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Environment-friendly Adhesives for Fancy Veneer Bonding of Engineered Flooring to Reduce Formaldehyde and TVOC Emissions[*1]

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ABSTRACT

The objective of this research was to develop environment-friendly adhesives for face fancy veneer bonding of engineered flooring. Urea-formaldehyde (UF)-tannin and melamine-formaldehyde (MF)/PVAc hybrid resin were used to replace UF resin in the formaldehyde-based resin system in order to reduce formaldehyde and volatile organic compound (VOC) emissions from the adhesives used between plywoods and fancy veneers. Wattle tannin powder (5 wt%) was added to UF resin and PVAc (30 wt%) to MF resin. These adhesive systems showed better bonding than commercial UF resin with a similar level of wood penetration. The initial adhesion strength was sufficient to be maintained within the optimum initial tack range. The standard formaldehyde emission test (desiccator method) and VOC analyzer were used to determine the formaldehyde and VOC emissions from engineered flooring bonded with commercial UF resin, UF-tannin and MF/PVAc hybrid resin. By desiccator method, the formaldehyde emission level of UF resin showed the highest but was reduced by replacing with UF-tannin and MF/PVAc hybrid resin. MF/PVAc hybrid satisfied the E_1 grade (below 1.5 mg/ℓ). VOC emission results by VOC analyzer were similar with the formaldehyde emission results. TVOC emission was in the following order: UF > UF-tannin > MF/PVAc hybrid resin.

Keywords : environment-friendly adhesive, engineered flooring, formaldehyde, VOCs

1. INTRODUCTION

With the rising economic standards in Korean, concerns about human health and the environment have been raised due to the increasing demand for a wide range of flooring products. PVC (polyvinyl chloride) flooring and laminated paper flooring treated with soy bean oil were the most common types for housing in the past. They, however, have begun to be replaced

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by wooden flooring, especially in the apartments. There are three types of wooden flooring: laminate, engineered and solid wood. The laminate flooring consists of high density fiberboard (HDF) as the core material, while the engineered flooring is composed of plywood with a thin fancy veneer bonded onto the face of the plywood using urea-formaldehyde (UF) and melamine-formaldehyde (MF) resins as hot-press adhesives (Kim and Kim, 2005a). Engineered flooring can be the cause of emitting formaldehyde vapors because the different wood layers, usually consisting of hardwood and/or softwood veneer, are normally glued together with formaldehyde-based adhesives. The hardwood top layer is most often treated with a formaldehyde-free UV-lacquer or an oil to protect the surface (Risholm-Sundman *et al.*, 1998). Two types of laminate flooring are commonly available: decorative plastic laminate bonded onto the substrate by means of a wet bonding agent, and several layers of specially saturated papers directly thermofused onto an HDF substrate. Some laminate flooring emits small quantities of formaldehyde and volatile organic compounds (VOCs) (Wiglusz *et al.*, 2002).

Many wooden flooring products containing formaldehyde-based resins release formaldehyde vapors, thus causing consumer's dissatisfaction and health-related complaints. Various symptoms such as the most common of which is irritation of the eyes and the upper respiratory tract are attributed to the emission of formaldehyde gases. Also, formaldehyde has been found to produce nasal carcinomas in mice and rats after a prolonged exposure at 14.1 and 5.6 mg/ℓ level, respectively. These findings have led to an intensified interest in the indoor environment. Consumer products, especially construction materials, are a major source of formaldehyde emissions in the indoor environment (Brown, 1999; Wolkoff *et al.*, 1991; Rothweiler *et al.*, 1992).

Formaldehyde-based resins, however, have the advantages of superb bonding properties and are inexpensive. Thus, they are used extensively as the adhesives in manufacturing various household products. As noted earlier, one prominent application of UF resin is in the manufacture of particleboard (PB), plywood, and fiberboard (FB). Several thin sheets of wood are glued together by UF resin to produce plywood, whereas PB and FB are manufactured by mixing wood chips and fibers with the resin and then pressing the mixture into its final form at a high temperature (Kim and Kim, 2005a; Kim *et al.*, 2006).

The greatest problem of formaldehyde and total VOC (TVOC) emissions in engineered flooring is attributed to the face fancy veneer bonding. UF resin is still used in industry in a large quantity. In this study, to reduce formaldehyde and TVOC emissions from the resin for bonding face fancy veneer on engineered flooring, UF resin was replaced by UF-tannin and MF/PVAc hybrid resin. Formaldehyde and TVOC emissions were measured by desiccator, 20 ℓ chamber method and VOC analyzer.

2. EXPERIMENTAL

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 Co., Ltd., South Korea. The decorative veneers were 0.5 mm thick maple, while the plywoods (7 mm thick) manufactured in China were used. Their moisture contents were 0.08 and 3.5%, respectively.

2.1.2. Urea Formaldehyde (UF) Resin and Tannin Additive

The UF resin with used for manufacturing PB was supplied by Taeyang Co., Ltd. in South Korea. The solids content of this UF resin was 49%. Commercial wattle tannin (*Acacia mearnsii*, mimosa) extracts were prepared by using the brand of Bondtite Co. Ltd. in Australia. These tannins, consisting of fine dark brown powders with the moisture content of 5%, were added at 5 wt% to UF resin to make UF-tannin. The mixture was stirred physically for 30 min.

2.1.3. MF/PVAc Hybrid Resin

Blends of various MF resin/PVAc compositions were prepared. To make MF/PVAc hybrid resin, 30 wt% PVAc was added to MF resin. The mixture was stirred for 20 min. 10% wheat flour by weight of adhesive was added as an extender. The viscosity measured using a Brookfield Viscometer Model DV-II+ was around 1000 cP at 21°C. 30 wt% was optimal value in the other work (Kim and Kim, 2005a).

2.1.4. Fabrication of Engineered Flooring Board

The engineered floorings for the formaldehyde and VOC emission tests were manufactured using UF resin, UF-tannin and MF/PVAc hybrid resin, with dimensions of 400 × 400 × 75 mm (length × width × thickness). After the resin was spread on the plywood, 0.5 mm thick maple fancy veneer was bonded by cold- and hot-pressing. The pressure-time diagram followed three-stage schedule, consisting of preliminary cold-pressing at 1 kgf/cm^2 for 2 min. for assembly, main hot-pressing at 5 kgf/cm^2 and 120°C for 160 sec. for resin curing, and final cold-pressing at 1 kgf/cm^2 for 2 min. for resin postcuring.

2.2. Methods

2.2.1. Surface Bonding Strength

The bonding strength between the fancy veneer and plywood was evaluated with a Universal Testing Machine (UTM, Hounds Co.) in the tensile mode. Samples were cut at 50 × 50 mm (length × width) and a knife mark of 20 × 20 mm (length × width) was made on the surface (fancy veneer face) to a depth of 0.5 mm. We bonded the upper device of UTM and the surface knife mark with hot-melt adhesive. Another face was bonded to the underneath of the device like the internal bonding strength test specimen. The tests were performed at a crosshead speed of 2 mm/min.

2.2.2. Light Microscopy and Scanning Electron Microscopy

For light microscopy (LM), small pieces containing glue line between maple fancy veneer and plywood were hand sectioned with a sharp razor blade to minimize artificial cell distortions by sectioning with a microtome. The sections were stained with Sudan 4 and toluidine blue to enhance the contrast between the glue line and the wood, respectively, prior to observation with the microscope (DW-BM, Korea) with photo camera. For scanning electron microscopy (SEM), small blocks containing glue line between fancy veneer and plywood were prepared using a sharp razor blade. The blocks were air-dried, mounted on stubs with an adhesive carbon tape, and then coated with gold particles in a vacuum evaporator. The coated samples were observed with a SIRIOM SEM (FEI Co.) using a backscattered detector (Singh *et al.*, 2002) to enhance the contrast between the glue line and the wood.

2.2.3. Initial Adhesion Strength

The initial adhesion strength was determined using a Texture Analyzer (TA-XT2i, Stable Micro Systems, Surrey, England) 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 sec. and test interval times of 1, 3, 5, 10, 20 and 30 min. Each of the adhesives was applied to stainless steel and decorative veneer. In the debonding process, the initial adhesion strength results were obtained at the maximum debonding force. Each value represents an average of five tests.

2.2.4. Formaldehyde Emission by Desiccator Method

The formaldehyde emissions from the engineered floorings bonded with each blend were determined with a desiccator (JIS A 1460) in accordance with JIS method using a glass desiccator. This 24-hour desiccator method used a common glass desiccator with a volume of 10 ℓ. Test specimens were positioned in the desiccator. The emission test lasted 24 hours in the covered desiccator at a temperature of 20°C. The emitted formaldehyde gases absorbed in a water-filled petri dish were analyzed by means of the chromotropic acid method (Kim and Kim, 2004). The quantity of formaldehyde was obtained from the concentration of formaldehyde gases absorbed in distilled or deionized water when the test pieces of the specified surface area were placed in the desiccator filled with a specified amount of water for 24 hours. The principle for determining the concentration of formaldehyde gases absorbed in the distilled or deionized water is based on the Hantzsch reaction in which the formaldehyde gases react with ammonium ions and acetylacetone to yield diacetyldihydrolutidine (JIS, 2001).

2.2.5. VOC Analyzer

The VOC analyzer is a portable device to measure the four main aromatic hydrocarbon gases: toluene, ethylbenzene, xylene and styrene. To prepare the samples for the VOC analyzer, the engineered floorings bonded with each blend were conditioned at 25°C and 50 ± 5% in a thermo-hygrostat for 15 days and then cut into 4 pieces of 50 × 50 mm and placed in a 3 ℓ polyester plastic bag. The polyester plastic bag was sealed with teflon tape, purged 3 times with N_2 gas, and then filled with N_2 gas by pulling up the plunger. For the blank control, an empty bag with N_2 gas was prepared. The gases for the VOC analyzer were collected from the 3 ℓ polyester plastic bag in a gas tight (0.5 cc) manner after 4 days, placed into the VOC analyzer and analyzed, as shown in Fig. 1. This 4-day period was chosen according to the authors' previous study for determination of the optimum method for VOC emission test by VOC analyzer (An *et al.*, 2006). The measurement procedure was comprised of three steps. First, the product was inserted into the 3 ℓ polyester plastic bag, after which the plunger was slowly pulled out, pushed in again, and pulled out for the second time before the syringe was removed from the plastic bag. If the top of the syringe was wet, it was wiped dry with a tissue. A dedicated needle was attached, and 0.5 cc (1/2 calibration) of the sampled gases was ejected by pushing in the plunger. The remaining gases were injected into the inlet on the main unit of the VOC analyzer, after which the measurement was automatically started.

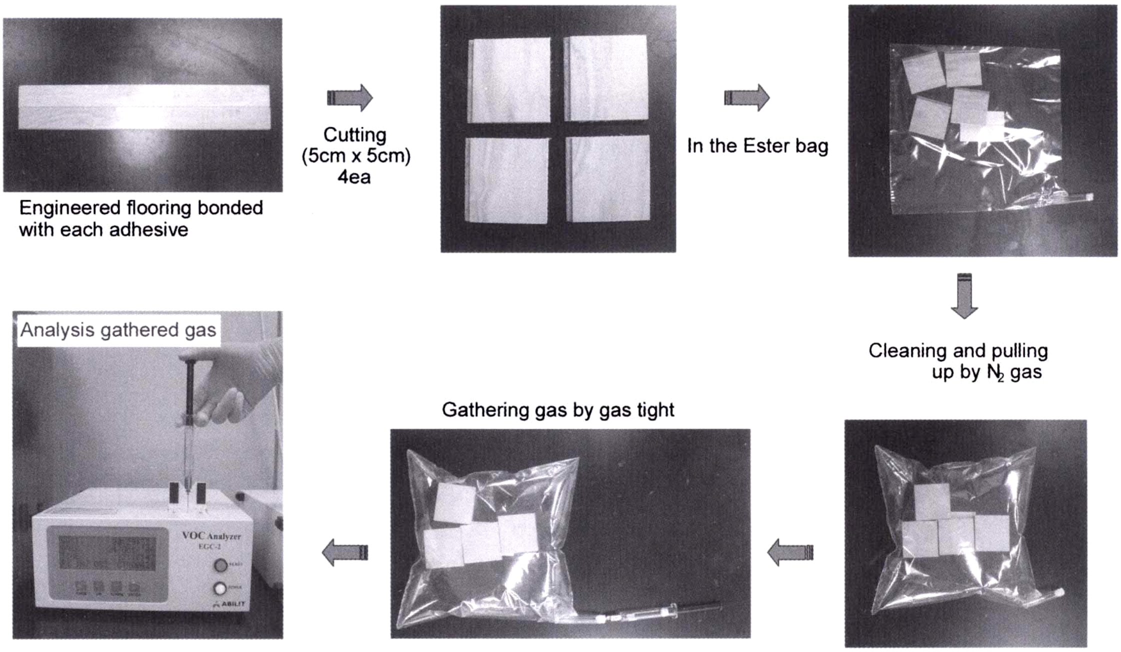


Fig. 1. Test method for VOC emissions from engineered flooring by VOC analyzer.

3. RESULTS and DISCUSSION

3.1. Bonding Strength and Microscopic Observation

The bonding strengths of the engineered flooring samples bonded with various adhesive systems at a press temperature and time of 120°C and 160 sec. are shown in Fig. 2. The bonding strengths of the non-treated (before boiling), engineered flooring samples made using UF-tannin and MF/PVAc hybrid resin were greater compared to those of the UF resin. The use of a tannin additive introduces reactive sites. The free C_6 and C_8 sites on the A-ring can react with formaldehyde because of their strong nucleophilicity to form the adhesive. The phenolic nuclei in tannins react with formaldehyde. This high reactivity of tannins towards formaldehyde is the result of their A-ring phloroglucinolic or resorcinolic nuclei, which have a rate of reaction with formaldehyde 10- to 50-fold higher than does phenol. Tannin functional groups are cross-linked to each other and are hardened. MF resin and PVAc are a miscible blend (Kim and

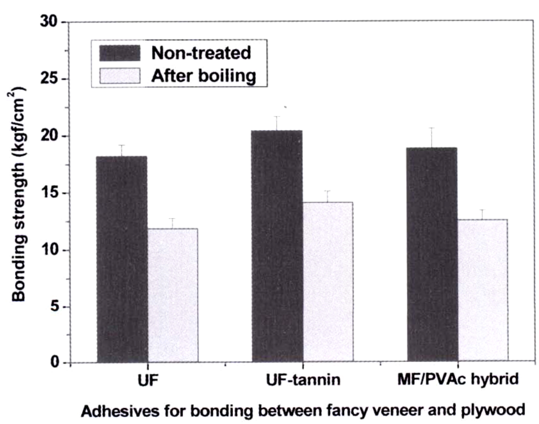
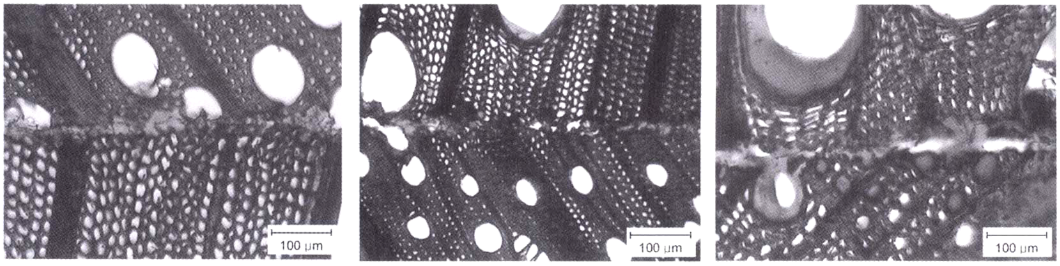
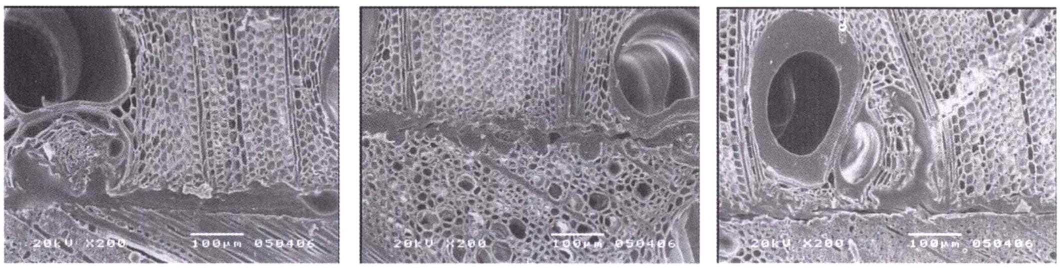


Fig. 2. Bonding strength between face fancy veneer and plywood substrate in engineered flooring: UF, UF-tannin and MF/PVAc hybrid.



UF resin UF-tannin MF/PVAc hybrid

Fig. 3. Glue line between maple fancy veneer and plywood by light microscopy.



UF resin UF-tannin MF/PVAc hybrid

Fig. 4. Glue line between maple fancy veneer and plywood by scanning electron microscopy.

Kim, 2007). Because it has a thermosetting tendency in hot-pressing condition, the adhesion strength was not lower than that of commercial UF resin in surface bonding. We boiled the samples at 60 ± 3°C for 4 h, dried them for 20 h, boiled them again for 4 h and finally dried them for 3 h to determine the waterproof property of each adhesive system. UF-tannin and MF/PVAc resin systems showed a similar waterproof property to that of UF resin. Especially, the tannin extract-added sample showed better waterproof adhesion property than the commercial UF resin. The similarity of the surface bonding strength was proved with the vivid glue lines shown in all adhesive systems. Glue lines between maple fancy veneer and plywood by LM and SEM are shown in Figs 3 and 4. The voids in wood near the glue line were filled with adhesives. Furthermore, the tracheids walls in the outer few layers were also ruptured in the MF/PVAc hybrid resin. The rays were also greatly distorted, with many broken and often compressed at the point of contact with the glue line, thus blocking the glue penetration. The glue penetration into tracheids was mainly confined to the outermost layer in direct contact with the glue line.

A small diameter probe was 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 was measured (Roos *et al.*, 2002). The probe tack was used for measuring the initial adhesion strengths of the adhesives. Fig. 5 shows the probe tack results for stainless steel and decorative veneer. With the increase of open assembly time, the probe tack of the UF, UF-tannin and MF/PVAc hybrid increased

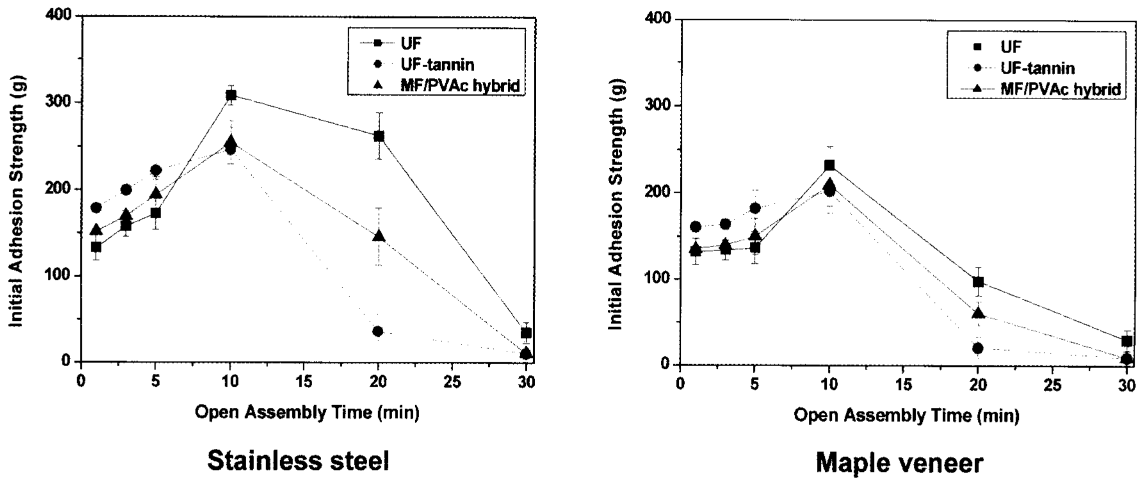


Fig. 5. Initial adhesion strength of UF, UF-tannin and MF/PVAc hybrid.

to a certain time and then decreased. The UF-tannin had the largest peak point at the first 5 min. from the spread on wood surface. MF/PVAc hybrid resin also showed a higher initial tack than commercial UF resin. These peak points indicate 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. According to the authors' previous work (Kim and Kim, 2006), the optimum initial tack range is between 100 and 200 g by probe tack force. On the stainless steal and maple veneer, the initial tack of the three resins was maintained within the optimum tack range.

3.2. Formaldehyde and TVOC Emission

MF resin is today mainly used as a thermosetting wood adhesive for wood panels. These thermosets of the family of amino resins are widely applied in the coating industry as resin crosslinkers such as hexakis(methoxymethyl)-melamine (HMMM), protective coatings, decorative laminates, and PB and FB for household products, and also as molding compounds in dinnerware (Graldine *et al.*, 2000). MF resin gives excellent adhesive performance, good moisture resistance, and tends to give a lower formaldehyde emission than UF resin. Before surface coating, formaldehyde emissions from the products glued with UF resin were more than 6 mg/ℓ and exceeded the E_2 grade of formaldehyde emission level in the Korean Standard, as shown in Fig. 6. When we coated the surface with a UV-curable, urethane acrylate coating for flooring, the emission level was reduced to less than half. In the MF/PVAc hybrid resin system, the role of PVAc was to reduce formaldehyde emission, by replacement of the formaldehyde system resin, and to increase the initial bonding strength through PVAc's high viscosity and room temperature curable property. The formaldehyde emission level of the coated sample of MF/PVAc hybrid appeared to satisfy the requirement of E1 grade.

Fig. 7 presents the concentrations of the four indicated VOCs from the engineered flooring bonded with each adhesive system, as determined by the VOC analyzer. For each substance, the concentrations were measured at 96 h

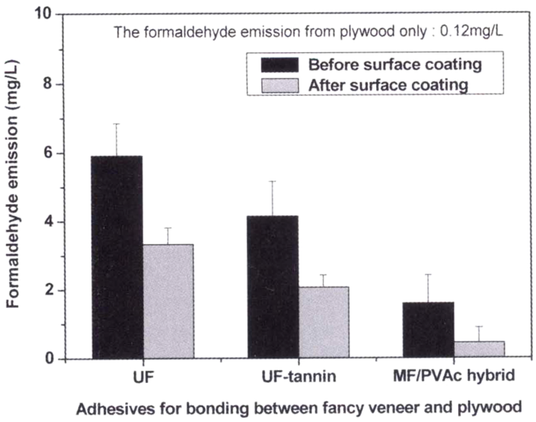


Fig. 6. Formaldehyde emission from engineered flooring bonded with UF, UF-tannin and MF/PVAc hybrid by desiccator method.

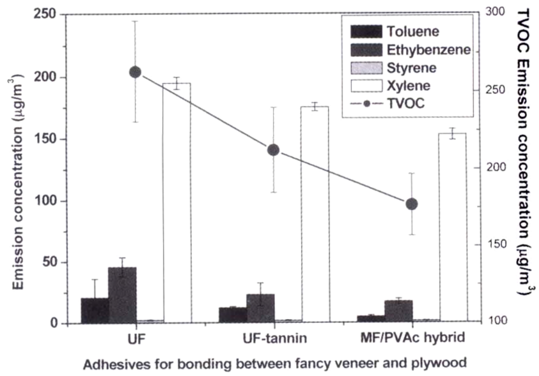


Fig. 7. VOC emission concentrations (toluene, ethylbenzene, xylene and styrene) from engineered flooring bonded with UF, UF-tannin and MF/PVAc hybrid resin as determined by the VOC analyzer.

after the start of the test. Three different phases are evident in the figures. In the first phase, the concentration in the 3 ℓ polyester bag increased due to the constant emission of organic compounds and was limited by the given air exchange rate. Xylene was the highest detected compound in all samples, followed by ethylbenzene and toluene in turn. Styrene, however, was not detected at all in any of the systems. Even from the blends with MF resin, no toluene was detected. But the UF resin adhesive system had the highest emission concentration, while MF/PVAc hybrid had the lowest.

In Korea, the Ministry of Environment provides TVOC guidelines for building materials. Even natural VOCs from wood are considered to be harmful and are included in the TVOC calculation. TVOC was calculated between C_6 and C_{16}. In the VOC analyzer test, however, we defined TVOC as the sum of the four detected main aromatic hydrocarbon gases: toluene, ethylbenzene, styrene and xylene. The VOC analyzer was found to be a suitable pre-test method for application as a TVOC emission test.

4. CONCLUSION

To discuss the reduction of formaldehyde and TVOC emissions from engineered flooring, UF-tannin and MF/PVAc hybrid resin were applied for the maple face veneer bonding on plywood instead of UF resin. The bonding properties of these environment-friendly resins were higher than those of commercial UF resin. By desiccator method, the formaldehyde emission, which was the highest for the UF resin, was lowered by adding tannin extract, and more greatly reduced by using MF/PVAc hybrid resin. The formaldehyde emission results by the 20 ℓ small chamber and FLEC methods showed a similar tendency with those from the desiccator method. In case of MF resin, PVAc addition exhibited great reduction of the formaldehyde emission. In the VOC test by analyzer, we defined TVOC as the sum of the four main detected aromatic hydrocarbon gases: toluene, ethylbenzene, xylene and styrene. The test by VOC analyzer was confirmed as a suitable pre-test method for evaluation of TVOC emission level. In conclusion, MF/PVAc hybrid resins successfully reduced formaldehyde and VOC emissions when applied as adhesives for manufacturing engineered flooring.

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