

Liquefaction of the Used Creosote-Treated Wood in the Presence of Phenol and Its Application to Phenolic Resin

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Abstract

A limited initial study was made to evaluate liquefaction of creosote-treated southern pine wood sawdust with liquefaction of birch wood powder as a control. The objective was to assess the feasibility of using creosote-treated southern pine wood as a raw material for the formulation of phenol-based resin adhesives. The liquefaction was conducted in the presence of phenol with sulfuric acid as a catalyst at reaction temperature and time of 150°C and 60 minutes, respectively. Novolac and resole resins were formulated from the liquefied wood, and their physical and mechanical properties of molding compounds made with them were determined. Residues obtained from samples of liquefied creosote-treated wood (5.8%) were significantly lower than those from non-treated birch wood powder (17.3%). Apparently, the residual creosote content of the treated-wood behaved as a reagent co-working with phenol to enhance the liquefaction. The flexural strength and the flexural modulus of moldings made from novolac resins prepared from liquefied creosote-treated wood were comparable to novolacs made from non-treated birch wood. Bond quality of southern pine plywood made from liquefied creosote-treated wood resin was only slightly lower than plywood made from conventional phenolic resin. Visual examination of the wood failure on broken shear specimens seemed to indicate overpenetration of the resin made from liquefied creosote-treated wood, and it was probably one of the major causes of lower bond quality. 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

Preservative-treated wood products are well known to significantly prolong their service life and thus extend the forest resource and enhance its sustainability. Inevitably however, treated products become unserviceable either due to mechanical damage or failure, biological deterioration, or obsolescence. Disposal of spent preserved wood increasingly has become a major concern because of its residual preservative content. Popular waste disposal options for spent preserved wood, such as combustion and land filling, are becoming more and more costly because of increasingly strict regulatory requirements. Thus, recycling options, particularly the one requiring zero discharge of preservative into waste streams, are of great importance to those concerned with the life cycle management of treated wood. Research in Pineville, Louisiana, laboratory of Southern Research Station has been focused on the development of a closed-loop recycling system (Fig. 1) with recycled composite products and liquefaction as the two key elements in the system. Three major steps toward determining the technological practicability of fabricating composite poles from used utility poles were accomplished with the determination of the residual preservative and its distribution (9), evaluation of the effects of residual preservatives on gluability (11) and decay resistance (12), and recycling of out-of-service utility poles for useful engineered wood products (10). This study, however, is the first in a series of studies on the liquefaction of preservative-treated wood. Despite

recent advancements in techniques of liquefying wood under mild conditions (6,7,13) and its promising potential for turning by-product wood wastes into new products (1,5,6,8,14,15), no study of liquefying preservative-treated wood has been reported. This study covers the evaluation of the liquefaction of two types of preservative-treated wood (i.e., chromated copper arsenate or creosote) using two liquefaction processes (i.e., in the presence of phenol and alcohols). The objective of the study is to develop an economically viable liquefaction process to either convert treated wood waste into useful products or to develop a novel new technique for the separation of residual preservatives from wood. The results of a preliminary study of liquefying recycled southern pine creosote-treated wood are presented in this paper.

Experimental Procedure

Materials

The recycled creosote-treated southern pine wood sample used in this study was the sawdust collected from sawing of recycled utility poles in a previous study (9). The sawdust, screened through No. 10 sieve (9 mesh), was used without further treatment. Wood meals used in the liquefaction as a comparison were of 20 to 80 mesh size prepared from the birch chips (*Betula maximowiczii* Regel). The filler used in the moldings of the phenolic resin was wood powder of 200-mesh pass size. All the other chemicals were of reagent grade and were used as received.

Liquefaction of Creosote-Treated Wood

Liquefaction Procedure.—Liquefaction reaction of the recycled creosote-treated wood was conducted as shown in Figure 2. To prepare liquefied wood, all used creosote-treated wood, phenol, and sulfuric acid (as a catalyst) were placed in a 300 ml three-branch flask equipped with a stirring system and a reflux condenser. To initiate the reaction, the mixture was heated in an oil bath maintained at 150°C. After the desired reaction time, the liquefied product was cooled to room temperature, and then diluted by methanol, followed by the filtration through a Toyo GA100 glass filter paper. The resulting filtrate was adjusted to a desired volume and measured for the un-reacted phenol content by high performance liquid chromatography (HPLC). The residue was dried in an oven at 105°C to a constant weight. The percent residue was calculated by the following equation:

$$\text{Percent residue (\%)} = W_r/W_o \times 100$$

where:

W_o = the weight of the starting amount of creosote-treated wood

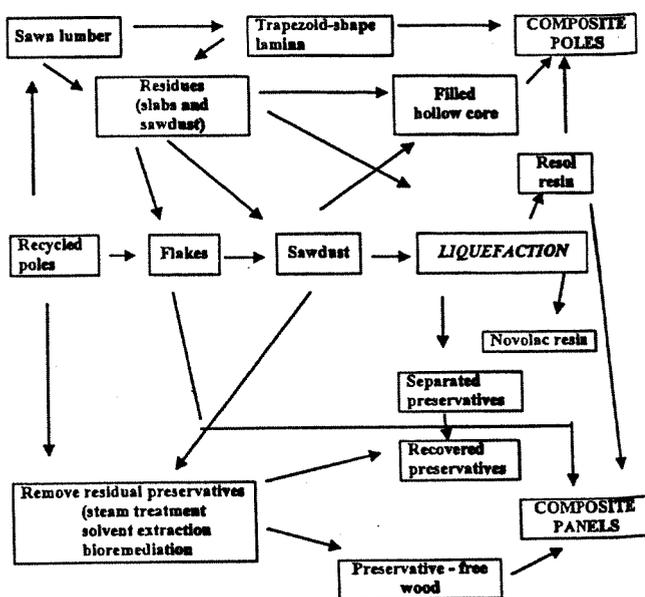


Figure 1.—Closed-loop recycling system for preservative-treated wood.

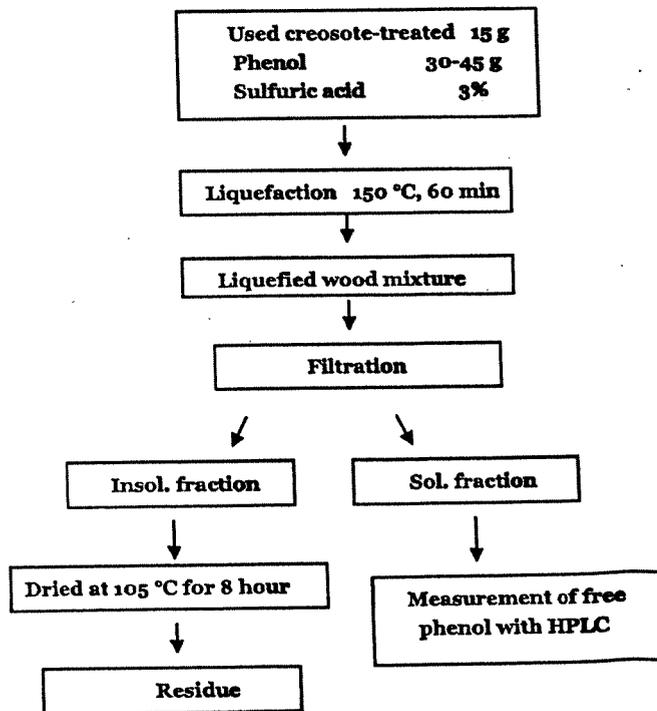


Figure 2.—Liquefying procedure for southern pine creosote-treated wood sawdust.

W_r = the weight of the unliquefied residue.

Determination of Un-Reacted and Combined Phenol.—The amount of un-reacted phenol (or free phenol) remained after liquefaction was measured by HPLC (Shimadzu LC-10A) equipped with CPD-10A

Used creosote-treated	15 g
Phenol	30-45 g
Sulfuric acid	3%

Liquefaction 150 °C, 60 min

cooling to 70 ~90 °C

Adding NaOH, formalin

Resinification (120min)

Test of PH value HPLC GPC Test of viscosity Test of gel-time

Figure 3.—Preparation of resoles from liquefied southern pine creosote-treated wood sawdust.

UV-vis detector. STR ODS-II reverse phase column was used for this study. The mobile phase was methanol/water (1/2, v/v) in a flow rate of 1.0 ml/min. The amount of combined phenol was calculated by the following equation:

$$\text{Combined phenol (\%)} = (W_1 - W_2) / (W_0 - W_r) \times 100$$

where:

W_0 = the weight of the starting amount of creosote-treated wood

W_r = the weight of the unliquefied wood residue

W_1 = the starting amount of phenol

W_2 = the amount of the unreacted phenol remained after liquefaction.

Preparation of Resole from Liquefied Creosote-Treated Wood

Resole Preparation Procedure.—The procedure for the preparation of resole and the determination of resole properties are summarized in Figure 3. The creosote-treated wood was liquefied first under the desired reaction conditions. At the end of liquefaction, the temperature of the liquefied product and the oil bath were decreased to 70° to 90°C and followed by the addition of the calculated amount of formalin (37% aqueous solution) and the 33.3% NaOH solution (for controlling the pH values to about 10.0 to 10.5) to the liquefied product. The molar ratios of formaldehyde to unreacted phenol ranged from 1.0 to 1.5. The resinification was conducted at 70° to 90°C for 10 to 120 minutes under reflux. At the end of resinification, the reaction was ter-

minated by rapidly cooling the reaction mixture to room temperature. Gel time, pH, amount of unreacted phenol, viscosity, molecular weight and molecular weight distribution were determined.

Characterization of the Resole.

pH.—The resole sample was dissolved in distilled water to make a 10 percent solution and the pH was measured.

Gel time and viscosity.—The gel time of the resole was evaluated according to Japanese Industrial Standard (JIS) K 6802, and its viscosity was measured according to JIS K 6833 by using a B-type viscometer.

Solids content.—Approximately 7 to 10 grams of resole was weighed and placed in a vacuum oven with temperature maintained at 70°C. The sample was dried without vacuum for 1 hour and then in vacuum for 8 hours. The dried sample was weighed and the solid content was calculated by the following equation:

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

where:

W_1 and W_2 = the weight of resole before and after drying, respectively.

Molecular weight.—Molecular weight and molecular weight distribution of the resole were determined by the gel-permeation chromatography (GPC) analysis. A Soda HLC-8020 GPC system equipped with a refractive index (RI) detector and TSK gel-G. 2000 HHR and -G. 1000HHR columns connected in series was used. Measurements were conducted at 40°C using THF (containing 0.4% trichloroacetic acid) as the mobile phase at a flow rate of 1.0 ml/min. The sample injection volume was 100 µL at concentration of 0.5 to 1.0 weight percent in the same solvent as the mobile phase. The molecular weights of the samples were calibrated by the monodisperse polystyrene standards.

Fabrication of Southern Pine Plywood and Evaluation of Bond Quality.—The liquefied wood resin used in fabricating plywood was prepared by the method as described in Figure 3 with the following conditions:

1. phenol to wood ratio was 2.0,
2. formaldehyde to liquefied wood ratio was 1.75, and
3. reaction time was 180 minutes.

In addition, two commercially available phenolic resins were included in the study as control. General gluing conditions were:

Glue mix: The adhesive mixture including resin, extender, and filler of a typical southern pine plywood mix was used. Total resin solids in the mix was 26 percent

Table 1.—Formula of the molding compound.

	(g)
Liquefied creosote-treated wood	37.7
Wood powder (filler)	49.5
Hexamine	9.4
Ca(OH) ₂	2.4
Zinc stearate	1.0

Glue application rate: 85 lb./1,000 ft.² of double glueline

Closed assembly time: 20 minutes

Hot press temperature and time: 4.5 minutes at 165°C

Specific pressure: 175 psi

Veneer were of southern pine, 1/8-in. thick. Three 12- by 12-in. three-ply panel were glued up for each of the resins, and 20 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 percent wood failure in specimens subjected to the vacuum-pressure cycle for exterior glue line (PS -I-66).

Preparation of Novolac with Liquefied Creosote-Treated Wood

Novolac Preparation Procedure.—The procedure for the preparation of the novolac resin was similar to the preparation of the resole with exception that no NaOH was added when reacting with formaldehyde. The liquefied products were dissolved in methanol and neutralized with magnesium oxide (MgO). After neutralization, the mixture was concentrated by successive reduced-pressure evaporation (about 20 mmHg) at 50°C and 180°C to remove all the diluting solvent and the unreacted phenol. The concentrated compound, called novolac resin, was stored in a desiccator.

Preparation of Novolac Moldings.—The formula for the moldings of the novolak-like resin is listed in Table 1. All ingredients without the resin were premixed sufficiently in a mixer. The resin, in an acetone solution, was then added and mixed thoroughly until a uniform compound was obtained. The resulting compound was dried in an oven at 70°C for 1 hour to remove the acetone. The dried compound was ground into powder and kept in a desiccator before molding.

About 6 grams of the powder resin were compression-molded into a 80 by 10 by 4 mm tested specimens with a laboratory molding press. The molding was accomplished under a pressure of about 30 MPa at 180°C for 5 minutes.

Table 2.—Liquefaction results of the recycled creosote-treated southern pine wood sawdust and birch wood powder.

Liquefied samples ^a	Residue	Combined phenol	Free phenol	Flow temp.
	----- (%) -----		(g)	(°C)
Recycled creosote-treated southern pine wood	5.8	120	12.9 (28.2%)	120
Birch wood	17.3	146.3	11.8 (25.8%)	150

^a All samples were prepared with wood-to-phenol-to-sulfuric acid ratios (w/w/w) of 15/30/0.9, reaction temperature of 150°C, and reaction time of 60 minutes.

Measurement of the Flexural Properties.—The flexural test of the molding specimens was conducted using a Shimadzu Autograph DCS-R-500 testing machine according to JIS K-6911 with a strain rate of 2 mm/min. The sample were conditioned at 20±0.5°C and 60 percent relative humidity for at least 48 hours before testing.

Results and Discussion

Liquefaction of Used Creosote-Treated Wood

A comparison of the liquefaction process between recycled southern pine creosote-treated wood sawdust and the birch wood powder is shown in Table 2. It is noted that the average residues obtained from the liquefaction of the creosote-treated wood (5.8%) are significantly lower than that from liquefied birch wood powder (17.3%), suggesting that liquefaction is more complete when recycled creosote-treated wood is involved than with untreated birch wood powder. On the other hand, the amount of combined phenol for the liquefied creosote-treated wood (120%) is lower than that of liquefied birch wood (140%). The lower combined phenol is desirable because several previous studies (1-4) have shown that the amount of combined phenol ranging between 90 to 120 percent was an ideal level for preparing a phenolic resin having excellent mechanical and flowing properties. The difference in the liquefaction results between the creosote-treated wood and the birch wood powder can be attributed to the presence of the creosote because the preexisting creosote behaved as a reagent co-working with phenol to enhance liquefaction. With lower flow temperature, the liquefied creosote-treated wood is also expected to have better flow properties. It is evident that the liquefied recycled creosote-treated wood had many of desirable properties as a raw material for the manufacture of phenol-based resin adhesives.

Table 3.—Reaction conditions and properties of the resoles made from liquefied creosote-treated wood.

Sample ID ^a	PF	LW-1	LW-2	LW-3	LW-5	LW-6
CH ₂ O/NaOH ^b	30/6	30/6	30/6.5	35/6.5	35/6	35/7
CH ₂ O/PhOH	1.5/1	1.15/1	1.15/1	1.34/1	1.35/1	1.34/1
Reaction temp. (°C)	70	70	70	70	90	70
Reaction time	120	120	120	120	60	120
Viscosity (MPa)	477	2,100	1,125	795	706	3,663
Free phenol (%)	2.65	0.33	0.71	0.56	0.55	0.77
pH value	10.36	10.30	10.08	10.05	10.04	10.43
Solid content (%)	52.4	60.1	59.8	61.8	58.9	59.3
Gel time (min.)	18.8	12.2	18.3	14.2	15.6	14.7
M _n	340	338	136	222	264	291
M _w	849	1,061	145	590	594	1,033
M _w /M _n	2.49	3.14	1.05	2.65	2.25	3.55

^a PF = phenol formaldehyde resin and LW = liquefied wood. All LW were made with creosote-treated wood-to-phenol-to-sulfuric acid (w/w/w) ratios of 15/30/9, at liquefaction temperature of 150°C, and reaction time of 60 minutes.

^b Concentration of formaldehyde and NaOH used were 37% and 33.3%, respectively.

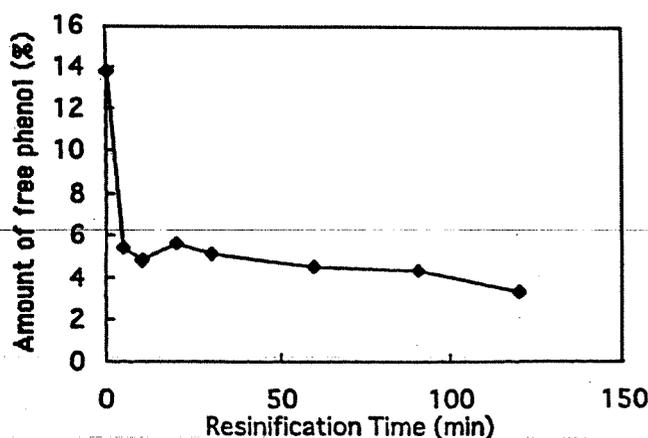


Figure 4.—Effect of resinification time on the amount of free phenol. Resinification temperature: 150°C; phenol/creosote-treated wood (w/w): 3/1; and sulfuric acid content: 3% based on the amount of phenol.

Properties of Resole Made with Liquefied Creosote-Treated Wood

The properties of the resoles prepared with the liquefied creosote-treated wood are shown in Table 3. In general, the results show that all properties are comparable to those of a conventional resole made in the laboratory (i.e., sample PF in Table 3). It is noted, however, the viscosities of the resoles made with liquefied creosote-treated wood (ranging from 706 mPa.s to 3,663 mPa.s) were significantly higher than that of conventional resole (477 mPa.s), indicating much faster increase in viscosity development of the resole made from liquefied creosote-treated wood. Because of its simplicity of the measurement, usefulness of the viscosity-mo-

lecular weight correlation, and value as an indicator of the working properties of resin adhesive, the viscosity measurement is widely used to control the reaction of conventional phenolic resins. Past experiences suggested the faster resin viscosity build up might influence the flexibility of reaction control. Thus, the need for optimum viscosity control is more evident for the liquefied creosote-treated wood than in conventional phenolic resins in optimizing resin formulation.

Table 3 also shows that, among the resoles made with liquefied creosote-treated wood, the formaldehyde/phenol ratio and NaOH content had rather minor effects on the gel time of the resole. On average, the gel-times for most of the resoles are below the level of JIS specification (i.e., 20 min.), suggesting good storage properties. Furthermore, all resoles in the study are soluble in water or a mixture of water/methanol.

The effect of reaction time on the amount of unreacted phenol remaining after resinification is shown in Figure 4. The unreacted phenol decreased sharply to about 4 percent within the first 10 minutes and then leveled off.

The effects of reaction time on the molecular weight distributions of resoles made with liquefied creosote-treated wood are shown in Figure 5. Based on the clear peak separation together with its molecular weight, it is suggested that peak 1 responds to the residual phenol, peak 2 to mononuclear, peak 3 to di-nuclear, and peak 4 to the tri-nuclear. As the reaction time increased, the low molecular weight fractions such as peaks 1 to 4 decreased and high molecular weight oligomers and polymeric fractions increased.

The effects of reaction time on the M_w and M_w/M_n are shown in Figure 6. The M_w decreased initially with increasing reaction time, and then increased after the

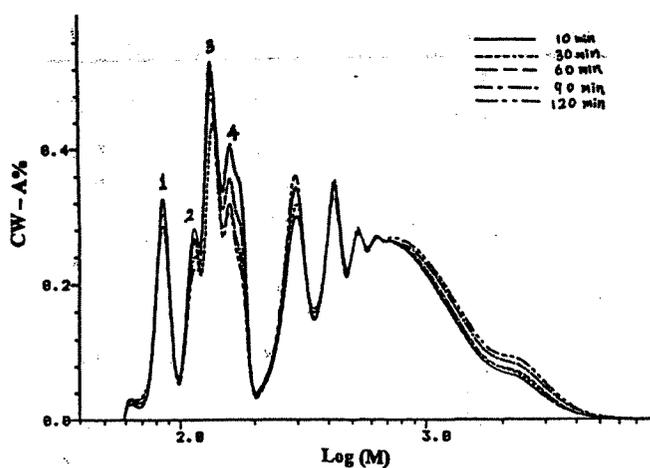


Figure 5.—Effect of reaction time on molecular weight distribution of resoles made from liquefied creosote-treated southern pine wood sawdust.

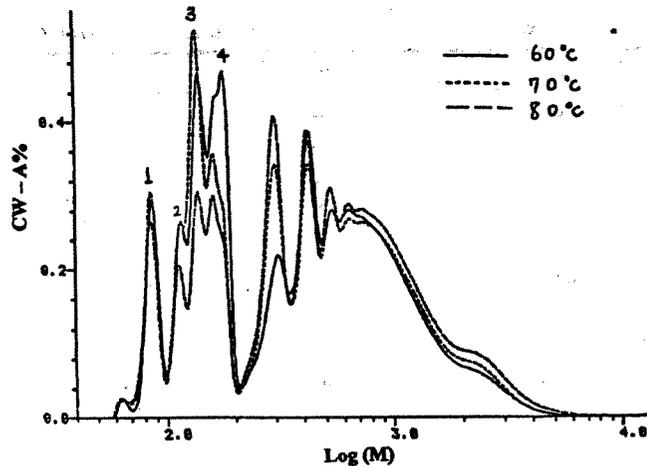


Figure 7.—Effect of resinification temperature on molecular weight distribution of the resole made from liquefied creosote-treated southern pine wood sawdust.

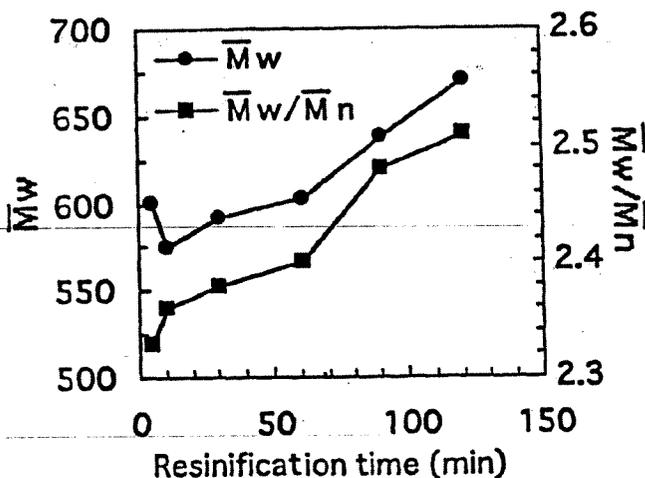


Figure 6.—Effect of resinification time on molecular weights of the resoles made from liquefied creosote-treated southern pine wood sawdust. Resinification temperature: 70°C; formaldehyde/phenol: 1.15/1.

reaction time reached 10 minutes. This trend is consistent with that of the unreacted phenol. As shown previously in Figure 5, the mono-, di-, and tri-nuclear phenols were produced rapidly due to the intense reaction between the free phenol and formaldehyde within the first 10 minutes, resulting in significant decrease in molecular weights. However, after the reaction time of 10 minutes, the free phenol was consumed up to an upper limit and the reaction of phenol and formaldehyde reached a minimum as shown in the leveling off of free phenol in Figure 4. Thereafter, the low molecular weight substances (e.g., peaks 1 to 4) continued to condense with each other or with the liquefied wood components to form large molecules.

Table 4.—Effect of resinification temperature on the molecular weights of resole made from recycled creosote-treated southern pine wood sawdust with a reaction time of 60 minutes.

Reaction temperature (°C)	M_n	M_w	M_w/M_n
60	252	591	2.34
70	251	603	2.40
80	285	711	2.49

Figure 7 showed the effect of resinification temperature on the molecular weight distributions of the resole made from liquefied creosote-treated wood. As expected, increase in the resinification temperature led to decrease in the low molecular fractions and increase in the higher molecular weight polymeric fractions. Consequently, the corresponding M_n , M_w and M_w/M_n also increased as the resinification temperature increased (Table 4). It is interesting to note that the average values of M_n , M_w and M_w/M_n of the resole made from liquefied creosote-treated wood at 60-min. reaction time (Table 4) approached those of conventional phenolic resin at 120-min. reaction time (sample PF in Table 3). This suggests a faster condensation reaction for the resole made from liquefied creosote-treated wood. This is in good agreement with earlier results that a faster increase in resin viscosity was shown with the resole made from liquefied creosote-treated wood.

It is well known that viscosity is sensitive to the shear rate. It was noted, however, the shear rate seemed to have little effect on the viscosity measured in the study (Fig. 8). In contrast, the shear period (rotating

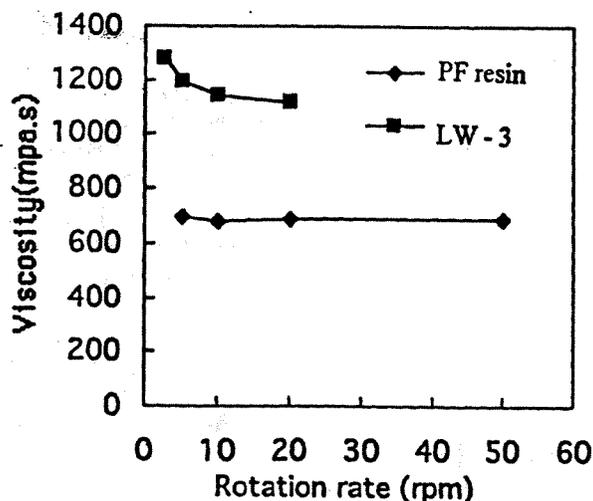


Figure 8.—Effect of rotation rate on the viscosity of resole made from the liquefied creosote-treated southern pine wood sawdust. Rotation time: 3 minutes.

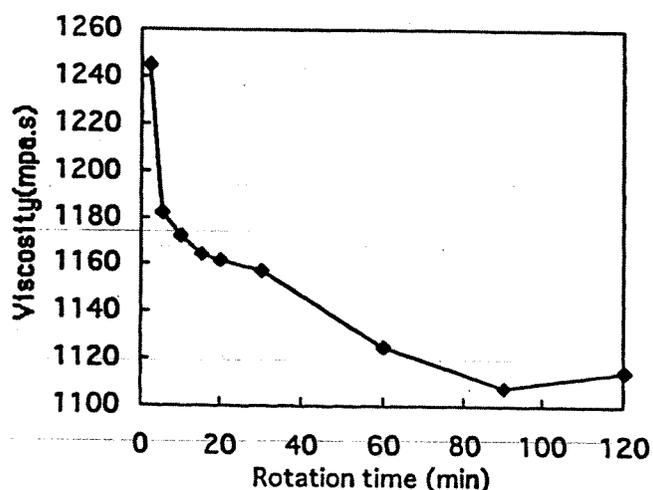


Figure 9.—Effect of rotation time on the viscosity of the resole made from creosote-treated southern pine wood sawdust. Rotation rate: 20 rpm.

time) was shown to have significant effect on the viscosity (Fig. 9), suggesting the possibility of thixotropic affect.

Bond Quality of Southern Pine Plywood

The average wet shear strengths and percent wood failures for southern pine plywood made with liquefied wood resin and two commercially available phenolic resins are summarized in Table 5. In general, the bond quality of southern pine plywood made with liquefied wood resin was slightly lower than that of commercial phenolic resins. Wet shear strength was about 22 percent lower and wood failure was about 9 percent lower than southern pine plywood bonded with commercial phenolic resins. Visual examination of the wood failure

Table 5.—Effect of resinification temperature on the molecular weights of resole made from recycled creosote-treated southern pine wood sawdust with a reaction time of 60 minutes.

Resin samples (°C)	Wet shear strength (psi)	Wood failure (%)
Liquefied wood resin ^a	243	79.2
PF resin A	313	87.6
PF resin B	311	86.0

^a Liquefied creosote-treated wood resin was made with phenol/wood ratio of 2.0 and formaldehyde/liquefied wood ratio of 1.75.

Table 6.—Physical and mechanical properties of the molding made from liquefied recycled creosote-treated southern pine wood sawdust and birch wood powder.

Properties	Recycled creosote-treated wood	Birch wood powder
Flow temperature (°C)	120	150
Flexural strength (MPa)	66	64
Flexural modulus (MPa)	7,572	7,794

on broken shear test specimens showed optimum resin transfer, and overpenetration of resin seemed to be one of the major causes of lower bond quality of the plywood made with the liquefied wood resin adhesive. Considering that this study is the first attempt to formulate resole adhesive from liquefied creosote-treated wood for gluing southern pine plywood, the results are very encouraging. With additional studies of resole formulation and glue mixing, the possibility for developing a satisfactory liquefied wood resin with improved bond quality is anticipated.

Mechanical Properties of Novolac Molding

The flow temperatures of the liquefied creosote-treated wood resin and properties of its moldings are shown in Table 6. The flexural strength and the flexural modulus of novolac moldings made with liquefied, used creosote-treated wood are comparable to those made with untreated liquefied birch wood resin.

Conclusion

Liquefaction of spent creosote-treated wood was studied to determine the technological practicability of its application in converting treated wood waste into resin adhesives. The liquefaction of creosote-treated wood was more complete than that of non-treated birch wood, because the residual creosote content in the treated-wood behaved as a reagent co-working with phenol to enhance the liquefaction.

The flexural strength and flexural modulus of novolac resin moldings made from liquefied creosote treated-wood were highly comparable with those made from liquefied birch wood. In the first attempt to make a plywood resin adhesive, the bond quality of southern pine plywood made with a liquefied creosote-treated wood resole resin was only slightly lower than that of plywood made with conventional phenolic resin. However, the results were very encouraging. With additional studies of resole formation and glue mix formulation, the possibility for developing a liquefied creosote-treated wood based adhesive with improved bond quality is anticipated.

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