalyst content, and the amount of reagent solvent on the liquefaction efficacy (i.e., extent of liquefaction) have been investigated. Additionally some chemical and physical characteristics of the liquefied wood, such as molecular weight and its distribution, and thermal flow property have also been studied (Lin et al. 1995, Alma et al. 1996, Lin et al. 1997). The liquefied products can be used to prepare polyurethane foams, phenolic resin, and adhesives (Yao et al. 1994, Lin et al. 1997). A comprehensive understanding of the mechanism of wood liquefaction, which is crucial for optimizing the physical and mechanical properties of the final products of liquefied wood, has not yet been clearly established due to the complicated structure and composition of wood.

The objectives of this paper were to investigate the effects of liquefaction temperature and cooking method on the physical and mechanical properties of compression molded bio-composites from wood particles and liquefied wood resin.

Experimental

Materials

Wood from Chinese tallow tree (*Triadica sebifera* syn. *Sapium sebiferum*) was sawn on a laboratory table saw and the sawdust was collected. The particles were oven-dried at 105°C to a moisture content (MC) of 3 to 5

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percent, and the sawdust was then ground to fine particles of 20 to 200 mesh. The ground wood particles were used as raw materials for wood liquefaction and wood filler for the wood composites. Liquid industrial grade phenol (90% concentration) was used as the liquefaction reagent solvent. All of the other chemicals used in this study were reagent grade.

Preparation of Liquefied Wood

Wood particles, phenol, and oxalic acid were premixed until a uniform mixture was obtained. Then the mixture was transferred to a Parr reactor or three-neck flask equipped with a condenser and a stirring system. The two variables chosen for this study were liquefaction temperature and cooking method (i.e., atmospheric and sealed). Based on our previous study (Pan et al. 2005), P/W ratio was set at 2/1(w/w). Liquefaction temperatures were 150° and 180°C. Oxalic acid was used as a catalyst and its content was 5 percent based on the amount of phenol.

Preparation of Liquefied Wood Resin and Composites from Wood Particle and Liquefied Wood Resin

Liquefied wood was mixed with formaldehyde and then refluxed under continued stirring for 80 minutes at 105°C. The 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. The weight percentage of the wood resin, hexamine, calcium hydroxide, zinc state, and wood filler were 37.7, 9.4, 2.4, 1.0, and 49.5 percent, respectively. After thoroughly mixing, the acetone was removed from the mixture under reduced pressure at 50°C. 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- by 5- by 1/8-in. panels using a 6- by 6-in. single-opening laboratory hot-press. The panels were hot pressed at 185°C for 3 minutes and then cooled under the same pressure for 10 minutes.

Test of Physical and Mechanical Properties

Flexural tests were performed using an Instron-4465 universal test machine in accordance with ASTM D-1037-96 (ASTM 1996). Each panel was cut to yield two static-bending specimens (1/2 by 5 in.) and two dimensional stability test specimens (1/2 by 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 from each panel were cut for the 24-hour soaking and 2-hour boiling test. The thickness of the specimens before and after the tests was measured. The percent of thickness swelling was calculated using Equation [1]:

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

where:

TS = the percent of thickness swelling and

T_0 and T_1 = the thickness of the specimen before and after the test, respectively.

Statistic Analysis

Analysis of variance (ANOVA) was used to analyze the effects of the variables in the studies of liquefied wood residue and the physical and mechanical properties of the molded composites.

Results and Discussion

Mechanical Properties

The results of the physical and mechanical properties of the composite from liquefied wood resin and wood particles are shown in **Table 1**. **Table 2** lists the two-way ANOVA results of the effects of selected variables on the MOR and MOE of the composite. Liquefaction temperature has significant effects on both MOR and MOE while the cooking method only has significant effects on MOE. In addition, these two variables showed significant interactions both on the MOR and MOE of the composites. As shown in **Table 1**, the composites from the higher liquefaction temperature have higher MOR and MOE than those from the lower liquefaction temperature when the liquefaction was in an atmospheric system. On the contrary, the composites from the higher liquefaction temperature yielded lower MOR and MOE than those from the lower temperature when the liquefaction was in a sealed Parr reactor. This result may be attributed to the different chemical compositions of the liquefied wood

Table 1. — *Physical and mechanical properties of the composites fabricated with liquefied wood resin.*

Cooking methods	Lique-faction temp.	MOR	MOE	Thickness swelling (%) 24-hour soaking	Thickness swelling (%) 2-hour boiling
	(°C)	----- (psi) -----			
Atmo[a]	150	8,008	934,279	3.3	10.9
	180	10,305	1,252,251	3.3	14.4
Sealed[b]	150	9,090	1,193,544	4.3	15.2
	180	8,890	1,131,397	4.6	18.7

[a] Atmospheric cooking.
[b] Sealed Parr reactor cooking.

Table 2. — *Two-way ANOVA results of mechanical properties of the composites.*

Source	df	*F* value	*p* value
1. Dependent variable: modulus of elasticity (MOE)			
Factor	3	102.35	<0.0001
M[a]	1	25.68	0.0003
T[b]	1	87.71	<0.0001
M*T[c]	1	193.65	<0.0001
2. Dependent variable: modulus of rupture (MOR)			
Factor	4	36.25	0.0040
M[a]	1	1.12	0.3109
T[b]	1	44.50	<0.0001
M*T[c]	1	63.15	<0.0001

[a] Cooking method.
[b] Liquefaction temperature.
[c] Interaction of cooking method and liquefaction temperature.

Table 3. — *Two-way ANOVA results of dimensional stability of the composites.*

Source	df	*F* value	Pr > F
1. Dependent variable: thickness swelling (24-hour soaking)			
Factor	3	20.59	<0.0001
M[a]	1	49.94	<0.0001
T[b]	1	5.81	0.0329
M*T[c]	1	6.03	0.0303
2. Dependent variable: thickness swelling (2-hour boiling)			
Factor	4	13.22	0.0004
M[a]	1	23.53	0.0005
T[b]	1	16.13	0.0331
M*T[c]	1	0.00	0.9802

[a] Cooking method.
[b] Liquefaction temperature.
[c] Interaction of cooking method and liquefaction temperature.

residues that were used as part of the filler in the composites. Our research on the characterization of liquefied wood residue showed that the liquefied wood residue had a higher a-cellulose content at a higher temperature in the atmospheric cooking system while it was lower in the sealed cooking system (Pan et al. 2006). Cellulose fibers can serve as a reinforcing material in a composite product, and it has a more regular chain structure than hemicellulose and lignin (Sarkanen 1963). Consequently, the panels with higher cellulose content wood filler yielded higher mechanical properties.

Dimensional Stability

Table 3 presents the two-way ANOVA results of the dimensional stability of the composites. Cooking method and liquefaction temperature showed significant effects on the thickness swelling of the composites in both 24-hour soaking and 2-hour boiling tests, and these two factors showed significant interaction in the 24-hour soaking test. The composites from sealed cooking liquefied wood consistently had higher thickness swelling than that from atmospheric cooking system in both 24-hour soaking and 2-hour boiling tests (**Table 1**). Liquefaction temperature showed different effects in the two tests. The composites from the higher temperature gave higher thickness swelling in the 2-hour boiling test while this factor interacted with cooking method in 24-hour soaking test; the higher temperature gave higher thickness swelling only in sealed cooked liquefied wood and gave similar results in the atmospheric cooked system. The possible reason for the higher thickness swelling can be the occurrence of less crosslinking in the liquefied wood resin with more complete liquefaction of the lignin. As indicated by our study on the chemical composition of liquefied wood residue, the composites had higher thickness swelling generally from liquefied wood that contained lower levels of lignin in its residue (Pan et al. 2006). Lignin is a highly branched biopolymer with phe-

nolic units in which the ortho, meta, and para positions on the benzene ring are mostly occupied. Therefore, when the lignin decomposed during the liquefaction reaction and further reacted with phenol and formaldehyde, the small unit of lignin cannot co-condense with phenol and formaldehyde as easily as the phenolic resin to form a highly crosslinked network.

Conclusions

The composites from the higher liquefaction temperature had higher MOR and MOE than those from the lower liquefaction temperature when the liquefaction was in an atmospheric system. On the contrary, the composites from higher liquefaction temperature yielded lower MOR and MOE than those from the lower temperature when the liquefaction was in a sealed Parr reactor. The composites from sealed cooking liquefied wood consistently had higher thickness swelling than that from the atmospheric cooking system in both 24-hour soaking and 2-hour boiling tests.

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