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Effects of natural-resource-based scavengers on the adhesion properties and formaldehyde emission of engineered flooring

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Abstract—In this study we investigated the effects of using four additives, wheat flour (WF), tannin, rice husk (RH) and charcoal, to melamine-formaldehyde (MF) resin for decorative veneer and base plywood in engineered flooring in order to reduce the formaldehyde emission levels and improve the adhesion properties. We determined the effects of variations in hot-press time, temperature and pressure on the bonding strength and formaldehyde emission. Blends of various MF resin/additive compositions were prepared. To determine and compare the effects of the additives, seven MF resin blends were prepared with the four different additives: four with a wt ratio of 8:2 (MF/WF, MF/tannin, MF/RH and MF/charcoal), and three in the wt ratio of 8:1:1 (MF/WF/tannin, MF/WF/RH and MF/WF/charcoal). The desiccator and perforator methods were used to determine the level of formaldehyde emission. The formaldehyde emission level decreased with all additives, except for RH. At a charcoal addition of only 20%, the formaldehyde emission level was reduced to nearly 0.1 mg/l. Curing of the high WF and tannin content in this adhesive system was well processed, as indicated by the increased lap-shear strength. In the case of WF, the lap shear strength was much lower due to the already high temperature of 130°C. The adhesive layer was broken when exposed to high temperature for extended time. In addition, both WF and tannin showed good mechanical properties. With increasing WF or tannin content, the initial adhesion strength increased. The MF resin samples with 20% added tannin or WF showed both good lap shear and initial adhesion strengths compared to the pure MF resin.

Keywords: Formaldehyde emission; flooring; decorative veneer; wheat flour; tannin; rice husk; charcoal; lap shear strength; initial adhesion strength.

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1. INTRODUCTION

Melamine-formaldehyde (MF) resins are thermosetting materials that have known rapid commercial development since the 1940s because of their low cost and good performance characteristics. These thermosets of the family of amino resins are widely used in the coating industry and are one of the most important industrial adhesives used in a number of applications such as paper laminates or as molding compounds in dinnerware. Melamine is the global leader in thermoset production [1, 2]. In the 1990s, about 28%, 196 000 tons, of the global melamine production was converted into wood adhesives. Melamine-based adhesive resins find wide application in high performance particleboards in Europe and moisture-resistant plywood in the Asia Pacific region. In North America, 3000 tons of melamine are used to manufacture predominantly flooring grade (medium-density fiberboard) MDF [3–5]. MF resins are incorporated in many coating formulations to improve their mechanical properties or humidity resistance, or to modify their adhesion to other materials. They can also be used in the same field as curing elements for other resins or as fire retardants. The basic melamine structure consists of an aromatic tri-amine ring with six substituent sites, two on each terminal nitrogen [6].

MF and melamine-urea-formaldehyde (MUF) resins are mainly used as thermosetting wood adhesives for wood panels providing excellent adhesive performance. The use of MUF resins has allowed the development of moisture-resistant panels with low formaldehyde emissions and excellent strength properties. The high cost of melamine compared to urea leads to an extensive use of specially tailored MUF resins which offer greatly enhanced performance at a lower cost than MF resins. In addition, MF or MUF resins are employed in applications where moisture resistance and a colorless glueline are required. The chemistry of MF and MUF resins is very similar to that of urea-formaldehyde (UF) resins, which permits panel manufacturers to easily convert between UF and MUF of MF resins [7, 8]. One possible difficulty experienced with melamine-containing resins is poor water dilutability resulting in more difficult clean-up. As compared to other formaldehyde resins, MF resins offer much higher crosslink density which provides cured polymers that are very hard, scratch resistant, and moisture resistant. Formaldehyde (HCHO) is emitted by many synthetic resins that are used as adhesives for wood and wood products [9, 10]. Recently, formaldehyde has been labeled as a suspect human carcinogen which is known to be released from pressed-wood products used in home construction such as particleboard, plywood, MDF and panelling. This study investigated the effect of using four scavengers abundantly available as a natural resource, tannin, rice husk (RH), wheat flour (WF) and charcoal, as additives to MF resin-based engineered flooring in order to reduce the formaldehyde emission levels and improve the adhesion properties. Already, tannin has been studied for many years in several countries and is considered as a possible replacement additive material not only because of its economic advantage but also due to its combination of high stability, high solubility in water and high reactivity with formaldehyde. RH, WF and charcoal have also been studied [11, 12]. In this study, the mechanical properties (single-lap shear strength) and initial adhesion strength (probe tack test) of MF resins mixed with four additive types were investigated. Formaldehyde emission levels were measured with both the desiccator and perforator methods.

2. MATERIALS AND METHODS

2.1. Materials

2.1.1. Plywood and decorative veneer. The plywood and decorative veneer used for fabricating the test samples were supplied by Easywood (South Korea). The decorative veneers were made of 0.5-mm-thick maple, while the plywoods (7 mm thick) were manufactured in China. The moisture contents were 0.08% and 3.5%, respectively.

2.1.2. Melamine-formaldehyde (MF) adhesive. The MF adhesive was used for decorative veneer and plywood in engineered flooring. The resin was prepared at an F/M molar ratio of 1.75, with a solid content of 49 wt%. After the addition of water to the formalin to give 38.5% by weight of formaldehyde in water, the pH was adjusted to 9.0 by adding 1 M NaOH solution (because the methylolated intermediates of the reaction rapidly condense under acidic conditions) and the melamine was added. As hardener, 10% NH_4Cl solution was used. The viscosity as measured using a Brookfield Viscometer Model DV-II+ was 140 cP by spindle No. 6 at 21°C.

2.1.3. Additives. Four additives were used as scavengers, WF, tannin, charcoal and RH, with moisture contents of 6%, 5%, 4% and 6%, respectively. WF was commercial grade, the tannin was prepared as a fine, dark brown powder, while the charcoal and RH were both supplied by Seoul National University (South Korea).

2.2. Methods

2.2.1. Fabrication of engineered flooring board. Engineered flooring boards of dimensions 40 cm × 40 cm × 0.75 cm (length × width × thickness) were fabricated using MF resin and four different additive materials. The content ratios of the total adhesive systems prepared with various MF resin and additive compositions are shown in Table 1. Resins were spread on the plywood at a density of 16 g/1600 cm^2 to bond the decorative veneer. The pressing schedule for the engineered boards was as follows: cold pressed at 1 kg/cm^2 for 2 min, in order to ensure the stability of the adhesive layer, hot pressed at 5 kg/cm^2 at 120°C for 120, 160 or 200 s, and finally cold pressed at 1 kg/cm^2 for 2 min.

Table 1.
Compositions of adhesive systems used

Additive	Ratio by wt (%)	Press time (s)
None	100	120
		160
		200
Wheat flour	80:20	120
		160
		200
Tannin	80:20	120
		160
		200
Rice husk	80:20	120
		160
		200
Charcoal	80:20	120
		160
		200
Wheat flour + tannin	80:10:10	120
		160
		200
Wheat flour + rice husk	80:10:10	120
		160
		200
Wheat flour + charcoal	80:10:10	120
		160
		200

In all cases, the adhesive was MF.

2.2.2. Formaldehyde emission.

2.2.2.1. Desiccator method. The Japanese Industrial Standard (JIS) and the Korean Standard (KS) were used for determining formaldehyde emissions from the engineered boards (Table 2). The 24 h desiccator method uses a common glass desiccator with a volume of 11 l. Ten test specimens, with dimensions of 50 mm × 150 mm, were placed in the desiccator. The sample total surface area was 1800 cm^2. The emission test lasted 24 h in the covered desiccator at a temperature of 20°C. The emitted formaldehyde was absorbed in a water-filled petri dish and analyzed using a UV spectrophotometer after treatment with acetyl acetone and ammonium, acetate solution.

2.2.2.2. Perforator method. This method is primarily used in Europe. The perforator value of formaldehyde emission was determined using the DIN EN 120 (European Committee for Standardization, 1991) method. About 110 g of the test piece was weighed to an accuracy of 0.1 g and placed in a round-bottom flask to

Table 2.
Comparison of standards for formaldehyde emission (mg/l) with the desiccator method used in Korea and Japan

Standard	Formaldehyde emission level (mg/l)			
	Under 0.3	Under 0.5	Under 1.5	Under 5.0
KS	Super E_0	E_0	E_1	E_2
JIS	F★★★★	F★★★	F★★	F★

KS, Korean standard; JIS, Japanese industrial standard (JIS A 1460).

Table 3.
Formaldehyde emission standard with the perforator method

Standard	Formaldehyde emission level (mg/100 g panel)		
	Under 0.8	Under 8.0	Under 15
DIN EN 120	E_0	E_1	E_2

DIN EN 120, European committee for standardization.

which 600 ml of toluene was added. One liter of distilled water was poured into the perforator attachment and boiled toluene was passed through the distilled water for two hours. In this process, the distilled water absorbed the formaldehyde and other volatile organic compounds (VOCs) stripped by the boiling toluene. The formaldehyde trapped by the water was then quantitatively determined using a UV spectrophotometer after treatment with acetyl acetone and ammonium acetate solution. According to KS, the perforator method is used for the evaluation of formaldehyde emission (Table 3).

2.2.3. Mechanical testing of adhesive bonds – single lap shear strength. Larch wood substrates with dimensions of 100×25 mm^2 were used to perform the single lap shear tests for the MF-based adhesive with four different additives. The thickness of the adhesive layer was 133 ± 1 μm. To form a uniform adhesive layer, we used polyimide film. Test specimens were cured at various temperatures (110, 120 and 130°C) and times (5, 10 and 15 min). Single lap shear strength was determined using a Universal Testing Machine (Hounsfield at Kookmin University) using the ASTM D 1002 method. The test speed was 2 mm/min. Each value represents an average of five measurements. Figure 1 shows the dimensions of a single lap shear test specimen.

2.2.4. Initial adhesion strength. The initial adhesion strength was determined using a Texture Analyzer (TA-XT2i, Stable Micro Systems, UK) with a 5 mm diameter, stainless steel, cylindrical probe. The measurements were carried out at a separation rate of 60 mm/min under a constant pressure of 100 kg with a dwell time of 1 s and test interval times of 1, 3, 5, 10, 20 and 30 min. Each of the adhesives with four additives was applied to stainless steel and decorative veneer.

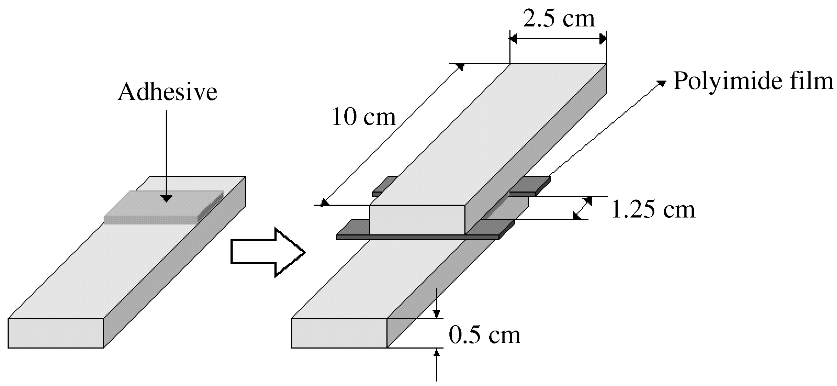

Figure 1. Diagram showing dimensions of a single-lap shear test specimen.

In the debonding process, the initial adhesion strength results were obtained at the maximum debonding force. Each value represents an average of four tests.

3. RESULTS AND DISCUSSION

3.1. Formaldehyde emission

These days, MF resin is mainly used as a thermosetting wood adhesive for wood panels. These thermosets of the family of amino resins are widely employed in decorative laminates and wood composite particleboards for household products, and also as molding compounds for dinnerware [3]. MF resin gives excellent adhesive performance, good moisture resistance and generally lower formaldehyde emission than UF resin. However, in this study, the formaldehyde emissions from the products glued with MF resin were slightly higher than our initial expectations before using the additive materials. They exceeded E_0 and F★★★ grade emission levels (under 0.5 mg/l) of formaldehyde emission levels in KS and JIS, respectively, as shown in Fig. 2. However, the emissions were reduced by the additives. The results obtained for the engineered boards are presented in Fig. 3. Formaldehyde emission decreased with increasing press time. The formaldehyde emissions of MF adhesives were 0.29, 0.21 and 0.30 mg/l at press times of 120, 160 and 200 s, respectively. The formaldehyde emission level varied only slightly depending on the mixture ratio. The role of the additive was to reduce formaldehyde emissions by partial replacement of the MF resin.

According to these results, the mixture ratio of additives did effectively reduce formaldehyde emission, with best reduction being achieved by the mix MF + charcoal (8:2), followed by MF/WF/charcoal (8:1:1) > MF/WF/tannin (8:1:1) > MF/WF (8:2) > MF/tannin (8:2) and MF/WF/RH (8:1:1) > MF/RH (8:2). According to JIS, all additives (except RH) satisfied Grade F★★★★ (emission level < 0.3 mg/l). Charcoal was an extremely effective scavenger among the four additives

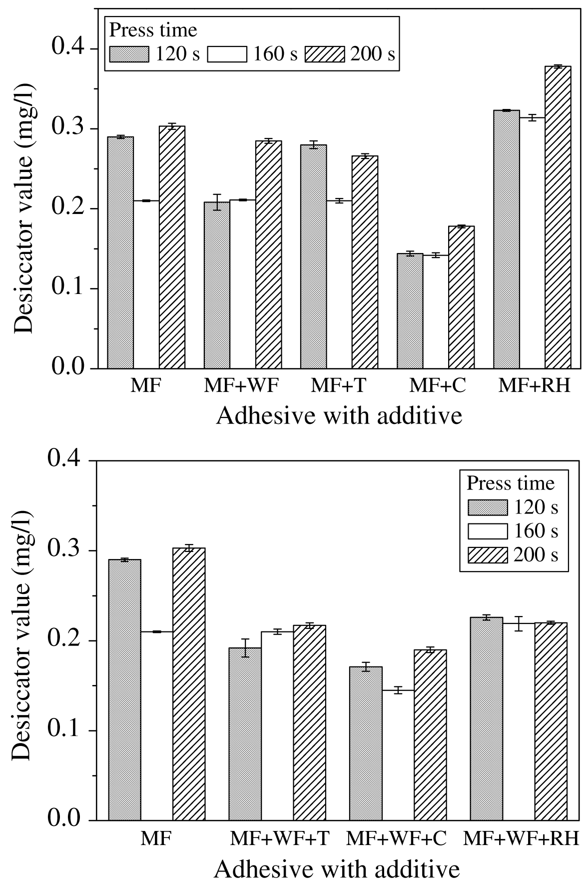

Figure 2. Desiccator values of formaldehyde emission from engineered boards using MF-based adhesive with additives. MF – Melamine formaldehyde resin; WF – Wheat flour; T – Tannin powder; RH – Rice husk flour; C – Charcoal.

due to its numerous minute holes capable of absorbing the molecular formaldehyde by acting as an absorbent [13].

3.2. Single-lap shear strength

MF adhesives are described as thermosetting adhesives [14]. Their strength is developed by the press time and temperature. Figures 4 and 5 show the single lap shear strengths of the MF-based adhesives at different curing temperatures (110, 120 and 130°C) and cure times (5, 10 and 15 min).

The lap shear strengths of all adhesives systems increased with increasing press time and temperature. In the case of WF, adhesion strength was higher than MF resin at all curing temperatures and times tested. For the tannin additive, the adhesion strength was initially the lowest, but it increased rapidly with increasing press time and temperature. WF molecules react with each other at short press time

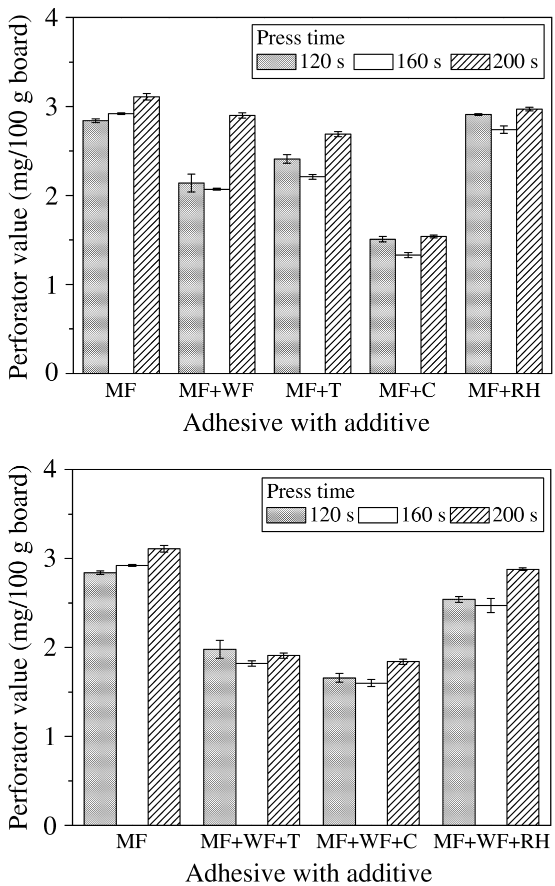

Figure 3. Perforator values of formaldehyde emission from engineered boards using MF-based adhesive with additives.

and low temperature, whereas tannin requires more energy to cross-link (Fig. 6) [5–9]. The order of the overall lap shear strength was tannin and WF > charcoal > RH. The lower results for RH and charcoal were due to their having components similar to the wood as well as inorganic substances. These inorganic substances hamper the adhesion strength of engineered board (Fig. 6).

3.3. Initial adhesion strength

Figure 7 shows the process of determining initial adhesion strength. A small diameter probe is brought into contact with the adhesive surface under a controlled pressure, held there for a controlled time, then withdrawn at a controlled rate, after which the separation force is measured [5]. The probe tack was used for measuring the initial adhesion strengths of the four MF-based adhesives. Figures 8–10 show the probe tack results for stainless steel and decorative veneer. With increasing open assembly time, the probe tack of the MF-based adhesives with WF and

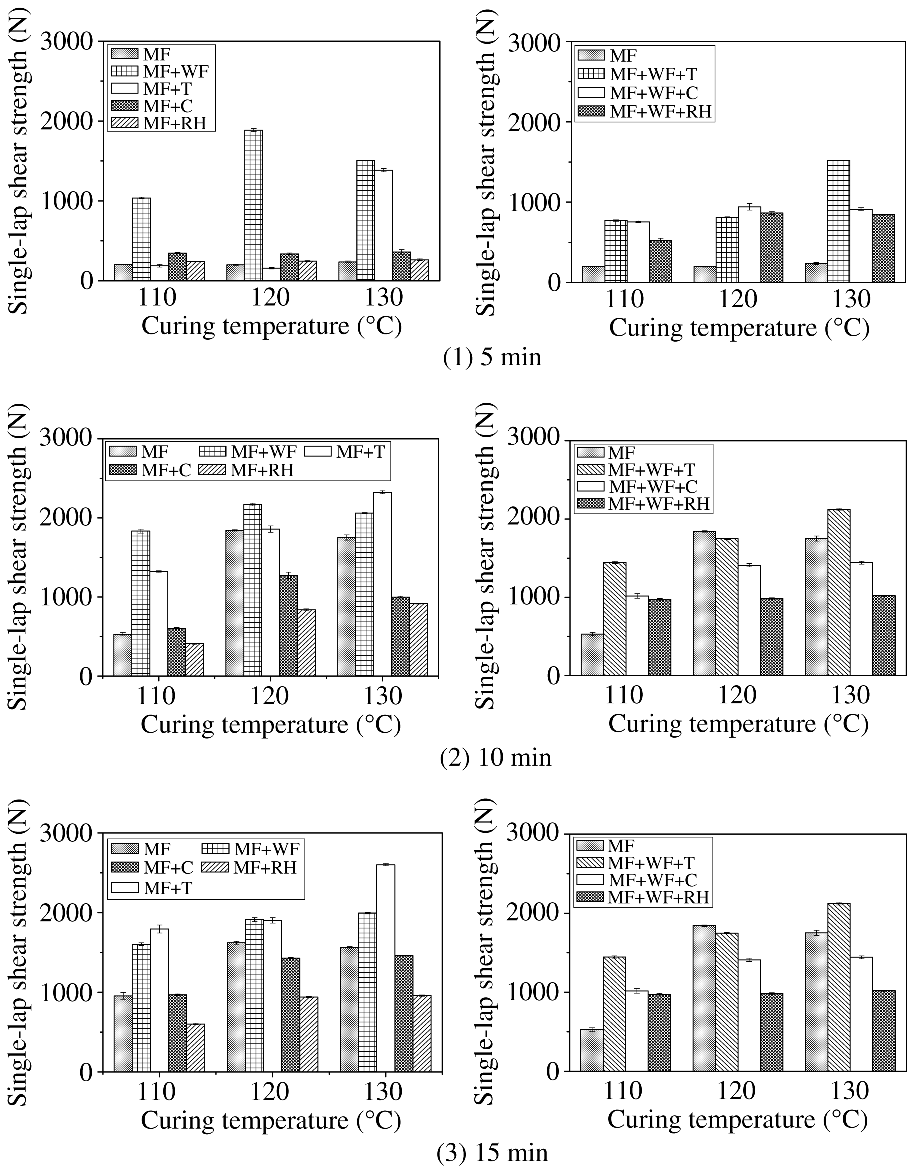

Figure 4. Single-lap shear strengths of all adhesives for different curing times.

tannin increased and then decreased. The MF-based adhesives with tannin and WF showed high initial adhesion strength. The high initial adhesion strength signifies the maximum open assembly time, which is a very important process condition in a manufacturing plant. Optimizing the open assembly time will enhance the work efficiency. Adhesives with tannin and WF additives had the longest open assembly time of 10 min, whereas those with RH and charcoal were impossible to measure because RH and charcoal have components similar to wood and inorganic

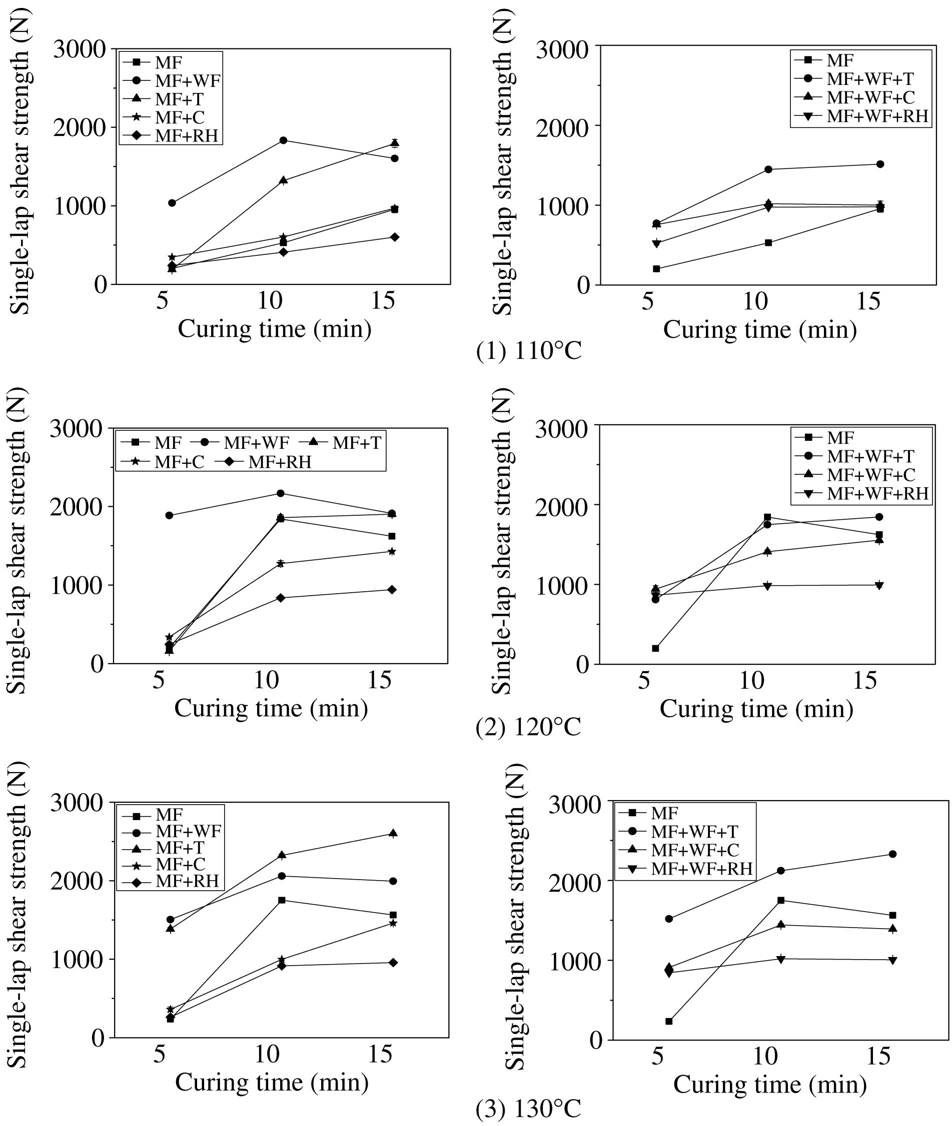

Figure 5. Single-lap shear strengths of all adhesives for different curing temperatures.

substances. These particles of the inorganic substances were present in the bonding layer and reduced the probe tack results of the engineered board.

Finally, Fig. 11 presents a diagram of the probe tack results for MF, MF + WF, MF + tannin and MF + WF + tannin.

4. CONCLUSIONS

The results from this study can be summarized as follows.

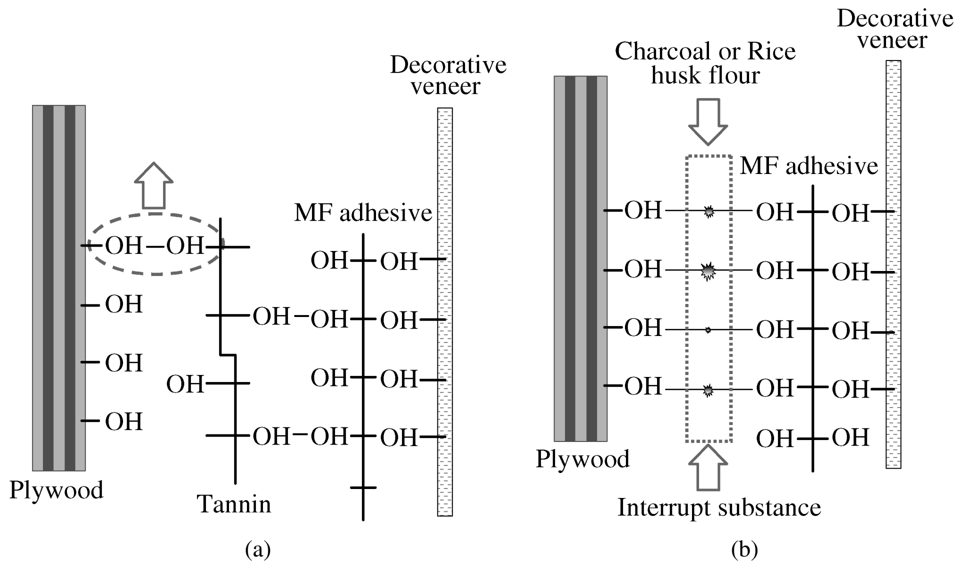

Figure 6. Schematic diagrams of adhesion between scavengers based on natural resources and MF adhesive. (a) MF adhesive + tannin powder. (b) MF adhesive + charcoal or rice husk flour.

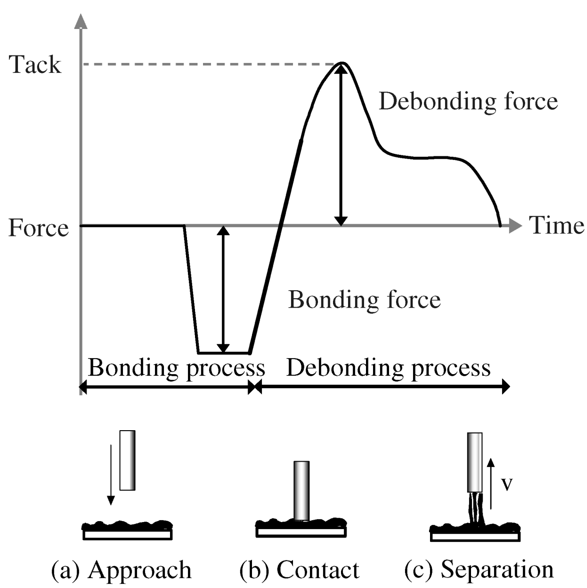

Figure 7. Process of determining the initial adhesion strength (probe tack).

In the desiccator test, the formaldehyde emission of all adhesive systems decreased with the use of additives. The charcoal additive reduced the formaldehyde emission most effectively. The same trend was shown in the perforator test results. The formaldehyde emissions of MF adhesive with charcoal (8:2) and of

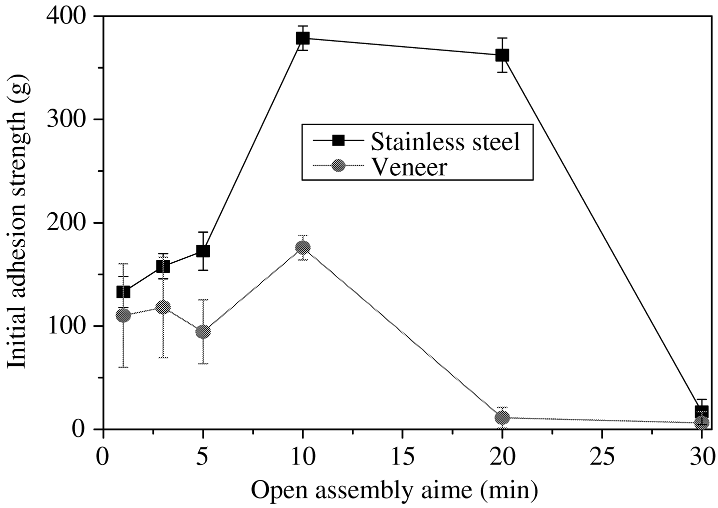

Figure 8. Initial adhesion strength of MF adhesive.

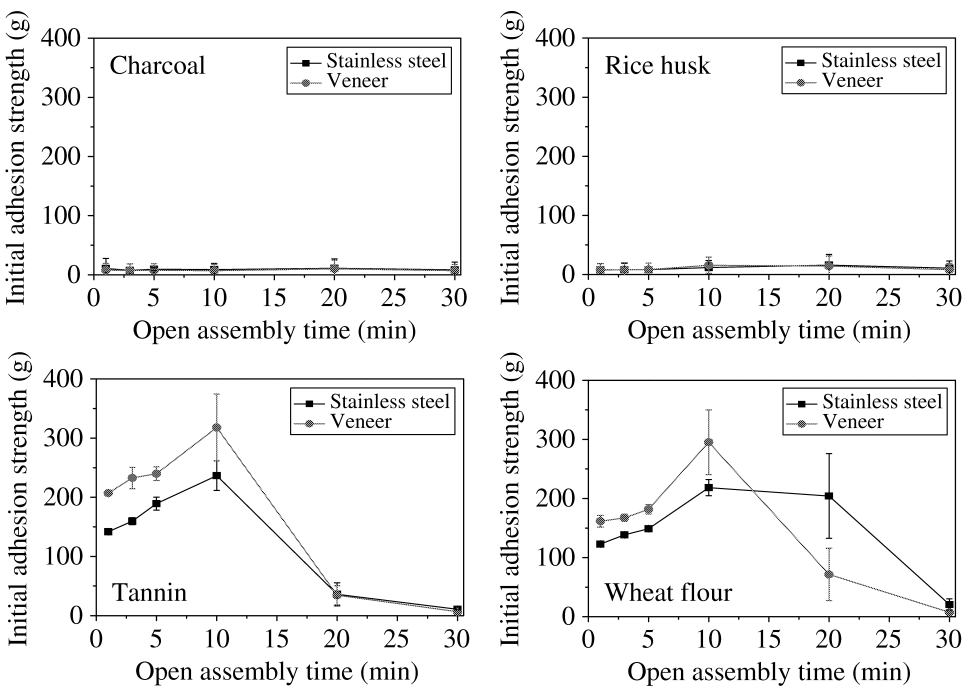

Figure 9. Initial adhesion strength of MF and scavengers based on natural resources (weight ratio 8:2).

MF/WF/charcoal (8:1:1) were both lower than 0.15 mg/l at a press time of 160 s. The reduction effect of charcoal on formaldehyde level was attributed to a probable reduction in absorption. Formaldehyde emission levels were not reduced with in-

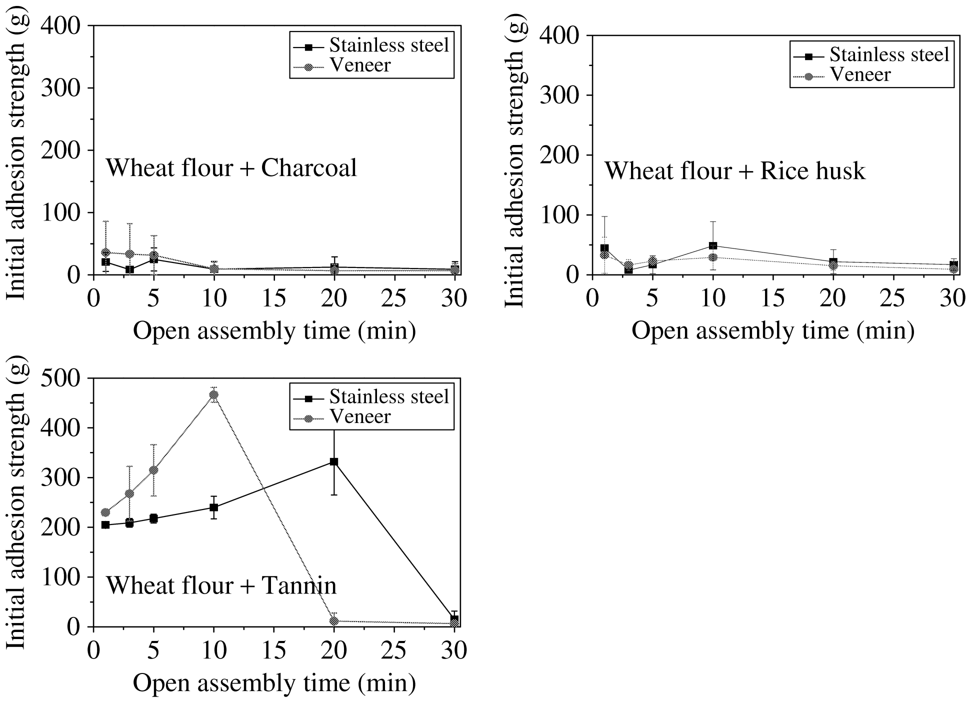

Figure 10. Initial adhesion strength of MF/wheat flour/scavengers based on natural resources (weight ratio 8:1:1).

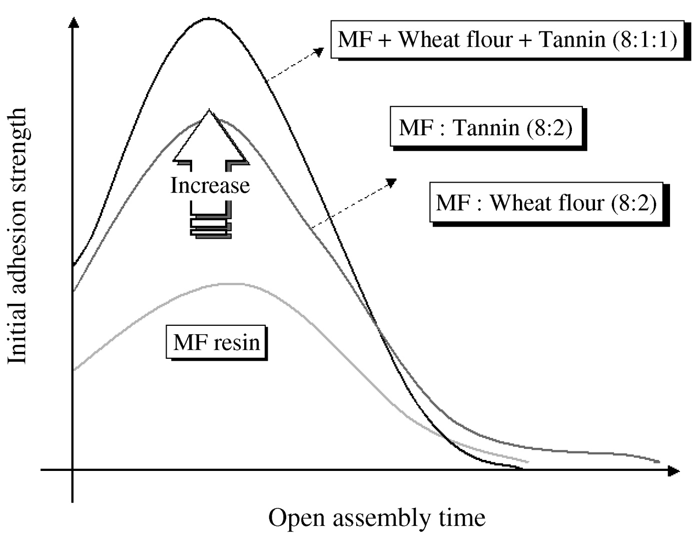

Figure 11. Diagram of initial adhesion strength with veneer for MF, MF + wheat flour, MF + tannin, and MF + wheat flour + tannin.

creasing press time because the adhesive layers were destroyed by excessive press time which allowed adhesive to flow out on the surface of the decorative veneer.

The probe tack test was used for measuring the initial adhesion strength with the highest result being achieved by MF/WF/tannin (8:1:1) at 10 min. MF/tannin (8:2) and MF/WF (8:2) had higher values at 10 min. However, the RH and charcoal blends had the lowest values. The test time of the probe tack indicates the open assembly time, which is a very important process condition in a manufacturing plant. To summarize the results, MF-based adhesives with WF and tannin were the most suitable for manufacturing times less than 10 min.

In terms of single-lap shear strength, the different engineered boards showed similar performance patterns, except for the tannin additive. In the case of tannin, the lap shear strength increased with increasing cure time and temperature, whereas for the other boards the increase was only maintained to 120°C. These adhesive properties of the tannin additive blend are explained by its role as a thermosetting adhesive. With increasing cure time and temperature, molecules of the tannin prepolymer and functional group are cross-linked to each other and are thereby hardened. Increased cure time and temperature provide more energy for cross-linking. In the case of WF, however, the lap shear strength was much lower due to the already high temperature of 130°C, which destroyed the adhesive layer. The use of RH and charcoal both reduced the adhesion strength between the decorative veneer and plywood. Figure 12 presents a schematic diagram showing the relationship between formaldehyde emission level and adhesion strength for the pure MF resin and seven different blends with additives.

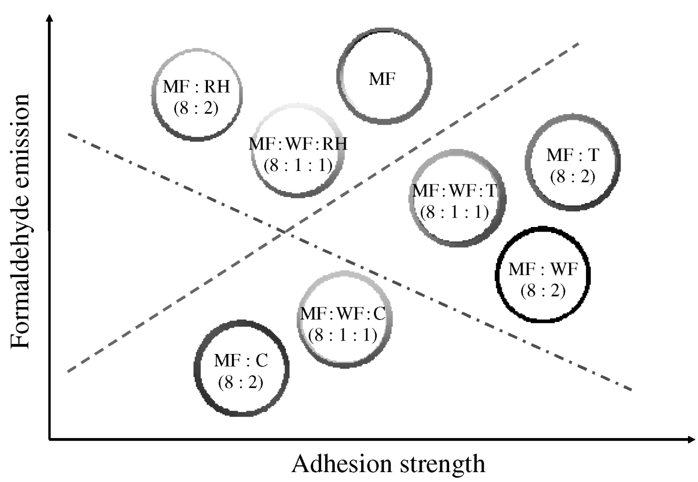

Figure 12. Schematic relationship between formaldehyde emission and adhesion strength of MF resin with different scavengers based on natural resources. MF – Melamine formaldehyde resin; WF – Wheat flour; T – Tannin powder; RH – Rice husk flour; C – Charcoal.

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