Bond Quality of Phenol-Based Adhesives Containing Liquefied Creosote-Treated Wood

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Abstract

Liquefaction of spent creosote-treated wood was studied to determine the technological practicability of its application in converting treated wood waste into resin adhesives. A total of 144 plywood panels were fabricated with experimental variables included 2 phenol to wood (P/W) ratios in liquefaction, 6 resin formulations (3 formaldehyde/liquefied wood (F/LW) ratios × 2 replications), 6 glue applications (2 glue spreads × 3 assembly times), and 2 panel replications. Average shear strength (235.6 psi) and wood failure (70.5%) for resin adhesives prepared from liquefied wood at P/W ratio of 2.0 were significantly higher than the shear strength (184.7 psi) and wood failure (53.1%) for that at P/W ratio of 1.5. On average, F/LW ratio of 2.25 yielded substantially lower shear strength and wood failure than that of F/LW ratios of 2.0 and 1.75. Differences in shear strength and wood failure between F/LW ratios of 2.0 and 1.75 were not significant. However, it is interesting to note that F/LW ratio interacted with P/W ratio to affect wood failure, but not shear strength. As shown in Fig. 2, at P/W ratio of 1.5, the F/LW ratio of 2.0 yielded the highest wood failure and the F/LW ratio of 2.25 resulted in the lowest wood failure. On the contrary, at P/W ratio of 2.0, the F/LW ratio of 2.25 resulted in highest wood failure and the F/LW ratio of 2.0 yielded the lowest wood failure. On the basis of wood failure, the resins prepared from liquefied wood at P/W ratio of 2., reacted at F/LW ratio of 2.25, and applied the glue at the rate of 90 pounds per 1000 square ft of double glue line met the standard of vacuum-pressure soak cycle for exterior glueline (PS-1-66). Nevertheless, the first attempt to formulate a phenol-based adhesive made from liquefied creosote-treated wood produced encouraging results. With additional studies of resole formation and glue mix formulations, it is anticipated that a resin adhesive from liquefied creosote-treated wood with improved bond quality can be developed.

Introduction

Recent advancements in techniques of converting wood into liquid materials under mild conditions have stimulated numerous studies focused on turning by-products wood wastes into new raw materials for products with promising potentials (Alma et al., 1998; Kobayashi et al., 2000; Lee et al., 2002; Lin et al., 1995; Pan et al., 2007; Pu et al., 1994; Yamada et al., 2001; Zhang et al., 2006). Our interest in wood liquefaction was related mainly to our effort in the development of closed-loop recycling system as described in Fig. 1. The liquefaction process provides the options for: (1) converting the residues to useful products such as resin adhesives and (2) removing residual preservatives from wood particles. This study focuses on utilizing the liquefied products as raw materials for resin adhesives. The objectives are to evaluate the glue bond performance of the phenol-based adhesives formulated from liquefied spent creosote-treated wood.

Experimental Procedure

Experimental design

The study involved the processes of liquefaction, resin formulation, and glue application. The variables considered in each of these processes are summarized as follows:

- Phenol (P) to wood (W) ratio (w/w) in liquefaction
  - 1.5 / 1
  - 2.0 / 1
- Resin formulation variables (Formaldehyde (F) to liquefied wood (LW) ratio)
  - 1.75 / 1
  - 2.0 / 1
  - 2.25 / 1
- Replications for resin: 2
- Glue application
  - Rate of glue application
    - 80 pounds per 1000 square feet of double glueline
    - 90 pounds per 1000 square feet of double glueline
  - Assembly time
    - 10 minutes
    - 20 minutes
    - 30 minutes

Panel replication: 2

Thus, with 2 phenol to wood ratio in liquefaction, 6 resin formulations (3 F/LW × 2 replications), 6 glue applications (2 glue spreads × 3 assembly times), and 2 panel replications, a total of 144 plywood panels were made.

Materials

Spent southern pine poles were obtained from a local utility company. After metal removal, the used poles were converted into sawdust with table saw. The portion of sawdust that passed through a number 10 sieve were collected, air dried, and used without further treatment. Average creosote content of the sawdust determined using toluene extraction in accordance with AWPA Standard A6-83 (1984) was 17 percent.

Liquefaction

Phenol, sawdust, water, acid catalyst, and polyethylene glycol 300 were premixed in a bench top mixer and transferred into Parr pressure reactor. To initiate liquefaction, the temperature of the reactor was increased to 120°C. After heating period of 40 minutes, the liquefied product was cooled to room temperature and stored before use in resin preparation.

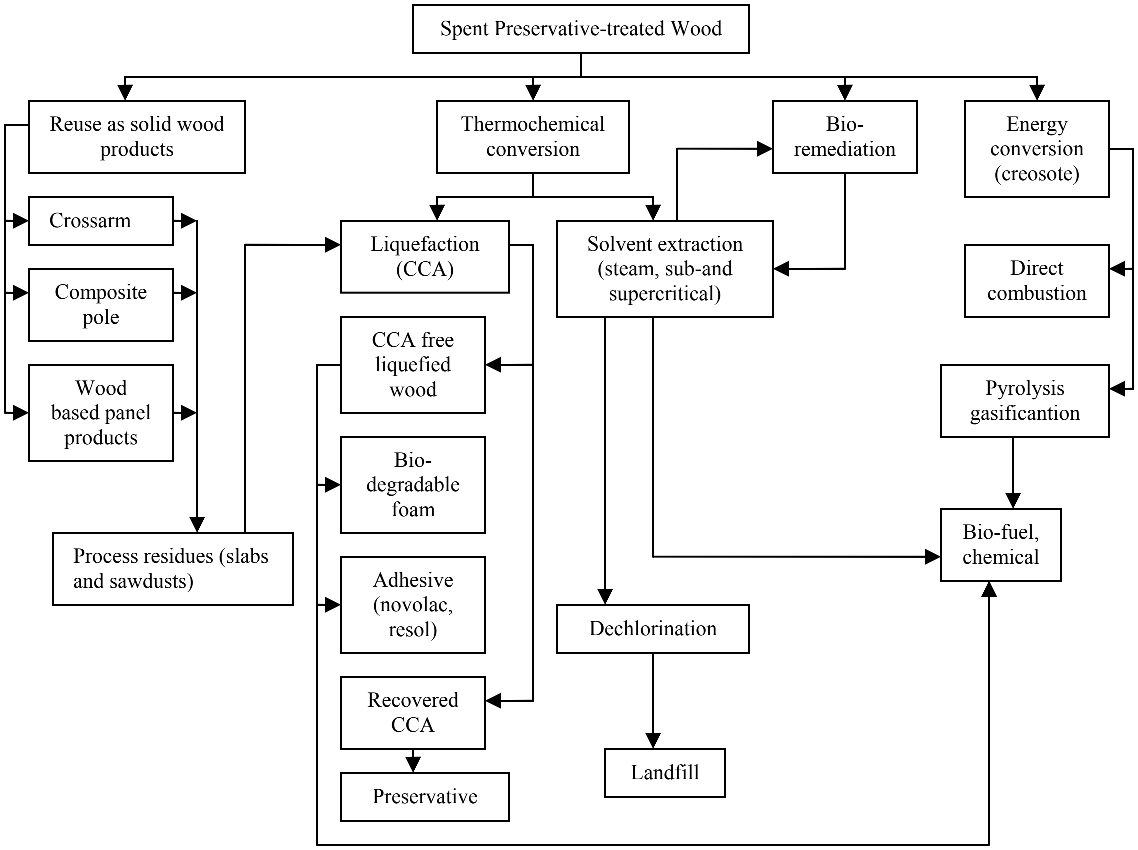

Fig. 1. Closed-loop recycling system for preservative-treated wood

Resin Preparation

All liquefied wood resins were prepared in the laboratory in a conventional resin reaction kettle. To calculate the F/LW ratio, the LW was assumed to have the same molecular weight as phenol. To prepare each resin, all of the LW, formaldehyde, and water were placed in the reaction kettle. The sodium hydroxide was added, as catalyst, in two steps; i.e., 0.4 mole of sodium hydroxide per mole of LW was added at the beginning, and the balance (0.2 moles) was added 60 minutes after the reaction began. To initiate the reaction, the mixture was quickly heated and maintained at 85°C. When viscosity reached 750 cps the reaction was terminated by rapidly cooling the mixture to 25°C.

Resin Characterization

Gel time and viscosity - The gel time of the resin was measured with a Sunshine gel timer at 100°C and the viscosity was measured with a Brookfield viscometer at room temperature (25°C).

Solids content - Approximately 5 grams of resin was weighed and placed in an oven with temperature maintained at 100°C. The sample was dried for 8 hours. The dried sample was weighed and the solid content was calculated by the following equation:

$$\text{Solids content (\%)} = W_2/W_1 \times 100$$

where W_1 and W_2 were the weight of resin before and after drying, respectively.

Preparation and Evaluation of the Plywood

All veneers were from mill-run southern pine bolts peeled at a plywood plant in Pollock, Louisiana. Average moisture content for the 3.18 mm veneer was 4 percent. T he veneers were sawn to yield 30- by 30-cm clear pieces. The pieces were randomly chosed for gluing into 3-ply panels.

Furafil and wheat flour were added to all resins to achieve 26-percent resin solids in the final mix. Ingredients of the glue mix are shown in Table 1.

Table 1. Ingredients of the glue mixes

Ingredient	52 % resin solids[1]	54% resin solids	57% resin solids
Water	11.0	15	19
Furafil	10.5	10.5	10.5
Wheat	1.5	1.5	1.5
Caustic	3.0	3	3.0
Resin	50.0	48.0	46.0
Total	100	100	1000

[1] percentage of solids in the resin

Glue was spread with a paint brush and the veneers were immediately assembled into three-ply panels. The glue spread and closed assembly time were specified in the experimental design. The panels were then pressed for 4 minutes at a temperature of 165°C, and a specific pressure of 120 N/cm^2. As the panels were removed, they were placed in a hot-stack box where they remained overnight.

Twelve standard shear specimens were cut from each panel in such a manner that half could be pulled open and half closed. Glue bond quality was evaluated by wet shear strength and wood failure in specimens subjected to the vacuum-pressure cycle for exterior glueline as specified in PS-1-66.

Results and Discussion

Resin properties

Table 2 summarizes average viscosity, solid content, and gel time for each combination of liquefaction variables and resin formulation variables. As expected, the gel times decreased consistently as F/LW ratio decreased for the resins made with both P/W ratios of 1.5/1 and 2.0/1.

Table 2. Physical properties of resin adhesives

P/W	F/LW	Viscosity	Solid Content	Gel Time
		Cps, 25 ^{o}C	%	Min.
1.5/1	1.75/1	1410	52	47.5
	2.00/1	1110	52	38.4
	2.25/1	1520	57	25.5
2.0/1	1.75/1	1600	57	43.2
	2.00/1	1050	57	39.5
	2.25/1	1880	54	22.6

In general, the resins made with P/W ratio of 2.0/1 yielded slightly higher viscosities than that of resin made with P/W ratio of 1.5/1 for all F/LW ratios with an exception for F/LW ratio of 2.0/1. The resin solid content ranged from 52 to 57 percent. The effects of P/W ratio and F/PW ratio on resin solid were not significant.

Bond quality

Table 3 summarizes average wet shear strength and percent of wood failure for each combination of liquefaction variables, resin formulation variables, and gluing variables. The results of the Turkey's test for significant means are summarized in Table 4. Analysis of variance indicated that bond quality, measured by wet shear strength and percent wood failure, differed significantly (0.05 level) with change in P/W ratio and F/LW ratio. Evaluation of gluing variable effect showed that the wet shear strength differed significantly with change in glue spray rate, while the percent wood failure differed significantly with change in assembly time.

Liquefaction effects

Average shear strength (235.6 psi) and wood failure (70.5%) for resin adhesives prepared from liquefied wood at P/W ratio of 2.0 were significantly higher than the shear strength (184.7 psi) and wood failure (53.1%) for that at P/W ratio of 1.5. Study on the properties of liquefied birch sapwood meals and its application to adhesives had also shown that P/W ratio of 2.0 was proved to be most useful (Pu et.al., 1991). Nevertheless, interest in liquefaction of wood at lower P/W ratio remained high due to its significant cost advantage. In this study, the P/W ratio of 1.5 was chosen on the assumption that the un-reacted residues may function as extender for resin adhesive system to enhance bond performance. The relatively poor bond quality for resin adhesives prepared from P/W ratio of 1.5 as compared to that of 2.0 seems to indicate that the assumption was not supported by the data obtained. It should be noted, however, that no attempt was made in the study to optimize the liquefaction within either the P/W ratios of 1.5 or 2.0 for the preparation for resin adhesives. Nor adjustment was made in the addition of extender in glue mixing to compensate for the higher residues in the liquefied wood of P/W ratio of 1.5 as compared to that of 2.0. Further study will be needed to determine the effect of P/W ratio in wood liquefaction on bonding properties of the plywood.

Table 3. Average plywood properties made with liquefied spent creosote wood resin adhesives

				Plywood properties			
				Shear strength		Wood failure	
F/LW	P/W	Glue spreading	Assembly Time	Aver.	Stdev.	Aver.	Stdev.
		[pls/1000ft^2]	[min]	[psi]		[%]	
1.75/1	1.5/1	80	10	197.7	32.3	44.2	21.7
1.75/1	1.5/1	80	20	191.7	28.8	61.0	16.0
1.75/1	1.5/1	80	30	164.6	29.4	57.9	17.3
1.75/1	1.5/1	90	10	209.4	24.9	48.5	13.3
1.75/1	1.5/1	90	20	189.6	46.7	59.4	23.1
1.75/1	1.5/1	90	30	192.7	18.3	77.7	10.6
2.00/1	1.5/1	80	10	203.8	13.9	67.1	10.7
2.00/1	1.5/1	80	20	188.8	12.6	61.0	16.6
2.00/1	1.5/1	80	30	158.3	22.1	51.7	21.3
2.00/1	1.5/1	90	10	207.9	42.1	54.4	17.9
2.00/1	1.5/1	90	20	206.9	36.0	71.0	9.3
2.00/1	1.5/1	90	30	194.2	30.7	64.8	14.7
2.25/1	1.5/1	80	10	162.1	41.8	33.8	10.6
2.25/1	1.5/1	80	20	154.0	52.3	35.2	16.4
2.25/1	1.5/1	80	30	159.4	36.9	48.5	18.8
2.25/1	1.5/1	90	10	191.3	20.4	41.3	7.7
2.25/1	1.5/1	90	20	205.0	16.7	47.9	15.6
2.25/1	1.5/1	90	30	147.9	41.0	40.8	17.1
1.75/1	2.0/1	80	10	215.7	21.9	62.5	22.9
1.75/1	2.0/1	80	20	251.3	24.4	81.3	12.6
1.75/1	2.0/1	80	30	222.9	33.9	73.5	10.0
1.75/1	2.0/1	90	10	257.1	15.7	59.4	17.0
1.75/1	2.0/1	90	20	260.6	31.6	75.6	14.3
1.75/1	2.0/1	90	30	265.0	30.7	75.4	13.5
2.00/1	2.0/1	80	10	241.5	11.1	59.8	20.9
2.00/1	2.0/1	80	20	218.3	25.3	66.9	16.4
2.00/1	2.0/1	80	30	222.7	17.7	68.3	16.3
2.00/1	2.0/1	90	10	250.4	16.3	58.1	21.4
2.00/1	2.0/1	90	20	248.3	27.2	78.8	13.7
2.00/1	2.0/1	90	30	220.8	18.7	76.9	14.3
2.25/1	2.0/1	80	10	244.8	16.4	59.8	24.6
2.25/1	2.0/1	80	20	210.2	39.2	70.0	17.6
2.25/1	2.0/1	80	30	207.7	38.8	69.2	20.2
2.25/1	2.0/1	90	10	236.3	28.4	80.2	17.3
2.25/1	2.0/1	90	20	230.8	32.5	79.2	14.7
2.25/1	2.0/1	90	30	221.9	19.2	74.2	23.2

F/LW ratio effects

On average, F/LW ratio of 2.25 yielded substantially lower shear strength and wood failure than that of F/LW ratios of 2.0 and 1.75. Differences in shear strength and wood failure between F/LW ratios of 2.0 and 1.75 were not significant. However, it is interesting to note that F/LW ratio interacted with P/W ratio to affect wood failure, but not shear strength. As shown in Fig. 2, at P/W ratio of 1.5, the F/LW ratio of 2.0 yielded the highest wood failure and the F/LW ratio of 2.25 resulted in the lowest wood failure. On the contrary, at P/W ratio of 2.0, the F/LW ratio of 2.25 resulted in highest wood failure and the F/LW ratio of 2.0 yielded the lowest wood failure. Experiences in synthesis of phenol formaldehyde resin indicated that the formaldehyde ratios of 2 moles per 1 mole phenol have been proved to be most useful. In general, additional formaldehyde, i.e., higher molar ratio, will not react effectively and thus contributes little to resin performance. Likewise, it raises the cost of the product without any attendant benefit. When the ratio of formaldehyde is less than 2 moles, the reactivity or cure speed of the resin is lengthened which was also indicated by the result of gel time determination (Table 2).

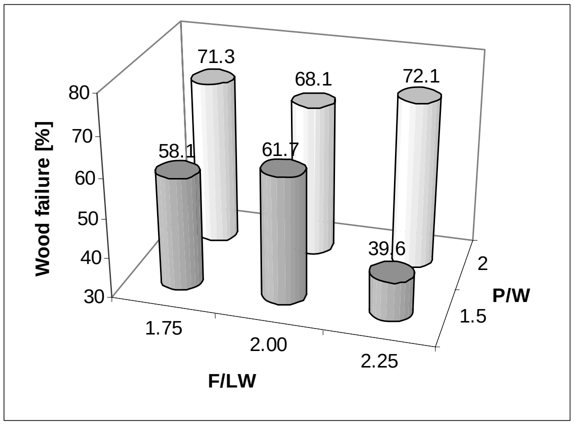

Fig. 2. Effect of phenol/wood ratio in wood liquefaction and formaldehyde/liquefied ratio in resin formulation on percentage wood failure

Table 4. Summary results of the least significant difference test

Factors	Levels	Plywood properties			
		Shear strength (psi)		Wood failure (%)	
F/LW	1.75/1	219.3	A*	64.7	A
	2.00/1	213.5	A	64.9	A
	2.25/1	197.6	B	55.8	B
P/W	1.5/1	184.7	A	53.1	B
	2.0/1	235.6	B	70.5	A
Glue Spreading	80	201.6	B	59.5	A
[*pls/1000ft*^{2}]	90	218.7	A	64.0	A
Assembly time	10	219.3	A	54.9	B
[*min*]	20	213.0	A	65.6	A
	30	198.2	B	64.9	A

* Means with the same capital letter are not significantly different by Tukey's test at 0.05 level

Gluing effects

It is noted that the effects of assembly time on wet shear strength differed to that of the percent wood failure. While the 30 minutes AT resulted in significant lower wet shear strength, the 10 minutes AT yielded significant lower percent wood failure. It is generally agreed that short AT tends to enhance over-penetration and long AT tends to cause dry-out and/or poor glue transfer. From the observations of the failure surface (Fig. 3), the results seem to suggest that, even with optimum glue transfer, the short AT yielded starved joints condition which resulted in lacking of the “resin-bite” necessary for yielding high wood failure (Fig. 3A). On the other hand, the glueline dry-out at long AT (Fig. 3C) resulted in low wood failure.

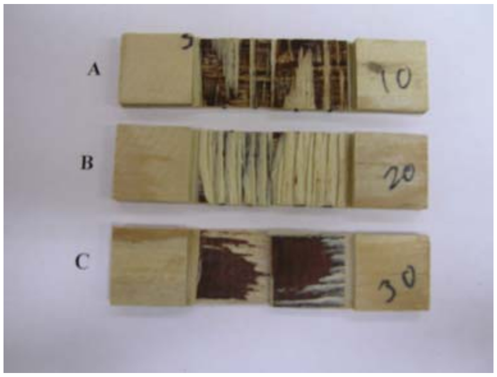

Fig. 3. Effects of assembly time on percent wood failure of the plywood shear specimens. "A" means 10 minutes AT, shallow and lighter color of the glue on surface indicating glueline over-penetration; "B" means 20 minutes AT, high percentage wood failure indicating optimum gluing conditions; and "C" means 30 minutes AT, deep and darker color of the glue on surface indicating dry-out glueline

Conclusions

Liquefaction of spent creosote-treated wood was studied to determine the technological practicability of its application in converting treated wood waste into resin adhesives. On the basis of wood failure, the resins prepared from liquefied wood at P/W ratio of 2., reacted at F/LW ratio of 2.25, and applied the glue at the rate of 90 pounds per 1000 square ft of double glue line met the standard of vacuum-pressure soak cycle for exterior glueline (PS-1-66). In the first attempt to make a plywood resin adhesive, the results were very encouraging. Considering that no pre-press was applied, the results suggest that, with additional studies of resole formation and glue mix formulation, the possibility of developing a liquefied creosote-treated wood-based adhesive with improved bond quality might be anticipated. Furthermore, there is strong indication that the creosote in the resin system might be beneficial to the liquefaction of the treated wood. A study of the role of creosote on plywood bond quality is in progress. Thus, the fine tuning on molecular development of the resin may also provide additional revenue for further improvement of the resin adhesives.

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