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Original Article

Evaluation of Anti-Sapstain Activity of Rice Powder Adhesives Modified with Wood Preservatives[1]

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ABSTRACT

Demand of natural interior finishing material has been widely sprayed in nowadays because many weak people as children, pregnant women, and elder people are being struggled with sick house syndrome due to volatile organic compounds such as formaldehyde, toluene, benzene, etc. Our research group developed a no-added formaldehyde adhesive for wood-based panels from mainly rice powder and some additives in the previous study for abating sick house syndrome. Since the rice powder adhesive provides a good source of nutrients with microorganisms, it was suspected a susceptibility of the rice powder adhesive to fungal and sapstain attack. We evaluated anti-sapstain activity of the rice powder adhesives modified by adding wood preservatives. We modified the rice powder adhesive by adding three different types of anti-sapstain preservatives at three different concentrations to assess their anti-sapstin activity. The bonding strengths of the modified rice powder adhesives were still outstanding performance on all samples. Moreover, the plywood manufactured with the modified rice powder adhesive satisfied outdoor use requirement for ordinary plywood (KS F3101, Korean Standard). The results obtained showed that at least 3% of preservative should be added to the rice powder adhesive to obtain effective anti-sapstain activity.

Keywords : adhesive, anti-sapstain activity, rice powder, plywood

1. INTRODUCTION

Demand of natural interior finishing material has been widely sprayed in nowadays because many vulnerable people as children, pregnant women, and elderly are being struggled with sick house syndrome due to formaldehyde, toluene, benzene, and more chemicals (Jaakkola *et al*., 1999; Krieger and Higgins, 2002). Wood-based panels have been known as major source of formaldehyde emission in indoor air. Most of wood-based panels are usually made with woody materials (veneer, particles, or fiber) and adhesive by mixing, forming, and hot pressing. One of most common adhesives used in wood-based panel manufacture is urea-formaldehyde (UF) resin adhesive, so wood-based panels emit formaldehyde through their lifetime

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by degrading of UF resin and free-formaldehyde (Lee *et al*., 2014, 2015, 2016; Chung *et al*., 1999; Jada, 1988).

However, formaldehyde-based wood adhesive such as UF and phenol-formaldehyde resin have been claimed that low formaldehyde emission may help to prevent fungal and sapstain activities due to its toxicity (Son and Park, 2013). Therefore, formaldehyde-based adhesive does not need to add any anti-fungal and -sapstain preservative. In general, however, wood-based panel and wood itself are somewhat susceptible to decay or sapstain when these are exposed to outdoor or wet environment. Therefore, for outdoor used, wood-based panels are distributed after anti-fungal and -sapstain treatments as wood preservatives.

Our research group developed a no-added formaldehyde adhesive for wood-based panels from mainly rice powder and some additives in the previous study (Lee *et al*., 2015). After then the rice powder adhesive was used to manufacture a plywood with pine veneer and tested its performance according to the Korean Standard for plywood (KS F 3101). As a result, the bonding strength satisfied the requirement of water-proof plywood as well as other requirements.

In the case of rice powder adhesive, however, a susceptibility to fungal and sapstain has been suspected at the beginning of the adhesive development. Rice could be a good feeding source for fungi and bacteria. In this study, therefore, to increase or assign anti-sapstin activity on rice powder adhesive, 3 different types of anti-sapstain preservatives with 3 different concentrations were added and evaluated its anti-sapstain activities. Effective concentration added adhesive was applied to make a plywood and then tested adhesive bonding strength.

2. MATERIALS and METHODS

2.1. Materials

Rice powder used in this study was a common commercial product (Gaemif Inc., Chungbuk Province, Korea, particle size: 150 ~ 250 μm, source: white rice). Polyvinyl alcohol (PVA, MW = 500) was purchased from Daejung chemicals (Korea) and polymeric methylene diphenyl diisocyanate (pMDIs, medel no. M11R) were provided from BASF Korea. The 3 anti-sapstain preservatives (called ITT45, ITT100, and WM) were purchased from the commercial market in Korea. These anti-sapstain preservatives were designed and used originally for wood. Normally these applied to wood by brushing. WM consists of tetrachloro isophthalonitrile, boric acid, chloro methyl isothlazolin, and water. ITT45 was 0.2% of octyl-isothiazolinone, and ITT100 contains 0.1% methylisothiazolinone.

2.2. Test organisms

Five fungi (*Aspergillus niger, aurebasdium pullulans, tricoderma viride, rhizopus nigrocans, penicillum funiculosum*) were selected to use in this test. *Aspergillus niger* is one of common fungus in the world. It is known as black fungus disease and occurred on specific fruit and vegetable. A spore of (*Aspergillus* spp.) is discovered in air, water, soil, rotten vegetable, food, animal body, and indoor atmospheric condition (Schuster *et al*., 2002). *Aurebasdium pullulans* belong to deuteromycetes and is yeast like fungus that can be found in different environments with round and eggshape form. Existing in indoor air condition of *aurebasdium pullulans* is prefer on wet surface of wood, leather, or clothes and cause allergic and asthma reaction to human (Deshpande *et al*., 1992). Also, *tricoderma viride* is most commonly reported fungus in soil and it can decompose organochlorineis as same as soil fungus (Mandels *et al*., 1962). As known as bread mold, *rhizopus nigrocans* is existing in rotten food and soil and can be found easily. Hot and dry weather can help wide dispersion of it and a spore contains allergenic protein. Therefore, *rhizopus nigrocans* can cause a respiratory disease or symptom of rhinitis (Sridhara *et al*., 1990). *Penicillum funiculosum* easily can be found in tropical and temperate zone and grows on paper, leather, soil, food, water, and etc. It contains toxicity and secretes gibberellin which can help growth and decomposition (Hasan, 2002).

2.3. Methods

Rice powder adhesive was synthesized according to Lee's method (Lee *et al*., Patented, 2016). To prepare rice powder solution, 30 g of PVA 500 was added to 850 g of water and stirred at about 60℃. While heating, 150 g (15 wt%) of rice powder was added gently to the hot PVA aqueous solution. The mixture was stirred for about 1 additional hour until rice powder was fully dissolved and then the rice powder solution was cooled at room temperature. The rice powder solutions and pMDIs were mixing for about 30 seconds. The pH of the adhesive solutions was maintained neutral.

Three anti-sapstain preservatives (ITT45, ITT100, and WM) were added individually in rice powder adhesive with 1, 3, and 5% of weight base to increase anti-sapstain activities. Each anti-sapstain preservative included rice power adhesive (5 g) was poured in a round shape mold (5.2 cm diameter) and then cured in an oven with 105 ± 5℃ for 1 h. Cured adhesive was 5 cm diameter and 0.3 mm thickness. The anti-sapstain activities test was conducted after CO_2 gas sterilization with 1 bar and 55℃ for 3 h. Through the five fungi, the anti-sapstain activities test of rice powder adhesive was conducted according to modified ASTM D4300-01.

A plywood with 3-ply (30 cm × 30 cm) was manufactured with anti-sapstain preservative included rice powder adhesive and pine (*Pinus radiata*) veneer and then determined its bonding strength according to KS F 3101. The Modified rice powder adhesives were applied on total 300 g/m^2 on the 3-ply plywood. Cold press was conducted with 10 kgf/cm^2 pressure for 30 minutes at room temperature and then hot press was obtained with 10 kgf/cm^2 pressure for 40

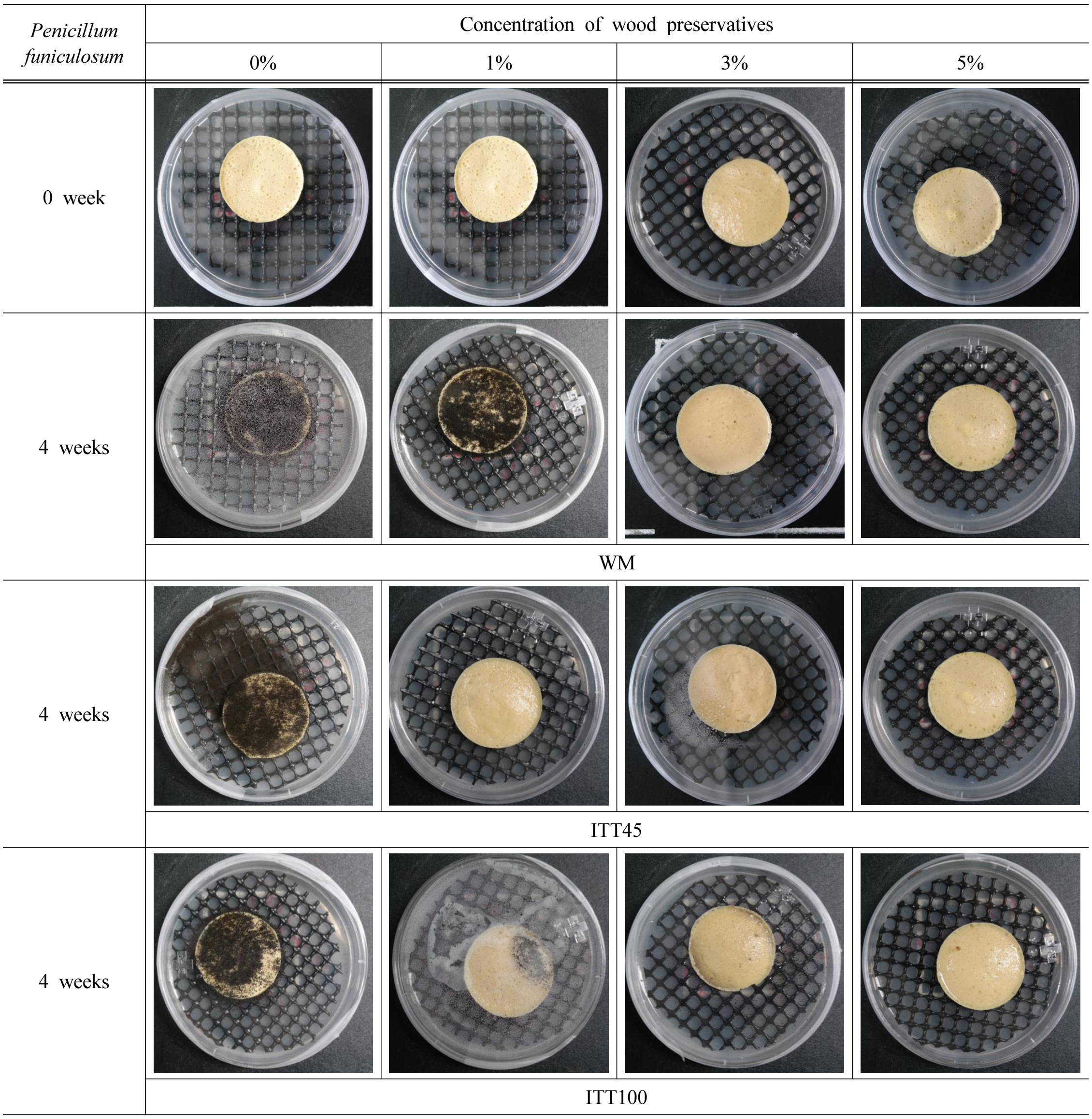

Fig. 1. The picture of rice powder adhesive during anti-sapstain activities test (*Penicillum funiculosum* only).

sec/mm at 120℃.

3. RESULTS and DISCUSSION

Cured rice powder adhesive (coin type, yellow color) are shown in Fig. 1. Table 1 summarized anti-sapstain activity of ITT45 on rice powder adhesive by using different concentrations. 5% ITT45 added samples showed good anti-sapstain activity for all fungi, while 3% ITT45 added samples were susceptible to *tricoderma viride*, and 1% ITT treated

Table 1. The results of anti-sapstain activities of ITT45 on rice powder

	ITT45 concentration (%)			
	0	1	3	5
Aurebasdium pullulans	+	–	–	–
Tricoderma viride	+	+	+	–
Rhizopus nigricans	+	+	–	–
Penicillum funiculosum	+	–	–	–
Aspergillus niger	+	–	–	–

※ "+" means fungus detected; "–" means no fungus detected

Table 2. The results of anti-sapstain activities of ITT100 on rice powder

	ITT100 concentration (%)			
	0	1	3	5
Aurebasdium pullulans	+	–	–	–
Tricoderma viride	+	–	–	–
Rhizopus nigricans	+	–	–	–
Penicillum funiculosum	+	–	–	–
Aspergillus niger	+	+	+	–

※ "+" means fungus detected; "–" means no fungus detected

samples were covered up by *rhizopus nigricans* and *tricoderma viride*. Therefore, more than 3% addition will be necessary.

ITT100 showed strong anti-sapstain activity to *aurebasdium pullulans, tricoderma viride, rhizopus nigricans*, and *penicillum funiculosum* with 1% treatment, but not *aspergillus niger*. Five percent ITT100 added samples were observed as same as initial samples which revealed ITT100 affected anti-sapstain activity for 5 types of fungus. However, *aspergillus niger* may have tolerance to ITT100 at low level, so above 3% will be needed to secure preservation effect from *aspergillus niger* (Table 2).

In the case of WM, 1% WM added sample did not show anti-sapstain activity on *rhizopus nigricans* and *aspergillus niger*. *Rhizopus nigricans* still grew up on 3% WM added sample, but not on 5% of that. Other fungi (*aurebasdium pullulans, penicillum funiculosum*, and *tricoderma viride*) did not grow up on 1% WM added samples after 4 weeks. *Aurebasdium pullulans*, and *penicillum funiculosum* were more sensitive and weaker fungi to all types of wood preservative than *tricoderma viride, rhizopus nigricans*, and *aspergillus niger* (Table 3).

Adhesion performance of rice powder adhesive was evaluated in order to understand effects of adding wood preservatives by making the plywood (3-ply). During the plywood manufacture process, no interfering was observed and the plywood was made as well as original rice

Table 3. The results of anti-sapstain activities of WM on rice powder

	WM concentration (%)			
	0	1	3	5
Aurebasdium pullulans	+	–	–	–
Tricoderma viride	+	–	–	–
Rhizopus nigricans	+	+	+	–
Penicillum funiculosum	+	–	–	–
Aspergillus niger	+	+	–	–

※ "+" means fungus detected; "–" means no fungus detected

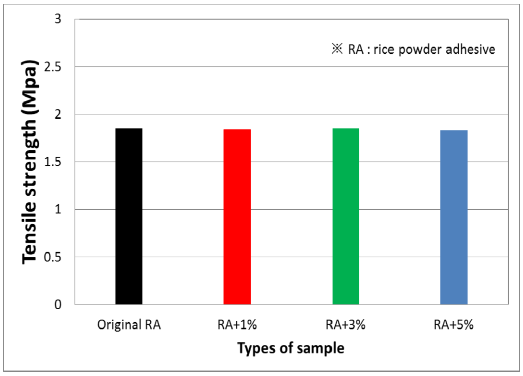

Fig. 2. The results of tensile strength of plywood with rice powder adhesive and rice powder adhesive (ITT100 only).

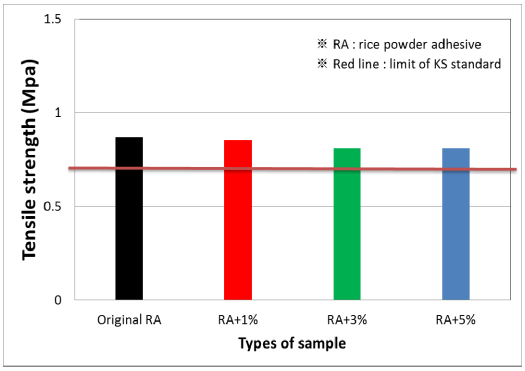

Fig. 3. The results of tensile strength (after water resistance test) of plywood with rice powder adhesive and rice powder adhesive (ITT100 only).

powder adhesive. Tensile shear strength was above 1.8 MPa for all samples. Therefore, wood preservatives did not influence adhesion performance of rice powder adhesive (Fig. 2.). Water resistance test was also conducted according to KS F 3101, which is after boiling for 4 h and drying 20 h at 60℃ then boiling additional 4 h. The plywood with wood preservative added rice powder adhesive was exceeded the water resistance requirement (above 0.7 MPa) and concentration of wood preservative did not affect significantly to water resistance performance (Fig. 3).

4. CONCLUSIONS

Above 3% of preservative should be added in rice powder adhesive to obtain effective anti-sapstain activity. However, each preservative showed different anti-sapstain activities to 5 fungi. ITT45 performed good anti-sapstain activity with only 1% addition for *aurebasdium pullulans, penicillum funiculosum*, and *aspergillus niger*, while ITT100 restricted the growth of *aurebasdium pullulans, tricoderma viride, rhizopus nigricans*, and *penicillum funiculosum* at 1% addition level. Based on results, ITT45 and ITT100 are combined together at 1% level and then added to rice powder adhesive. It will show a good anti-sapstain activity with low level chemical addition.

Through the adhesive bonding strength of rice powder adhesive, bonding strength showed still outstanding performance on all samples. Therefore, the plywood manufactured with rice powder adhesive satisfied outdoor use requirement for ordinary plywood (KS F 3101) as water-proof plywood which correspond to type 1 plywood. Wood preservatives did not affect to adhesion performance of rice powder adhesive.

In the general view of wood, wood itself is susceptible to fungi, so even adhesive has anti-sapstain activity, wood-based panels still be possible to damage from fungi. This data may be able to diminish the doubt that fungi can grow faster than wood-based panels bonded with formaldehyde based adhesives due to the characteristic of rice.

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