

CHARACTERISTICS OF PHENOL-FORMALDEHYDE ADHESIVE BONDS IN STEAM INJECTION PRESSED FLAKEBOARD

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ABSTRACT

A better understanding of the mechanisms involved in phenol-formaldehyde resin-wood bonding is needed to design adhesive systems that can adequately develop bond strength in a humid environment. This study was performed to determine how the molecular weight distribution of a liquid resole phenol-formaldehyde adhesive affects mechanical properties and adhesive flow in flakeboard bonded during steam injection pressing. The performance of three adhesives, differing only in molecular weight distribution, was studied. For all adhesives, mechanical properties of specimens located on the edge of the panel were found to be superior to those located in the center of the board. Excessive moisture present in the center of the mat was believed to be responsible for poor bonding. Edge internal bond strength improved with higher weight average molecular weight adhesive. Fluorescence microscopy and image analysis techniques were used to measure flow of adhesive into the wood substrate before and after exposure to a steam injection pressing environment. Flakes wetted with adhesive and not exposed to a pressing environment had more adhesive penetration with the lowest weight average molecular weight adhesive. Deeper and less concentrated adhesive penetration was measured in flakes exposed to a steam injection environment, with a smaller apparent difference between the three adhesives.

Keywords: Phenol-formaldehyde, steam injection pressing, fluorescence microscopy, image analysis, wood bonding.

INTRODUCTION

Recent commercial applications of steam injection pressing have renewed interest in this pressing technique. Steam injection during pressing rapidly transfers heat throughout the wood particulate mat, facilitating faster cure of thermosetting adhesives. Thus, steam injection pressing has the advantage of reduced press times as compared to conventional hot

pressing, allowing production of thicker wood products. The injection of saturated steam into a mat creates a host of steam-related pressing variables, as well as introducing an adhesive curing environment that is different from the mat environment that exists during conventional hot pressing. During steaming, some steam condenses, thus releasing the heat of condensation in the mat. However, conden-

sation creates a humid environment and perhaps a substantial quantity of liquid water, which is not desirable for curing condensation polymers such as urea-formaldehyde and phenol-formaldehyde resins. Steam injection environments are believed to affect phenol-formaldehyde (PF) adhesive bonding in at least two areas: (1) moisture-induced effects on condensation polymerization kinetics, and (2) excessive flow of the adhesive from the bondline during and after steaming due to its solubility in water.

The objectives of this project were to determine how the mechanical properties and adhesive flow in flakeboard panels produced with steam injection pressing were affected by the molecular weight distribution of a liquid resole PF. Fluorescence microscopy and image analysis techniques were used to quantify flow of the adhesive into unpressed wood flakes and flakes exposed to a severe steam injection pressing environment.

BACKGROUND

The responses of a steam injection mat environment to adjustment of steam time, steam pressure, board thickness, adhesive type, and mat density range during the injection of steam have been measured (Geimer et al. 1991; Hata et al. 1989). Saturated steam conditions prevail through most of a steam injection pressing cycle, except for a brief period following the injection of steam and prior to venting the press manifold to atmosphere (Geimer et al. 1991). During the period immediately following steam injection, vapor pressure measurements indicate that significant condensation may occur in the mat. Acceptable board properties can be formed in that type of mat environment with a liquid resole PF by using high temperatures with a long steaming schedule.

Efforts have been made to simulate steam injection bonding conditions and monitor thermoset adhesive cure (Geimer and Christiansen 1991). A high humidity environment (91% RH) could accelerate development of ad-

hesive stiffness and degree of chemical cure of a non-aqueous PF as judged by dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC), respectively. Moisture-induced plasticization of the adhesive in a humid environment may increase polymer chain mobility and facilitate crosslinking. However, with lap shear specimens prepared using aqueous PF at 115 C, bond strength development was greatest when bonds were formed in an intermediate relative humidity (41%), while bonds that were formed in the highest humidity (91%) were the weakest. Measured hardness of an aqueous PF adhesive cured in a steam environment in which temperatures ranged from 120 C to 200 C showed that the PF adhesive required long steam times and high temperatures to cure, and the adhesive had less than 20% of the hardness of a PF adhesive fully cured in a 160 C oil bath (Surbiyanto et al. 1989).

Mechanical properties of panels and adhesive flow characteristics have been shown to be affected by the molecular weight distribution of liquid resole PF adhesives used in conventional hot-pressing. Laminated veneer lumber (LVL) loaded to failure after accelerated aging tests has indicated that higher wood failure can be obtained with neat PF resins that have low weight average molecular weight (Gollob et al. 1985). Poor neat adhesive performance has been obtained with a high weight average molecular weight adhesive with a large degree of molecular branching. When extenders and additives are used with the adhesive, the effects of individual variables are masked in a complex interrelationship (Gollob et al. 1985). Low molecular weight adhesive fractions may penetrate wood cell walls in veneers and serve as a primer by facilitating adsorption of higher molecular weight fractions (Nearn 1974).

The weight average molecular weight of PF adhesives used in veneered panels is several orders of magnitude larger than in PF adhesives used with nonveneered panels. Internal bond strength has been shown to increase using

larger proportions of high molecular weight fractions of PF adhesive during conventional hot-pressing of oak flakeboard. Low and medium molecular weight fractions are hypothesized to over-penetrate the wood substrate, thus “starving” the bondline (Wilson et al. 1979). Low molecular weight fractions of an aqueous PF adhesive alone serve poorly as a binder or as a solvent to aid in penetration of higher molecular weight adhesive molecules (Stephens and Kutscha 1987). It is believed that the primary function of the low molecular weight adhesive is to cross-link between the higher molecular weight adhesive molecules. In addition, the low molecular weight PF adhesive fraction has been shown to have the greatest gross adhesive penetration into the wood substrate when wetting.

METHODS AND MATERIALS

Panel manufacturing

Three replicate steam injection flakeboard panels were manufactured for each adhesive. The panels were manufactured with *Liriodendron tulipifera* flakes cut with a 91-cm (36-in.) CAE disc flaker to target dimensions of 13 mm by 76 mm by 0.51 mm (0.5 in. by 3 in. by 0.020 in.). The flakeboard panels had dimensions of 610 mm by 610 mm by 25.4 mm (24 in. by 24 in. by 1 in.) with a specific gravity of 0.64. The mats were hand-felted with random orientation. Flake moisture content was approximately 3.4%, and mat moisture content going into the press was approximately 9.3%. The panels were pressed in a 300-ton, 610-mm by 610-mm (24-in. by 24-in.) Clifton hot press controlled by a programmable YEW process loop controller. Steam was supplied by a dedicated Coates 45 kW electric boiler. Platens were independently heated by a Sterlco Model F6026-D high temperature oil heater. The platens had 1.59-mm (0.0625-in.) diameter steam injection port holes spaced 57.2 mm (2.25 in.) apart. The outer 102 mm (4 in.) of the platens did not contain steam injection port holes.

A steam injection schedule similar to one used successfully with a liquid resole PF adhesive by Geimer et al. (1991) was used. Total press time was approximately 400 seconds, with 27 seconds of 1.37 MPa (200 psi) steam injected during press closing. Due to the finite steam supply, steam pressure declined throughout the steaming period. Steaming was initiated in a 15-sec hold stage in which press closing ceased when the mat reached a specific gravity of 0.27. Press closing was again started and steaming continued until approximately 5 seconds after the mat reached final platen position. A 25.4-mm wide by 6.35-mm thick (1-in. by ¼-in.) steel dam was inserted into the outer edge of the mat to help maintain internal gas pressure, mimicking a commercial scale press. Steel screens with dimensions of 610 mm by 610 mm by 1.78 mm (24 in. by 24 in. by 0.070 in.) were used on top and bottom of the mat to help distribute the steam more evenly. The outer 102 mm (4 in.) of the screens were sealed with a high temperature silicone RTV sealant to slow leakage of steam. The press platens were heated to 200 C. Press conditions as well as temperature in the mat were recorded through a computer-based data acquisition system. After steaming ceased, the solenoid steam valve system remained closed, and steam was allowed to dissipate from the press manifold through the mat for 82 sec. Afterwards, the steam control valve was opened, and the press manifold was allowed to vent to atmosphere for 10 sec. A pneumatic vacuum ejector was then employed through the press manifold for the rest of the pressing cycle to aid in removal of moisture from the mat.

Adhesive characterization

Three liquid resole phenol-formaldehyde adhesives were used to manufacture the panels. The adhesives used were identical, except for the degree of polymerization. The molecular weight distribution of the three adhesives was characterized by gel filtration chromatography (GFC) as performed by Sellers and

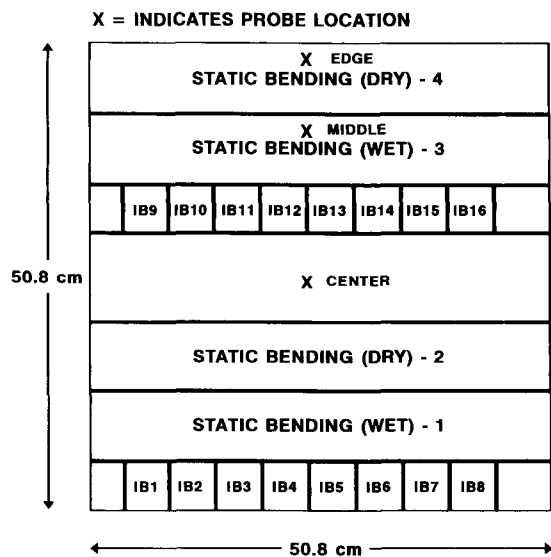


FIG. 1. Cutup diagram of flakeboard panels and location of thermocouple and gas pressure probes.

Prewitt (1990). The gel packing material was Sephacryl S-200, and an aqueous 0.1N NaOH eluent was used. Sodium polystyrene sulphates and phenol were used as calibration standards. The UV detector was equipped with a 280-nm filter. Other pertinent adhesive physical properties such as viscosity, pH, and gel time were also measured. Resin solids were applied at 5% weight basis. No wax or sizing was added. The adhesive was applied to the flakes in a 45.7-cm by 122-cm (18-in. by 48-in.) rotating drum blender with a pneumatic atomizing nozzle. Air pressure to the nozzle was 152 kPa (25 psi) and the blender rotated at 0.27 rps (16 rpm).

Mechanical tests

Figure 1 shows the panel cutup diagram. Internal bond and static bending tests were performed according to ASTM D-1037-89 (1990). Sixteen internal bond specimens and four bending specimens were cut from each panel. Half of the internal bond specimens were cut from the edge of the panel (specimens 1-8) and half were cut from near the center of the panel (specimens 9-16). Two static bending speci-

mens were tested dry (specimens 2 and 4), and two were tested wet (specimens 1 and 3). Both wet bending specimens were from similar locations in the panel, but dry bending samples 2 and 4 were cut from locations close to the board center and edge, respectively.

Quantifying adhesive penetration

Flakes of *Liriodendron tulipifera* were sliced from the same log that was used to produce the panel furnish. The flakes were sequentially sliced from the relatively permeable sapwood of a water-saturated block with the width orientation as close to the pure tangential plane as possible. The flakes were dried in a convection oven at 104 C to oven-dry condition. Target flake dimensions were 25.4 mm by 25.4 mm by 0.635 mm (1 in. by 1 in. by 0.025 in.). Five minutes after removal from the oven, three drops of liquid phenol-formaldehyde adhesive were placed across the width of each flake with a micropipette set at 0.50 microliters volume. The flakes and each adhesive drop were weighted on an analytical balance. The flakes had a 5-min open assembly time. Half of the flakes were placed in a convection oven heated to 104 C overnight. These flakes will later be referred to as unpressed flakes. The other flakes, which contained adhesive drops, were mated with an opposing flake that contained no adhesive and were placed in a teflon fabric envelope. The envelope was produced from Spectrum® fluorocarbon macro filter with 174- μ m mesh opening, 180- μ m thickness, and 24% open area. The envelope containing the flake assemblies was placed in a flakeboard mat, exposed to a steam injection pressing environment, and later recovered from the panel. These flakes will be referred to as pressed flakes in later discussion. The press and steaming schedule that was used to produce this panel was similar to the one used to produce the nine flakeboard panels.

Cross sections of the cured adhesive on flake specimens were cut 80 μ m thick on a sliding microtome. These cross sections were stained with 0.5% Toluidine Blue O solution. After

staining, a fluorescence microscope interfaced with an image analysis system was then used to quantify adhesive penetration into the flakes. The staining and image analysis techniques have been described previously (Johnson and Kamke 1992). A Carl Zeiss Axioskop microscope with 50W mercury burner and halogen bulbs was used for observing the sections. The sections were viewed under incident light with a 10× Plan Neofluar objective providing a microscopic magnification of 80×. Total magnification on the image analysis system was 320×. An UV G365/LP420 excitor-barrier filter set was used. Measurements were performed with a (Universal Imaging) Image 1/AT Image Processing and Analysis System. The system consisted of a CCD solid-state camera, a 30 lines per millimeter 330 mm color monitor, a WIN 386 personal computer with monitor, a frame grabber board, and the Image 1/AT software. The staining technique used in this project suppresses the autofluorescence of the wood, while allowing the nonabsorbent adhesive to fluoresce brightly. Therefore, measurements conducted in this experiment are of adhesive area on the transverse plane, herein referred to as adhesive penetration area. The sections were positioned such that the left edge of the image consisted of the wood-adhesive interphase region, with the flake thickness in the radial direction lying across the long axis of the monitor screen. The target flake thickness was 635 μm, while the monitor screen corresponded to an area 623 μm high by 800 μm wide. Therefore, the flake thickness (in most cases) was less than 800 μm and lay completely within the image. Measurements of any adhesive that did not penetrate beneath the flake surface were also made. One-half of a bondline was analyzed in the pressed flake assemblies. Each image was analyzed as a whole, and then in individual segments 100 μm wide by the monitor screen height (623 μm). Up to 8 segments were analyzed for each image, starting at the wood-adhesive interface and analyzing 100-μm wide segments across the flake thickness.

TABLE 1. Analysis of liquid resole phenol-formaldehyde physical properties and molecular weight parameters as measured by gel filtration chromatography.

	Adhesive 1	Adhesive 2	Adhesive 3
pH	9.20	9.20	9.20
Nonvolatiles (%)	45.81	46.18	46.28
Viscosity (cP at 25 C)	82	138	200
Gel time (min)	23.50	20.90	19.96
NaOH (%)	1.45	1.45	1.45
Molecular weight averages			
Weight average (Mw)	2,964	3,680	4,366
Number average (Mn)	1,322	1,298	1,153
Z average (Mz)	6,159	7,713	10,440
Polydispersity (Mw/Mn)	2.241	2.835	3.786
	Area Adhesive 1	Area Adhesive 2	Area Adhesive 3
Molecular weight range			
73,500–35,000	0.00	0.00	0.11
35,000–18,000	0.40	1.14	2.95
18,000–10,000	3.89	6.50	8.94
10,000–5,000	12.70	15.50	16.47
5,000–3,000	15.06	16.33	13.89
3,000–2,000	15.27	15.63	14.63
2,000–1,000	25.95	24.17	21.13
1,000–500	20.29	16.22	15.58
500–100	6.44	3.46	7.73

RESULTS AND DISCUSSION

GFC results

GFC analysis results and other resin physical properties are listed in Table 1. The weight average molecular weight (Mw), and Z average molecular weight (Mz) increase from Adhesive 1 to Adhesive 3. These parameters, as well as the discrete molecular weight ranges, viscosity, and gel time, all indicate that Adhesive 3 is more highly developed than Adhesive 2, and Adhesive 2 is more highly developed than Adhesive 1. The number average molecular weight (Mn) decreases slightly from Adhesive 1 to Adhesive 3. This parameter is determined by the number of molecules in a molecular weight range, which is influenced by the large proportion of low molecular weight molecules found in all three adhesives. Polydispersity (Mw/Mn) increases from Adhesive 1 to Ad-

