ISOCYANATE REACTIVE HOT-MELT ADHESIVE FOR VENEER LAMINATES

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ABSTRACT There is a need for new wood adhesives to eliminate heat transmission time loss and steam blow wood rupture in hot-pressed laminated veneer lumber (LVL). This is most important in LVL that is 40 mm thick or greater. A total of 15 single-component isocyanate hot-melt adhesives were evaluated for water and heat resistance in preliminary screening tests. No external heat was applied and laminate consolidation was by nip roll. Plywood bond testing procedures were used. The results showed that 8.6 percent active isocyanate formulations could pass a single boil-dry-boil water resistance test and achieve wood failure greater than 80 percent when tested hot at 150°C. The research calls attention to a technological need and identifies a possible starting point for adhesive and process development.

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There is a need for new wood adhesives for use in thick laminates made from veneer where heat is very slow to diffuse to the inner gluelines. In addition to being a production bottleneck, heating causes internal steam pressure from water originating in wood and adhesive moisture. This leads to poor adhesion. Another result is severe wood rupture in weaker species such as spruce. These difficulties are especially critical in making laminated veneer lumber (LVL) and plywood greater than 40 mm thick. Special adhesive developments might enable these products to be made without heating or lengthy cold-press or clamping times. The curvilinear dynamics of heat diffusion encourages the investigation of reactive hot-melt adhesives (RHM) only in thick laminates. Thin - laminate manufacturing, including ply- wood, has endured for over 40 years using various phenol-formaldehyde (PF) hot-press adhesives and will likely remain unchallenged in the near future.

This preliminary paper examines single-component RHMs and reports on their current status relative to bonding thick laminates. The high tack and rapid green strength of RHMs offers tight laminate consolidation for prompt release from nip rolls or short cold-press periods.

ISOCYANATE REACTIVE HOT MELTS

Huber (8) and Souza (11) have examined RHMs. RHMs are currently used in such applications as metal-faced wood-based panel and floor laminates; window and door building components; edge banding and vinyl wrapping of profiles; and furniture and automotive assembly.

Most industrial RHMs are formulated using monomeric, difunctional, methylene diphenyl diisocyanate (MDI). Polymeric MDI is designated as PMDI, and has been used for years as a structural adhesive for oriented strand- board (OSB). Functionality is defined as the number of reactive groups per molecule. This averages to 2.2 to 2.8 for PMDI.

There are features of a melt-applied, high-tack isocyanate that make its use desirable:

1. Room-temperature cure with an advanced level of thermoset character in the final bond. Curing coreactants of MDI include wood moisture and cell wall material. Conventional hot melts depend entirely on melt fusion.

2. High tack during open time and hot-melt fusion green strength development make the laminate suitable for handling after nip roll or short press consolidation. These features are relied upon to hold the assembly during isocyanate reaction, which may not be completed for several hours.

3. Reductions in glueline blistering and wood rupture are expected because heat input to the assembly is very small compared to hot-press lamination.

4. Problems associated with dielectric heating, such as arcing and glue conductivity are removed when RHM is used.

The properties of RHM offer potential high production rate advantages to makers of automated assembly glued wood products. In fact, the short open assembly time of RHM requires high- speed assembly. Current RHM single- component adhesives are not usually...
claimed by manufacturers to be fully structural. Therefore, an RHM with an increased isocyanate content was included in this research.

*TABLE 1. - Materials - **RHM** adhesives*

Property Range	Application
Temperature	110° to 175°C
Application viscosity	6,000 to 50,000 cps
Open time (unsolidified or tacky)	15 to 600 sec.
Percent elongation at failure (25°C)	10% to > I 00% (estimated)
Wood's typical green shear strength	0.2 MPa in IS sec. to 1.4 MPa in 120 sec.
Solids	100%
Color	White to light brown

EXPERIMENTAL SCOPE

Simple bond quality screening was chosen for this introductory study of 15 formulations. The experimental units were Douglas-fir plywood shear bond specimens having three veneer lamina that were cut according to American Society for Testing and Materials (ASTM) test D 906 (2). An industrial PF hot-press adhesive was the reference control. Wood failure percentage and shear bond strength were the response variables. The first treatment consisted of a single boil-dry-boil cycle (ASTM D 3110 (3)). The second treatment was a heat resistance temperature test at 150°C (ASTM D 1151 (4)). Success in these simple treatments was considered prerequisite to more rigorous tests such as ASTM D 2559 (5), which deals with duration-of-load and accelerated-age testing.

The term structural bond used here is broadly defined as a bond manufactured to endure in outdoor exposure as long as the wood itself, which is also able to transfer stress between wood elements near universally as well as the wood itself. A comprehensive review by River (10) discusses structural bonding of wood. Conclusions from these studies indicate that a structural Douglas-fir plywood bond should have 80 to 90 percent wood failure. These values must not occur on specimens of unusually weak wood, resulting in low shear strength. Wood failure in Douglas-fir was considered uncompromised if shear strengths were greater than 0.7 MPa.

ASTM D 906 shear test does not apply a pure shear stress to the glueline. The stress is combined with tensile stress perpendicular to the glueline. Therefore, the test is not useful as a good measure of shear strength but has proven highly useful for comparing adhesives.

RHM ADHESIVE

Ten single-component RHMs were evaluated as received from the formulators. Typically, industrial products range from 0.5 to 2.5 percent free isocyanate content (NCO). Five of these were also tested at added isocyanate levels. These were increased to about 8.6 percent free NCO by the addition of 25 percent (by weight) of PMDI to the original formulations. **Table 1** provides the estimated ranges and expected properties covering a spectrum of commercial proprietary products and the PMDI-added versions. Estimates were not confirmed by tests in this preliminary work. A typical RHM formulation is disclosed in United States Patent 4,891,269 (H.B. Fuller, 1990). More complete information on RHM specification was obtained from the manufacturers.[1] The manufacturers were re- quested to provide formulations that tended to be rigid, not elastomeric, in cured form at room temperature.

PMDI-ADDED FORMULATIONS

An important criterion in selecting prepared formulations for isocyanate extension was retaining a high tack upon PMDI addition. Adding liquid PMDI to the formulation melts gave cooled cartridge solids that were stable for storage for at least 1 month. No reactive gelling was observed after mixing. Presumably, this was because all hydroxyl and other sites capable of reacting with isocyanate were consumed by the original difunctional MDI used in the industrial formulations. The weight ratio of the MDI addition was 75 parts RHM formulation to 25 parts of PMDI crosslinking enhancement. A rule of mixtures yields an estimated 8.6 percent free NCO in the modified formulations assuming the industrial formulations contained a typicall.5 percent NCO and the PMDI was at 30 percent NCO.

PF ADHESIVE

The standard plywood hot-press glue mix was based on PF resin, IB- 334, from Neste Resins, Inc.

The mix was:	PF	26.0%
	Wheat flour, bark filler solids	12.3%
	NaOH solids	6.6%
	Water	55.1%
		100%

The purpose of the PF control was to provide a structural bond performance benchmark using veneer from a common set of veneer sheets.

WOOD VENEER

Rotary-peeled interior Douglas-fir heartwood was used. Moisture content (MC) was 7 to 9 percent, nominal thickness was 3.2 mm on pieces cut 205 mm square. The standard deviation of thickness calculated between pieces of veneer using piece averages was 0.178 mm. The average primary roughness texture was estimated to be 0.38 mm in peak-to-valley relief, measured as stylus amplitude, with a range of 0.25 to 0.50 mm. This is considered acceptable veneer for use in sheathing-grade softwood plywood. Veneer with a primary texture amplitude greater than 0.510 mm is considered rejection veneer in normal plywood hot-pressing (9).

EQUIPMENT

A hand-held, heated, pressurized, hot-melt gun with a swirl spray nozzle was selected for RHM application because of the convenience of changing formulations quickly using preloaded 310-ml aluminum cartridges. The fine swirl spray distribution of the gun was not as controlled or uniform as a heated roll spreader, but the gun's utility in evaluating several formulations without using large volumes of sample formulations and extensive flushing was important. The PAM 500KS cartridge hot- melt applicator with a spray/swirl nozzle was used. The consolidation of the 3-ply plywood lay-ups was in a set of nip rolls 150 mm in diameter and 660 mm long. The rubber-covered rolls exerted an estimated 7 x 104 N force per lineal meter of nip roll pressure. (400 lb./in.)

[1] H.B. Fuller, Vadnais Heights, Minn.; Jowat Corp., High Point, N.C.; Klebchemie, Lenoir, N.C.; Na- can National Starch and Chemical Corp., Bridge- water, N.J.; PAM division of Buehnen Group, Charlotte, N.C.; and Swift Division, RCI, Downer's Grove, III.

METHODS AND SPECIMEN PREPARATION

Adhesive application was by regular hand movement over a single face of room-temperature veneer surface. Veneer receiving the RHM was placed on a tared weigh scale and application stopped at a single glueline target spread of 0.029 g/cm^2. The open assembly time from adhesive application until nip rolling the two veneers was about 20 seconds. This process was repeated to bond the third veneer to the first bonded pair, completing the 3-ply plywood. Nominally, six replicate panels were made for each adhesive formulation. Adhesive temperatures were set at 175°C to give the best swirl spray distribution. This temperature causes the MDI vaporization to exceed the level acceptable in an unventilated work space and any operations at this temperature would require extensive ventilation typically found in industrial high vapor pressure isocyanate operations. All specimens were stored at ambient conditions for 1 month prior to testing.

The PF control panels were made on a small laboratory press under the following conditions: press temperature = 156°C; press pressure = 1.05 MPa; press time = 2.5 minutes; single PF glueline target spread = .014 g/cm^2 (28Ib./l,000 ft.^{2} single glueline); and open assembly time = 8 minutes.

The test pieces were hot-stacked for 24 hours and stored at ambient conditions for 3 weeks prior to tests.

TESTING METHODS

Water-resistance testing methods used elements of the ASTM D 3110 standard for adhesives in nonstructural glued lumber products and product standard PS-l for plywood (1). The boil-dry-boil test procedure featured in these standards evaluates wet-use bond performance. The 25.4- by 79-mm plywood specimens are boiled for 4 hours, dried at 63°C for 20 hours, again boiled for 4 hours, followed by cooling in water for 1 hour, and wet shear tested at the cross ply to failure. Percentage wood failure and failure shear stress are recorded on five samples per test panel and these five are averaged to give each replicate mean.

The dry heat resistance test refers to ASTM D 1151 (effect of moisture and temperature on adhesive bonds). Deficient heat resistance is evidenced by much diminished shear bond performance when bonding specimens are tested while hot. Number 18 test condition in D 1151 specifies a dry temperature of 150°C. This was chosen because it is a point of departure where remitting of conventional thermoplastic hot melts typically occurs.

Both these tests were performed on shear specimens tested according to ASTM D 906 that were 25.4 by 79 mm and 9.75 mm thick. According to this method, the face and back of the 3-ply specimens were kerf cut to a depth nearly through the core so that the sheared area was 25.4 mm square. Shear load rate was 7560 g/second, with shear in the tangential grain direction.

TABLE 2. - Boil-dry-boil tests, woodfailure.[a]

Adhesive	Mean wood failure	Standard deviation	No. of replicates
	- - - - - (%) - - - - -		
I	56.0	38.2	6
2	81.0NS[b]	18.9	3
3	77.3NS	28.7	3
4	50.7	19.8	6
5	73.7 NS	29.1	6
6	65.3 NS	18.4	6
7 (3 + PMDI)	82.0 NS	23.4	3
8 (2 + PMDI)	86.0 NS	15.1	3
9	42.3	30.1	6
10	79.1 NS	27.0	3
11	59.5	26.7	6
12 (5 + PMDI)	71.5NS	29.1	6
13	48.3	30.8	6
14 (15 +PMDI)	30.2	25.5	6
15	75.3 NS	24.7	3
16 (PF control)	93.70	7.8	6

[a] Replicates were composed of five repeated measures, from five shear samples/replicate.
[b] NS = no significant difference when tested against PF control (adhesive 16) at the 0.05 level of significance.

TABLE 3 - Boil-dry-boil tests, bond strength [a]

Adhesive	Mean strength	Standard deviation	No. of replicates
	- - - (MPa) - - -		
1	0.43	0.12	6
2	O.84NS[b]	0.10	3
3	0.68 NS	0.34	3
4	0.44	0.10	6
5	0.85 NS	0.27	6
6	0.75 NS	0.22	6
7 (3 + PMDI)	0.92 NS	0.12	3
8 (2 + PMDI)	0.79 NS	0.03	3
9	0.61	0.19	6
10	0.66 NS	0.15	3
11	0.76NS	0.29	6
12 (5 + PMDI)	0.80 NS	0.27	6
13	0.73 NS	0.24	6
14 (15 + PMDI)	0.51	0.27	6
15	0.40	0.07	3
16 (PF control)	0.89	0.07	6

[a] Replicates were composed of five repeated measures, from five shear samples/replicate.
[b] NS = no significant difference when tested against PF control (adhesive 16) at the 0.05 level of significance.

EXPERIMENTAL DESIGN

The experimental design sought to resolve significant differences in mean bond performance between test adhesives and to provide comparison to a PF control. Wood failure and shear strength were used as random variables. The primary experiment was on the set of boil- dry-boil specimens featuring 15 RHM formulations and a PF control. All veneers in the specimens were randomly selected from two successive rotary- peeled veneer sheets cut from the same tree. Complete randomization was continued in the ordering of specimen preparation.

TABLE 4. - Heated I50ac - bond strength.

Adhesive	Mean strength	Standard deviation	No. of replicates
	- - (MPa) - -		
2	0.55	0.04	3
3	0.45	0.08	3
7 (3 + PMDI)	0.94 NS[2]	0.10	3
8 (2 + PMDI)	0.88 NS	0.27	3
16 (PF control)	1.03	0.13	3

NS = no significant difference when tested against PF control (adhesive 16) at the 0.05 level of significance.

TABLE 5. - Bond strength, 150°C, least significant difference multiple range test.

Formulation Comparison	Bond Strength—difference	Significance
	(MPa)	
2 vs. 3	0.10	Not significant
2 vs. 7	0.39	Significant
2 vs. 8	0.34	Significant
0 2 vs. 16 (PF)	0.48	Significant
3 vs. 7	0.50	Significant
3 vs. 8	0.43	Significant
3 vs. 16 (PF)	0.58	Significant
7 vs. 8	0.06	Not significant
7 vs. 16 (PF)	0.09	Not significant
8 vs. 16 (PF)	0.15	Not significant

This dispersed any un- known systematic errors such as temperature drift in the application gun or in veneer properties. In this fashion, the experiments were completely randomized. The single factor in the analysis of variance was the percentage wood tear with 16 fixed, qualitative treatment levels (types of adhesive). Post-hoc comparisons between pairs of adhesives including the PF control were made using Fisher's Protected Least Significant Difference Multiple-Range Test Method for Means. The experimental analysis was repeated with the shear strength as the dependent variable.

A similar design was used for the second experiment in which four selected RHMs were evaluated in heated dry shear bond tests and compared with the PF control and each other. A significance level of less than 0.05 was considered acceptable in the overall experiment analyses of variance and the multiple range testing.

RESULTS:

ADHESIVE SPREADS

The RHM spreads averaged 0.028 g/cm2 on single gluelines with a standard deviation of 0.006 g/cm2 between formulations. The PF single glueline spread was 0.014 g/cm2 with a standard deviation of 0.001 g/cm2. The spread rate for RHM was derived from the PAM applicator's ability to swirl spray a deposit that would become a reason- ably continuous glueline after nip rolling. Gap filling was also a consideration because of dependence on hot-melt tack to hold the assembly tight as fusion occurred. Several RHMs would have tolerated lower spreads.

BOIL-DRY-BOIL TESTS - WOOD FAILURE (TABLE 2)

Least significant difference multiple range testing on the wood failure means gave the following results at the 0.05 significance level.

1. RHM adhesives 2,3,5-8,10,12, and 15 were not significantly different from the PF control (adhesive 16). This group comprised 9 of the total survey of 15 RHM formulations and included all the PMDI-added formulations except adhesive 14.

2. In the previous group, RHMs 2,3,5,10, and 15 were unmodified industrial formulations showing no significant difference in boil-dry-boil test wood failure compared to PF control 16.

3. RHMs 1,4,9,11, and 13 were un- modified industrial formulations that formed solid, well-consolidated contact bonds emerging from the nip roll. How- ever, after curing, this bonding did not survive the boil-dry-boil cycle. Wood failure was significantly poorer com- pared to the PF control.

4. PMDI-added formulations 6-8 and 12 were not significantly different from the PF control. The highest per- forming RHM adhesives were numbers 7 and 8, which were PMDI-added formulations. Diminished glueline tackiness and poorer nip roll consolidation due to PMDI addition contributed to the poorer performance of PMDI-added formulation 14 compared to 15, which was the same RHM formulation but without PMDI. Formulation 6 was thought to be similarly affected to a lesser extent.

BOIL-DRY-BOIL TESTS - BOND STRENGTH (TABLE 3)

1. RHMs 2,3,5-8, and 10-13 were not significantly different from the PF control in bond strength performance after the boil test. This group comprised 10 of the total survey of 15 RHM formulations.

2. In the previous group, RHMs 2,3,5,10,11, and 13 were unmodified industrial formulations.

3. RHMs 1,4,9, and 15 were un- modified industrial RHMs that were significantly lower in bond strength relative to the PF control.

4. PMDl-added formulations 6-8 and 12 were not significantly different from the PF control. RHM 14 was the only PMDI-added formulation that per- formed poorly. The low shear strength result for RHM 14 shear bond strength was confirmed by a poor wood failure in **Table 2**.

HEAT RESISTANCE TESTS

Four RHM formulations were selected for heated, dry shear testing at 150aC. These were formulations 2 and 3, together with their PMDI-enhanced complements, designated as 8 and 7, respectively. The reason for selecting these formulations was because they were not significantly different from the PF controls in the previous boil-dry- boil tests in both wood failure and shear strength.

HEATED SPECIMENS - BOND STRENGTH (TABLES 4 AND 5)

The significance of the overall experimental analysis of variance on dry, heated shear strength was 0.002. The multiple range test comparisons were therefore considered valid. Tables 4 and 5 show that PMDI had a very positive effect on the formulations' heat resistance and that the PMDI-added formulations performed as well as the PF control at 150aC.

HEATED SPECIMENS - WOOD FAILURE (TABLE 6)

The overall experimental analysis of variance was significant only at the 0.16 level of confidence when the wood failure was examined in the heat resistance tests. Therefore, the associated derivative inferences from multiple range testing were discounted in validity. Increased replicate observations should improve this in future studies. **Table 6** data for heated wood failure show the means data for heated wood failure.

Grouping formulation 2 with 3 and 7 with 8 creates a sample that is large enough to validly infer that the 7 and 8 set had higher wood failure than the 2 and 3 set. This confirms the earlier bond strength result that the addition of PMDI enhances the bond quality significantly.

TABLE 6. - *Woodfailure of heated (150°C) specimens.*

Adhesive	Mead wood failure	Standard deviation	No. of replicates
	------------------------------(%)---------------------------		
2	83.3	4.8	3
3	63.6	23.0	3
7 (3 + PMDI)	97.0	2.6	3
8(2+PMDI)	79.3	27.2	3
16 (PF	94.6	4.5	3

DISCUSSION

Hot-pressing places excessive limits on the practical ranges of density, mechanical properties, and species utilization in LVL. It also imposes restrictions on laminate thickness and production rates. These constraints are reduced by using adhesives with process capabilities similar to RHM. RHM bonding may be of interest to manufacturers wanting the ability to custom assemble LVL at sales service depots by using thin LVL sub-units (blanks) that are 10 to 20 mm thick. Stress-rated veneers for blanks can be hot-pressed in existing facilities making 1220- by 2440-mm plywood panels. This takes advantage of hot-pressing where it is best suited. Blanks are presently cold-pressed to make thick LVL by one major manufacturer using adhesives with extended cure times. The assembly of finger- jointed sub-unit blanks allows an expanded variety of LVL products to be made in terns of species, density, modulus, and dimensional stability. This method permits thick LVL products to be made at competitive inventory costs, with local service depot emphasis on the customer. Heavy LVL beams and custom laminates using fibers, metal, foams, and overlays would be relatively easy to manufacture using high tack and high green strength nip roll adhesive systems with plywood press sub units. Other possibilities for RHM lamination of low value 1- by 4-inch lumber to larger sizes and lamination of balanced laminate lumber exist (6).

At present, the largest single use for LVL is in I-beam flanges (7). An estimated 44 percent of LVL is used in flanges approximately 40 mm thick. An estimated 9 million kg of hot-press PF polymeric solids were used in 1993 in LVL adhesives.

CONCLUSION

Single-component isocyanate RHM adhesives having 8.6 percent free isocyanate performed favorably in preliminary evaluations. The potential of high production rates and freedom from hot- pressing thick laminates was demonstrated in concept, using RHM. Future development should focus on two-component high tack, high green-strength systems that give the adhesive formulator more latitude in meeting performance, hygiene, and cost criteria. Two-component systems would also be easier to extend to foam for application or economic advantages. Research should start with selecting the best polymer system for the adhesive, through equipment and process development, to final qualification of the veneer laminates as structural products. The research should be guided by a business plan that exploits the processing and marketing advantages of this method of LVL manufacture.

LITERATURE CITED

1.American Plywood Association. U.S. Products standard PS 1-83 for construction and '
industrial plywood. APA, Tacoma, Wash.
2. American Society for Testing and Materials. 1991. Strength properties of adhesives in plywood type construction in shear by tension loading. ASTM D 906-82.Vo1. 15.06. ASTM, Philadelphia, Pa., pp. 31- 33.
3. ._____1991. Specification for adhesives used in nonstructural glued lumber products. ASTM D 3110-90. Vol. 15.06. ASTM, Philadelphia, Pa. pp. 208-213.
4. _____.1991 Test method for effect of moisture and temperature on adhesive bonds. ASTM D 115-1-90. Vol. 15.06. ASTM, Philadelphia, Pa. pp. 66-67.
5. .______1991. Specification for adhesives for structural laminated wood products for use under exterior (wet use) expo- sure conditions. ASTM D 2559-84. Vol. 15.06. ASTM, Philadelphia, Pa. pp. 174- 178.
6. Bodig, F. 1991. United States Patent 5,002,105.
7. Guss, L. 1994. Engineered wood products: a bright future or a myth? *In:* Proc. 28th Inter. Particleboard/Composite Materials Symp. Forest Prod. Soc., Madison, Wis. pp.71-88.
8. Huber, H.F. and H. Muller. 1987. Shaping reactive hot melts using LMW copo1yesters. Adhesives Age 30(12):32- 35.
9. Northcott, P.L., L.C. Palka, and W.V. Hancock. 1967. Commercial softwood veneer quality. Project VP-134-2, Short Rept. VP- 5. Forintek Canada, Vancouver, B.C.
10. River, B.H. 1991. Wood as an adherend. Treatise on adhesion and Adhesives, Vol. 7, J.D. Minford, ed. Marcel Deker, New York.
11. Souza, P.A. 1993. PUR technology offers expanded application opportunities. Adhesives Age 36(9):20-23.