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TVOC and formaldehyde emission behaviors from flooring materials bonded with environmental-friendly MF/PVAc hybrid resins

Abstract Polyvinyl acetate (PVAc) was added as a replacement for melamine-formaldehyde (MF) resin in the formaldehyde-based resin system to reduce formaldehyde and volatile organic compound (VOC) emissions from the adhesives used between plywoods and fancy veneers. A variety of techniques, including 20-l chamber, field and laboratory emission cell (FLEC), VOC analyzer and standard formaldehyde emission test (desiccator method), were used to determine the formaldehyde and VOC emissions from engineered flooring bonded with five different MF resin and PVAc blends at MF/PVAc ratios of 100:0, 70:30, 50:50, 30:70 and 0:100. Although urea-formaldehyde (UF) resin had the highest formaldehyde emission, the emission as determined by desiccator method was reduced by exchanging with MF resin. Furthermore, the formaldehyde emission level was decreased with increasing addition of PVAc as the replacement for MF resin. UF resin in the case of beech was over 5.0 mg/l, which exceeded E_2 (1.5–5.0 mg/l) grade. However, MF30:PVAc70 was $\leq E_1$ (below 1.5 mg/l) grade. Because formaldehyde emission is caused by formaldehyde-based resin, the engineered floorings bonded with PVAc only had emissions of just 0.25 mg/l. The results of formaldehyde emission by the 20-l small-chamber and FLEC methods showed a similar tendency with those from the desiccator method. After the replacement of UF resin by MF resin, PVAc addition further reduced formaldehyde emission. With increasing installation time, formaldehyde emission factors (EFs) were decreased. Furthermore, the results of the desiccator method correlated with those of the 20-l chamber and FLEC methods. VOC emission results by 20-l small-chamber and FLEC methods were similar to the formaldehyde and aldehyde emission results. VOCs were calculated between C_6 and C_{16} as total VOC (TVOC). The TVOC EF results by 20-l small-chamber and FLEC methods were comparable with that of formaldehyde emission by FLEC. Although the major emitted harmful gas from wood-based composites was formaldehyde, it was followed by VOC emission. Although it was hard to compare directly the 20-l chamber and FLEC results because the data were based on the sum of only four VOC compounds, the VOC analyzer can be applied as a pre-test method for TVOC emission test. The TVOC emission results were also similar to the FLEC results. Due to its good correlation with the TVOC emission levels obtained from the standard desiccator, FLEC and 20-l chamber methods, the VOC analyzer can be successfully applied to the measurement of TVOC emissions from adhesives used in building materials.

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Practical Implications

This paper presents TVOC and formaldehyde emission behaviors from the engineered floorings that used in Korean housing recently. To reduce emissions, MF/PVAc hybrid resins were used as bonding material. Normally, TVOC and formaldehyde emissions in indoor conditions are caused by interior materials. The results explained 'materials control' of interior materials are the first way to improve indoor air quality. There is a need to study about environmental-friendly materials for solving indoor air quality problem.

Introduction

Building and furnishing materials and consumer products are important sources of formaldehyde and other volatile organic compounds (VOCs) in the indoor environment. There is a growing concern about the significance of these indoor pollutants for the health and comfort of building occupants. Exposure during time spent indoors can account for most of the total personal exposure of inhabitants to these pollutants. The slow release of VOCs from polymeric materials can affect the performance and durability of products and can adversely affect the indoor air quality (IAQ) and the 'well being' of occupants.

Indoor air pollutants mainly include nitrogen oxides (NO_x) and VOCs, which can cause adverse health impacts on occupants (Pickrell et al., 1986). VOCs are primarily composed of BTEX (benzene, toluene, ethylbenzene, and *o*-xylene) and halogenated hydrocarbons (Afshari et al., 2003). Among the numerous VOC compounds, toluene, ethylbenzene, *o*-xylene and styrene were chosen for this study because they are the major VOCs found in indoor environments in different countries (Risholm-Sundman and Wallin, 1999). Wolkoff (1999) stated that it is necessary to know the nature of the primary and secondary emissions from building products. The primary emissions are free (non-bound) VOCs and are generally of low molecular weight such as solvent residues, additives and non-reacted raw products, e.g. monomers. Secondary emissions are chemically or physically bound VOCs and several of these are emitted or formed by different processes under special chemical or physical conditions. Many of the building products that are based on natural raw materials, as opposed to synthetic building products, behave as a secondary emission source and generally continue to emit VOCs. These emissions appear to be partly caused by oxidative degradation to lower molecular weight VOCs with low odor thresholds, such as (unsaturated) aldehydes and fatty acids from C1 to C10, and alcohols like 2-ethylhexanol (Risholm-Sundman, 1999).

In the past, urea-formaldehyde (UF) and phenol-formaldehyde resin binders have contributed greatly to the progress made by the wood industry. These adhesives are widely used as a major component in the production of building and furniture materials, such as medium density fiberboard (MDF), particleboard (PB), and plywood. However, decreasing the emission levels of formaldehyde fumes from PB manufactured using UF resins has now become one of the major concerns of the timber and wood adhesives industry, particularly in the case of adhesively bonded wood products. Recently, attention has turned to other VOCs that may be emitted from wood products. These VOCs include chemicals naturally present in the wood, as well as those added during processing. In new energy-efficient buildings, air exchange rates are low, permitting concentrations of VOCs to accumulate beyond detectable and possibly to harmful levels. The adverse health effects associated with these increased VOC concentrations include eye and respiratory irritation, irritability, inability to concentrate and sleepiness. Moreover, health and the environment constitute two key concerns of the 21st century (Lee and Kim, 2002; Meyer et al., 1986; Milota and Wilson, 1985).

Formaldehyde-based resins also have superb bonding properties and are inexpensive. As a result, they are used extensively as adhesives in the manufacture of a variety of household products. Examples of formaldehyde use in the manufacture of selected products are listed in Table 1. As noted earlier, one prominent use of UF resin is in the manufacture of PB, plywood, and chipboard. Several thin sheets of wood are glued together by the UF resin to produce plywood, whereas PB and chipboard are manufactured by mixing wood chips and sawdust with the resin and then pressing the mixture into its final form at a high temperature (Kim and Kim, 2005b,c).

The standard method for measuring emission from wood-based panels is to use a test chamber. Three different sizes, ≥12, 1 and 0.225 m^3, are proposed in the new European standard prEN 717-1 (prEN 717-1, 1997) for formaldehyde emission determination. In Sweden, the emission test is performed in a 1-m^3 chamber according to standard SS 27 02 36 (SS 1988). As measuring the formaldehyde emission in a chamber takes time and requires specialized and expensive equipment, simpler laboratory methods which can be used for inhomogenous products with good correlation to the chamber methods are needed. Several methods have been mainly used for the determination of formaldehyde emission from PB and a good correlation has been found between the chamber, perforator and flask methods (Risholm-Sundman and Wallin, 1999).

The Korean government started controlling IAQ in 2004. The regulation prepared by the Ministry of Environment regulates the use of building materials which emit pollutants. The use of materials with total

Table 1 Uses of formaldehyde and potential indoor sources

Products	Example
Pressed wood products	Plywood, particleboard, decorative paneling
Paper products	Grocery bags, wax paper, facial tissues, paper towels, disposable sanitary products
Stiffeners, wrinkle resisters, and water repellents	Floor cover material (rugs, linoleum, varnishes, plastics), carpet backings, adhesive binders, fire retardants
Insulation	Urea-formaldehyde foam insulation
Combustion devices	Natural gas, kerosene, tobacco smoke
Other	Cosmetics, deodorants, shampoos, fabric dyes, inks, disinfectants

VOC (TVOC) emission levels above 4.0 mg/m^2/h (JIS A 1901, small-chamber method) is prohibited. TVOC is calculated between C_6 and C_{16}. Most suppliers and people are concerned about how to reduce pollutants from building materials and how to control IAQ (Kim and Kim, 2005a; Kim et al., 2006b).

In renovated or completely new buildings, levels of indoor air pollutant emissions from construction and building materials, especially of VOCs, are often several orders of magnitude higher than the VOC levels in existing buildings under normal use (Brown, 1999; Rothweiler et al., 1992; Tuomaninen et al., 2001; Wolkoff et al., 1991). Furthermore, the emission test has been standardized and chemical analyses using the 20-l small-chamber method have been conducted by the Ministry of Environment. The 20-l small-chamber method was developed in Japan and its performance complies with ASTM (1996, 1997), ECA reports (1989, 1991, 1993, 1995), and ENV 13419-1 (1999).

Although there are larger chambers, the 20-l chamber with desiccator method (JIS A 1460) was used in this paper because it has become standardized in Korea. The air control system consisted of an air supplying unit, a humidifier, and pumps. A 20-l small chamber was set up in a temperature-controlled climate chamber. Purified air was used for ventilation. A stainless steel seal box was used to prevent the cut edge effect, which allowed chemical emission only from one side surface of the test piece. When two seal boxes were used, the total surface area was 0.044 m^2 and the loading was 2.2 m^2/m^3 (Funaki and Tanabe, 2002). To reduce formaldehyde emission from surface adhesion on flooring and furniture, UF resin was replaced by melamine-formaldehyde (MF) resin and polyvinyl acetate (PVAc) was added to the MF resin. Furthermore, as PVAc can also improve the initial tack of the decorative veneer, the production productivity of the engineered flooring was increased.

In this study, we use a variety techniques, including 20-l chamber, field and laboratory emission cell (FLEC), VOC analyzer and standard formaldehyde emission test (desiccator method), to determine VOC and formaldehyde emission levels from engineered flooring bonded with MF/PVAc hybrid resin.

Experimental

Materials

Resin was prepared at a formaldehyde/melamine molar ratio of 1.75, with a solid content of 60%. After the addition of water to the formalin to give a formaldehyde content by weight of 38.5%, the pH was adjusted to 9.0 by the addition of 1 M NaOH solution (because the methylolated intermediates of the reaction rapidly condense under acidic conditions) and melamine was added. As hardener, 10% ammonium chloride solution was used. The viscosity as measured using a Brookfield Viscometer Model DV-II+(Brookfield Engineering Laboratories, Inc., Middleboro, MA, USA) was 75 cP at 21°C. Liquid-form PVAc was used with a density of 1.1 g/cm^3, viscosity of 2000 cPs at 21°C, pH value of 5% and ash ratio of 3%. PVAc adhesive was supplied from Tae Yang Chemical Co. Ltd (Incheon, Korea).

Preparation of blends

To determine and compare the effect of PVAc content, five different composition blends with MF resin/PVAc content ratios of 0%, 30%, 50%, 70% and 100%, by weight of MF resin, were prepared. The blends were merely stirred together physically and all were five-blending systems.

Flooring materials preparations

The engineered floorings for formaldehyde and VOC emission test were manufactured using five blends of MF/PVAc hybrid resins, with dimensions of 400 mm × 400 mm (length × width). After resin was spread on the plywood, three species of fancy veneers, beech, oak, and walnut, were bonded by cold and hot press. The thickness of these fancy veneers was 0.5 mm. The pressing schedule was cold pressed at 1 kgf/cm^2 for 2 min, to ensure the stability of the adhesive layer, then hot pressed at 5 kgf/cm^2 and 120°C for 160 s, followed by cold press at 1 kgf/cm^2 for 2 min.

Formaldehyde emission by desiccator method

The formaldehyde emissions from the engineered floorings bonded with each blend were determined with a desiccator (JIS A 1460; ASTM-D6007-96, 1996) according to the JIS method using a glass desiccator. The 24-h desiccator method uses a common glass desiccator with a volume of 10 l. Test specimens were positioned in the desiccator. 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 was analyzed by means of the chromotropic acid method (Kim and Kim, 2005c. The emitted quantity of formaldehyde was obtained from the concentration of formaldehyde 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 h. The principle for determining the concentration of formaldehyde absorbed in the distilled or deionized water is based on the Hantzsch reaction in which the formaldehyde reacts with ammonium ions and acetylacetone to yield diacetyldihydrolutidine (JIS, 2001).

20-l chamber test and emission factor

The 20-l small-chamber method was developed in Japan with its performance in compliance with ASTM (1996, 1997), ECA reports (1989, 1991, 1993, 1995), and ENV 13419-1 (1999). Although there were larger chambers, the 20-l chamber was used in this study because it has been standardized in Korea. The air control system consisted of an air supply unit, a humidifier, and pumps. The 20-l chamber was set up in a temperature-controlled climate chamber. Purified air was used for ventilation. The stainless steel seal box was used to prevent the cut edge effect, which allowed chemical emission only from one side surface of the test piece. When two seal boxes were used, the total surface area was 0.044 m^2 and the loading was 2.2 m^2/m^3 (Funaki and Tanabe, 2002).

Before setting up the chamber and seal boxes, they were washed with water and baked out in an oven at 260°C to eliminate any pollutants from the chamber itself. The 20-l small chamber was supplied with purified and humidified air at a given ventilation rate. The temperature and relative humidity (RH) inside the chamber were kept constant. The test conditions are shown in Table 2. Test pieces, all sealed with seal boxes, were set in the chamber, and the air inside the chamber was sampled after 12 h. Sampling conditions are shown in Table 3. Throughout the measurements, the air temperature and RH inside the test chamber, which was ventilated at 0.5/h, were kept constant at 25 ± 1°C and 50 ± 5% respectively. Aldehydes were analyzed by HPLC, and TDS/GC-MS was used for VOCs, as shown in Tables 4 and 5. In this paper, TVOC was defined as the conversion of all areas of the peaks between C_6 and C_{16} to concentrations using the toluene response factor. A peak area under 10 was defined as the limit of detection. The sample gas was taken by Tenax-TA and 2,4-DNPH cartridge 7 days after the sample specimens were installed into the 20-l small chamber, according to the regulation of the Ministry of Environment, Korea.

Table 2 Test conditions in the 20-l small-chamber method

Variables	Condition
Chamber volume	20 l
Sample size	0.0432 m^2 (0.147 m × 0.147 m × 2)
Air flow rate	0.01 m^3/h
Air exchange rate	0.5/h
Sample loading factor	2.16 m^2/m^3
Temperature	25 ± 1°C
Humidity	50 ± 5%

Table 3 Sampling condition in the 20-l small-chamber method

	Formaldehyde	VOCs
Sampler	2,4-DNPH Cartridge (Supelco, USA)	Tenax-TA (Supelco, USA)
Air flow rate	167 ml/min	167 ml/min
Total volume	10 l	3.2 l

Table 4 Analysis conditions for formaldehyde

Variables	Condition
HPLC	Agilent HP1100
Detector	UV/Vis 365 (Bw.30), ref. 590 (Bw.10)
Column	Supelco C18. 4.6 × 250 mm
Mobile phases	Acetonitrile:water = 45:55
Analysis time	25 min
Injection volume	20 μl
Column temperature	40°C
Mobile phase flow rate	1.0 ml/min

Table 5 Analysis conditions for VOCs

Variables	Condition
TDS	Perkin Elmer ATD400
GC/MS	HP6890/Agilent5973
Column	RTX-1 (105 m × 0.32 mm × 3 μm)
Carrier gas and flow	He (99.99%)
Temperature program	40°C (5 min) → 70°C (5 min) → 150°C (5 min) → 200°C (5 min) → 220°C (5 min) → 240°C (5 min)
MS condition	EI (Electron ion)
Mode	70 eV
Electron energy	TIC (scan), *m/z* :
Detection mode	35/350

The calculation of emission factor (EF) is explained in ASTM D5116. Two technical terms are commonly used to describe the rate of emissions from indoor materials, EF and ER, which are related as follows:

$$ER = A(EF) \quad (1)$$

where ER is the emission rate (mg/h), A is the source area (m^2), and EF is the emission factor (mg/m^2 h).

Thus, ER can be applied to both area sources and non-area sources, whereas EFs are reported as mass/area/time, or in the case of caulk beads, mass/length/time, when a standard bead diameter is used. In the remainder of the cases, only EF is used in the examples.

Field and laboratory emission cell

The inner surface was formed with a lathe and was hand polished. The cell was circular with a diameter of 150 mm, providing a maximum test material surface area of 177 cm^2 and a volume of 35 ml. By placing the FLEC on top of the material specimen, the surface becomes the bottom part of the cell. The loading factor (test material area to emission cell volume) was a maximum of 506 m^2/m^3. An emission-free, silicon rubber foam was used to seal the interface between the FLEC and the test material surface. All tubes and couplings were made of high-quality stainless steel. The air (or nitrogen) was introduced through two diagonally positioned inlets into a circular shaped channel (depth 7×7 mm) at the perimeter of the cell, from where the air was distributed over the test material surface through the circular air slit (1 mm). The air exited the cell at the top of its center. Such an arrangement provided a constant and efficient air velocity over the entire surface, apart from a smaller part near the center, because the cylindrical cross-sectional area is constant from the perimeter. The FLEC was supplied with clean and humidified air (or nitrogen) from an air supply control unit as outlined. The unit was coupled to the FLEC with teflon tubing. The outlet of the FLEC was connected to a 90° union coupled to a union cross with a 90-mm outlet tube protruding to avoid false air intake during testing and sampling. The two sample outlets were closed with metal rods during conditioning of the test material. The standard cleaning procedure for the FLEC was heating to 75–100°C for 1 h in a vacuum oven at about 50 mbar. A detailed protocol for the cleaning and sampling procedures can be found in the reports by Wolkoff et al. (1991, 1995). The FLEC was supplied with purified and humidified air at a given ventilation rate. The temperature and RH inside the chamber were kept constant. The emission sample was collected after 5 min of equilibration time and 5 min of cleaning time under the FLEC lid at an air flow of 250 ml/min. For formaldehyde, 4.5 l of gas was collected in a 2,4-DNPH cartridge for 30 min under a gas flow rate of 150 ml/min, while 1.5 l of gas was collected in a Tenax-TA tube for 30 min under a gas flow rate of 50 ml/min. The condition of correction gas is shown in Table 6. The formaldehyde and VOCs emitted were collected at 1, 3, 5 and 7 days after sample installation. HPLC and TDS/GC-MS were used for formaldehyde and VOCs. The instruments used were the same as those for the 20-l chamber.

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 to four pieces of size 50 mm × 50 mm and placed in a 3-l polyester plastic bag. The polyester plastic bag was sealed with teflon tape, purged three 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 cm^3) manner after 4 days, placed into the VOC analyzer and analyzed. This process is shown in Figure 1. This 4-day period was determined by the authors' previous study to find the optimum method for VOC emission test by the VOC analyzer (An et al., 2006). The measurement procedure comprised three steps. First, the product was inserted into the 3-l polyester plastic bag. Then, the plunger was slowly pulled, 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 cm^3 (1/2 calibration) of the sampled gas was ejected by pushing the plunger. The remaining gas was injected into the inlet on the main unit of the VOC analyzer, after which the measurement was automatically started.

Table 6 Conditions for field and laboratory emission cell

Variables	Condition
Chamber volume	0.035 l
Sample size	0.0177 m^2
Air flow rate	50 ml/min (VOCs), 150 ml/min (formaldehyde)
Air collects	1.5 l (VOCs), 4.5 l (formaldehyde)
Air exchange rate	428.6/h
Sample loading factor	506 m^2/m^3
Temperature	25 ± 1°C
Humidity	50 ± 5%

Results and discussion

Formaldehyde and aldehyde emission

Formaldehyde is well known to be emitted from wood-based products such as PB, MDF and plywood bonded with formaldehyde-based resin. Especially, UF resin has the highest formaldehyde emission rate because of incompletely cured, UF resin-bonded, wood-based products. To reduce formaldehyde emission from the surface adhesive used on flooring and furniture, UF resin was replaced by MF resin and PVAc was added to MF resin at various ratios in this study. Figure 2 shows the reduction of formaldehyde emission by the replacement of UF resin with MF and PVAc. The formaldehyde emission of engineered flooring determined by desiccator method can be seen to vary with different adhesive types and three fancy veneer species (oak, beech, and walnut). Although UF resin had the highest formaldehyde emission, the emission was reduced by exchanging with MF resin. Furthermore, the formaldehyde emission level was decreased with increasing addition of PVAc as the replacement for MF resin. UF resin in the case of beech was over 5.0 mg/l, which exceeded E_2 (1.5–5.0 mg/l) grade. However, MF30:PVAc70 was $\leq E_1$ (below 1.5 mg/l) grade. Because formaldehyde emission is caused by formaldehyde-based resin, the engineered floorings bonded with PVAc only had emissions of just 0.25 mg/l. As shown in Figure 3, because melamine has more $-NH_2$ groups to react with formaldehyde in the same molar ratio, formaldehyde emission when UF is replaced by MF is lower than that for pure UF resin.

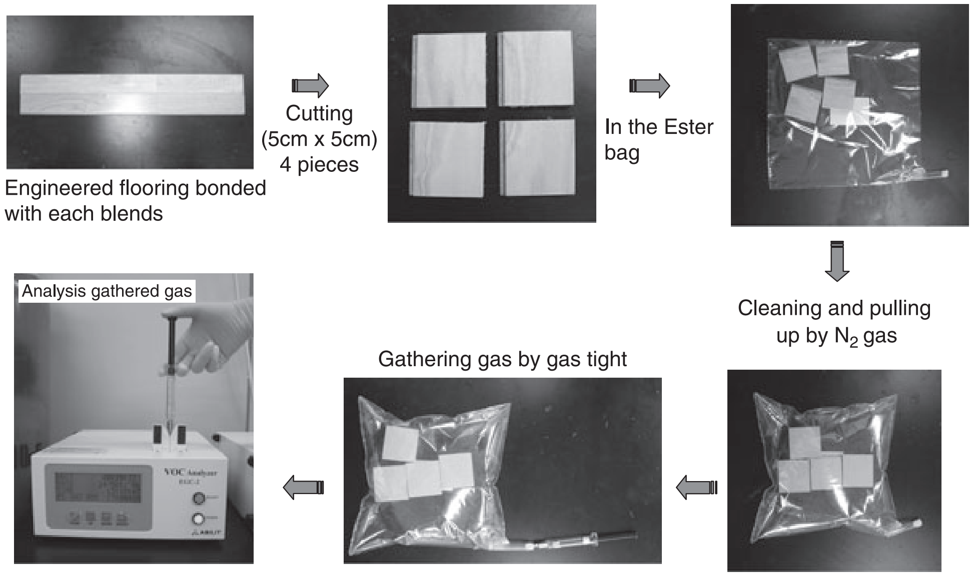

Fig. 1 Test method for volatile organic compound (VOC) emissions from engineered flooring by the VOC analyzer

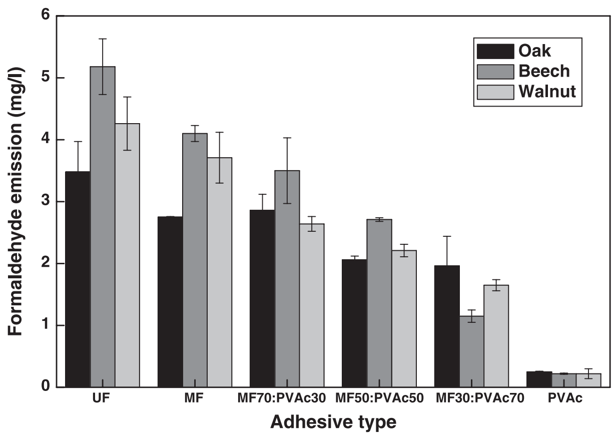

Fig. 2 Formaldehyde emission variation with different adhesive types and fancy veneer species, by desiccator method

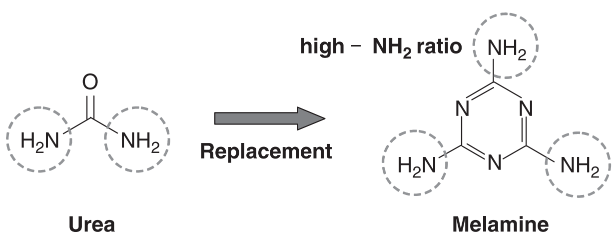

Fig. 3 Comparison of urea with melamine on the NH_2 group to react with formaldehyde

Although the formaldehyde emission varied slightly across the three fancy veneer species, the tendency for reduced formaldehyde emission was similar for all three fancy veneers. Because only beech was the highest emission species, other emission tests such as 20-l small-chamber, FLEC and VOC analyzer were carried out with beech fancy veneer.

The testing method used to test formaldehyde emission in the furniture and flooring industries, the desiccator method, is the most basic method. This desiccator method is defined in KS F 3104 and KS F 3200, which are similar to JIS A 1460 (Building Boards Determination of Formaldehyde Emission-Desiccator Method; JIS A 1460-2001, 2001). This method is inexpensive and simple to carry out. When we consider the small-scale nature of the building, flooring and furniture-related businesses in Korea, we need to develop several practical testing methods and establish the correlations among them. The Korean government started controlling IAQ in 2004. The law from the Ministry of Environment regulates the use of pollutant emitting building materials. The use of materials with a formaldehyde emission level above 1.25 mg/m^2/h (JIS A 1901, small-chamber method) is prohibited. This is E_2 grade (> 5.0 mg/l) when converted to the desiccator method.

The formaldehyde EFs are shown in Figure 4. The samples were tested for 7 days, as mandated by the Korean Ministry of Environment, in the 20-l small chamber and the formaldehyde emissions in the 2,4-DNPH cartridge were sampled after 1, 3, 5, and 7 days. The results showed a similar tendency with those from the desiccator method. After replacement of UF resin by MF resin, the addition of PVAc reduced the formaldehyde emissions. With increasing installation time, formaldehyde EFs decreased. At 7 days after sample installation, the result was 0.527 mg/m^2/h for UF resin, but under 0.25 mg/m^2/h for MF30:PVAc70.

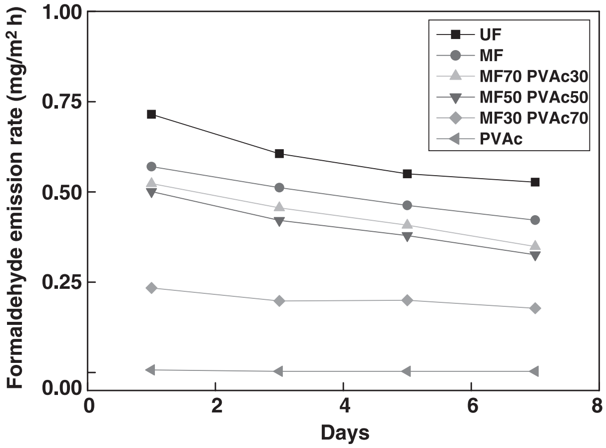

Fig. 4 Formaldehyde emission from engineered flooring bonded with different adhesive types, as determined by 20-l small chamber, for 7 days after installation of the samples in the chamber

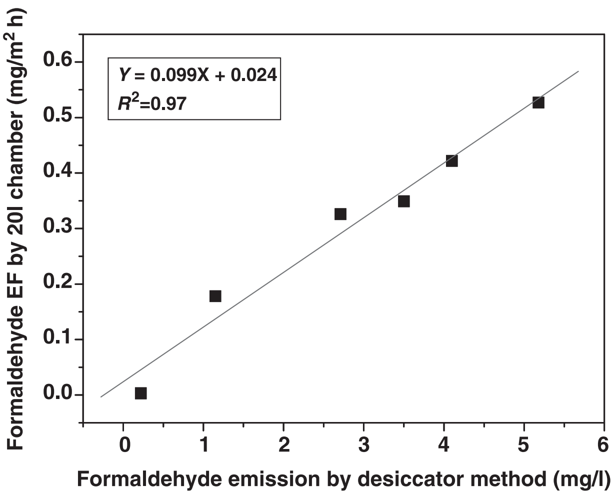

Fig. 5 Correlation of the determined formaldehyde emission from engineered flooring between desiccator method and 20-l chamber

The results of the desiccator and 20-l chamber methods showed good correlation, as shown in Figure 5. The formaldehyde contents measured by 20-l chamber method were directly proportional to the desiccator method. From the report by Marutzky (1989), wood-based panels show sufficient correlation between the emission values determined in large-chamber tests, which are used for the fundamental classification procedures and for basic research on wood products, and their actual formaldehyde content, to allow the use of the formaldehyde content value as a basis for their classification. Based on the correlation between the large-chamber and perforator values, the perforator method was the second method to gain acceptance for the determination of the emission class of PBs in Germany. The desiccator and perforator methods are standard formaldehyde emission test methods which have been deemed to be satisfactory for determining formaldehyde emission. Therefore, the results produced by the chamber method, which were well correlated with the standard methods, can be successfully applied to the pre-test measurement of formaldehyde emission.

Although the test and analysis method are the same as with the 20-l small-chamber method, by HPLC, FLEC has the advantage of reduced testing time; only a few hours are required compared with 7 days for the 20-l chamber method. The FLEC results for formaldehyde emission, shown in Figure 6, present are similar to those from the 20-l chamber. Furthermore, the correlation with the desiccator method was as high as that for the 20-l chamber. As shown in Figure 7, the correlation between the FLEC and desiccator was described by the equation $Y = 0.262X - 0.162$, and r^2 was 0.92.

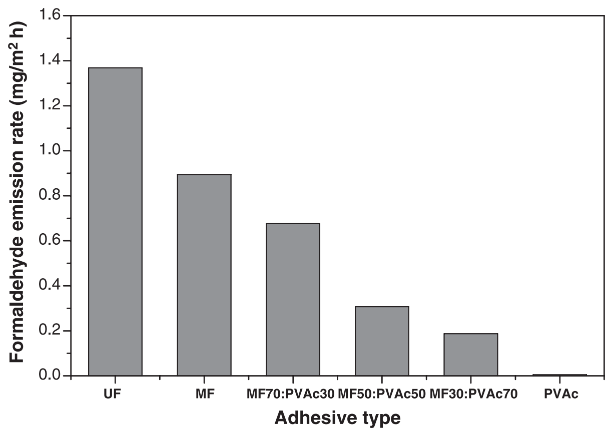

Fig. 6 Formaldehyde emission from engineered flooring bonded with different adhesive types, as determined by field and laboratory emission cell

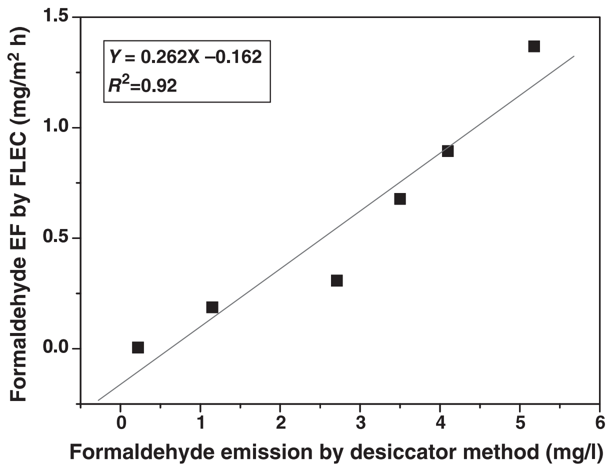

Fig. 7 Correlation of the determined formaldehyde emission from engineered flooring between desiccator method and field and laboratory emission cell

The results, in the form of a formaldehyde chromatogram, of formaldehyde emission from engineered flooring bonded with MF resin by the HPLC analysis are shown in Figure 8. This peak was determined from the gathered gases in the 2,4-DNPH cartridge for the FLEC. Formaldehyde, detected at a retention time of 5.2 min, was the first detected compound from the aldehyde chromatograms. The difference of each peak height and area for the engineered flooring was checked. Table 7 presents the peak areas from all engineered flooring samples bonded with different adhesive systems used in this study and calculated from these chromatograms.

As these engineered floorings were made with formaldehyde-based resins such as UF and MUF, as is common in industry, formaldehyde was the aldehyde with the highest emission from the engineered flooring. In addition, formaldehyde was detected at the early retention time of 5.2 min because it is an aldehyde with a simple molecular structure: HCOH. Not only formaldehyde, but also acetaldehyde, acrolein/acetone, propionaldehyde, benzaldehyde and tolualdehyde were detected as aldehyde compounds. The authors' previous study (Kim et al., 2006a) reported that aldehyde emission from wood-based composites, such as PB, MDF, engineered flooring and laminate flooring, showed similar results for the kind of aldehydes emitted. The order of peak area of aldehydes from the wood-based compounds was formaldehyde > acrolein/acetone > acetaldehyde > benzaldehyde. However, tolualdehyde was not detected from the PVAc, and all aldehydes were detected at much lower levels than in the other adhesive systems. The aldehyde EFs tested for 7 days in the 20-l small chamber are shown in Figure 9. These are the total aldehyde results for 7 days. Although the results from blends of MF resin and PVAc showed a complex variation with changing blending rate of each resin between pure MF resin and PVAc only, UF resin showed the highest EF, while PVAc showed the lowest, similar to the results of formaldehyde emission. In addition, these aldehyde emissions decreased as installation time was increased from 1 to 7 days. Despite these differences of test principle between the standard, 20-l small-chamber and FLEC methods, the results for aldehyde emissions showed a similar trend.

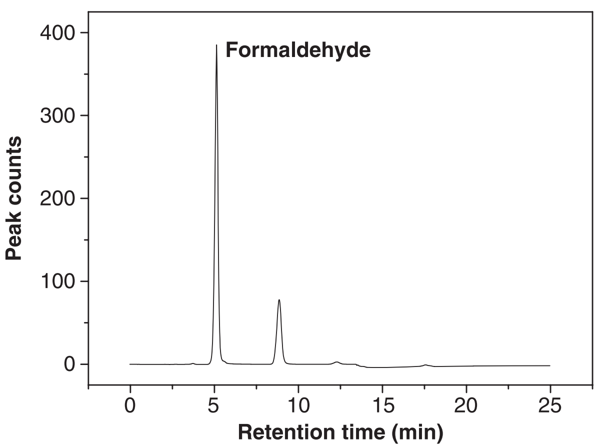

Fig. 8 Formaldehyde chromatogram of engineered flooring bonded with MF resin (determined by HPLC)

Table 7 Aldehydes from the FLEC method detected by HPLC analysis (unit: μg/m^{2}h)

	UF	MF	MF70PVAc30	MF50PVAc50	MF30PVAc70	PVAc
Acetaldehyde	0.106	0.079	0.038	0.06	0.078	0.022
Acrolein	0	0	0	0	0	0
Acetone	0.197	0.185	0.172	0.096	0.115	0.042
Propionaldehyde	0.032	0.011	0.009	0.054	0	0.009
Crotonaldehyde	0	0	0	0	0	0
Butyraldehyde	0	0	0	0	0	0
Benzaldehyde	0.041	0.043	0.055	0.041	0	0.036
Isovaleraldehyde	0	0	0	0	0	0
Valeraldehyde	0	0	0	0	0	0
Tolualdehyde	0.021	0.025	0.026	0.02	0.019	0
Hexaldehyde	0	0	0	0	0	0
Dimethylbenzaldehyde	0	0	0	0	0	0
Total	0.398	0.343	0.3	0.271	0.211	0.109

TVOC emission

Representative TVOC chromatograms at 7 days after sample installation of engineered flooring bonded with MF resin are shown in Table 8. Koontz and Hoag (1995) reported that unfinished PB and MDF from North America emitted many VOCs in addition to formaldehyde, and often at greater concentrations than formaldehyde. Major VOCs reported were (in approximate order of amounts emitted): acetone, hexanal, pentanal, benzaldehyde, pentanol, heptanal, pinenes, nonanal, and octanol. In this experiment, it was found that the PB specimens emitted hexanal, pinenes, pentanal, nonanal, heptanal, and octanol.

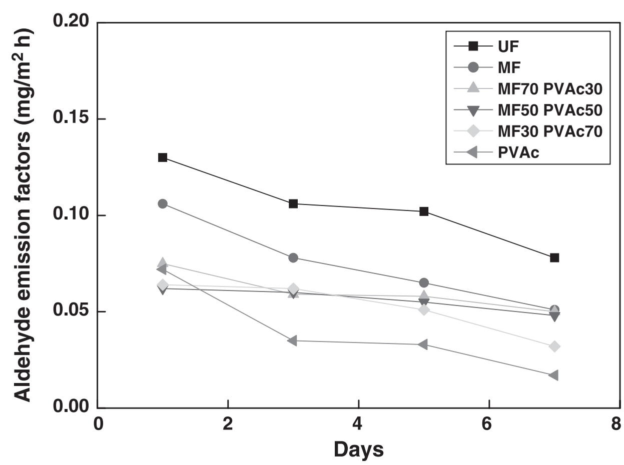

Fig. 9 Aldehydes from the 20-l chamber method as detected by HPLC analysis recorded 7 days after sample installation

Table 8 Volatile organic compounds from engineered flooring bonded with MF resin tested with the 20 l chamber method, as detected by GC/MS analysis (unit: $\mu g/m^2h$)

Resin	MF			
Sample installation day	1	3	5	7
Chloroform	0.000	0.000	0.000	0.000
1,2-Dichloroethane	0.000	0.000	0.000	0.000
Benzene	0.136	0.160	0.159	0.148
1,2-Dichloropropane	0.000	0.000	0.000	0.000
Trichloroethylene	0.000	0.000	0.000	0.000
cis-1,3-Dichloropropene	0.000	0.000	0.000	0.000
trans-1,3-Dichloropropene	0.000	0.000	0.000	0.000
1,1,2-Trichloroethane	0.000	0.000	0.000	0.000
Toluene	2.854	2.648	11.920	3.065
1,2-Dibromomethane	0.000	0.000	0.000	0.000
Tetrachloroethylene	0.000	0.000	0.000	0.000
Chlorobenzene	0.000	0.000	0.000	0.000
Ethylbenzene	0.666	0.631	0.535	0.301
Styrene	0.337	0.255	0.621	0.600
1,1,2,2-Tetrachloroethane	0.000	0.000	0.000	0.000
o-Xylene	0.831	0.751	0.519	0.403
m,p-Xylene	1.604	1.444	1.269	0.719
Benzyl chloride	0.000	0.000	0.000	0.000
1,3,5-Trimethylbenzene	0.630	0.582	0.217	0.182
m-Dichlorobenzene	0.000	0.000	0.000	0.000
o-Dichlorobenzene	0.000	0.000	0.000	0.000
p-Dichlorobenzene	0.000	0.000	0.000	0.000
1,2,4-Trichlorobenzene	0.000	0.000	0.000	0.000
Hexachlorobutadiene	0.000	0.000	0.000	0.000
Known total	7.057	6.470	15.239	5.419
Unknown total	195.383	151.180	136.301	103.091
Total concentration	202.440	157.650	151.540	108.510

Besides formaldehyde, wood emits a variety of volatile compounds such as terpenes and some organic acids. The amount of other VOCs released from wood depends highly on the wood species. Hardwoods like beech and oak release mainly a high amount of acetic and formic acid and less terpene compounds, whereas softwoods release much less organic acids but much more terpene compounds (Risholm-Sundman et al., 1998). Monoterpene compounds such as α-pinene, β-pinene and 3-carene originating from softwoods and products are the most important VOCs. Diterpene compounds, which are less volatile, can be emitted at a relatively high temperature and in comparatively small amounts (McDonald et al., 2004). Sundin et al. (1992) studied the VOCs from wood and wood products and found that about 80% of the VOCs from green wood are monoterpenes and only 1% free aldehydes. In PBs, the authors found a different pattern with monoterpene compounds comprising only 20–22% and aldehydes as much as 27–32%. The emission of VOCs from softwoods depends upon a number of factors including the age of wood (Roffael, 2006). However, many natural VOCs such as α-pinene and β-pinene are emitted from wood-based panels. In Korea, the Ministry of Environment provides guidelines for VOC emissions from building materials in terms of TVOC. Even natural VOCs from wood are considered to be harmful and are included in the TVOC calculation. Consequently, it is necessary to consider natural VOCs when reassessing the regulations governing VOC emissions from building materials. Because more than 90% of the emissions are unknown VOCs, high emission VOCs need to be regulated and included in the TVOC emission calculations. Furthermore, non-harmful VOCs, such as natural VOCs from wood, α-pinene and β-pinene, are selected as harmful VOCs when TVOCs are calculated. TVOC was calculated between C_6 and C_{16}, as shown in Figure 10. Unlike the formaldehyde EF results, the TVOC result was unclear during the test time from 1 to 5 days. The final data at 7 days were similar to the formaldehyde and aldehydes data.

Total volatile organic compound results by FLEC shown in Figure 11 show comparable data with the formaldehyde emission results by FLEC. Although the harmful gas with the highest emission from the wood-

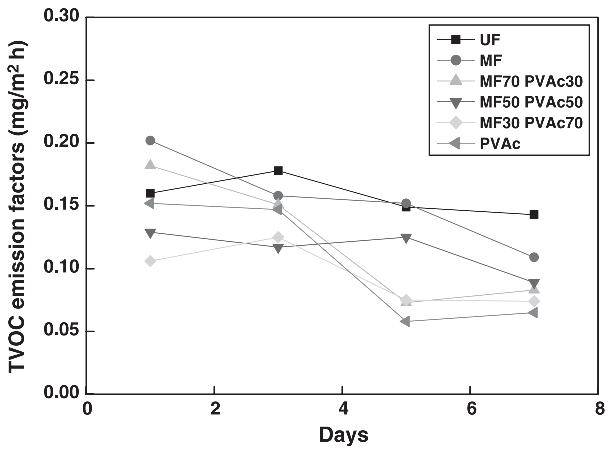

Fig. 10 Total volatile organic compounds from the 20-l chamber method as detected by GC/MS analysis recorded 7 days after sample installation

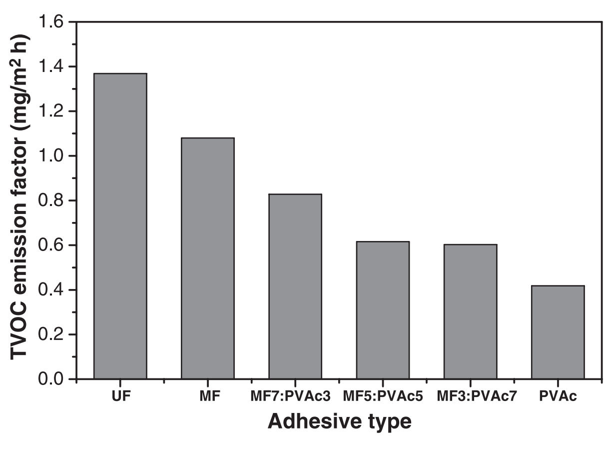

Fig. 11 Total volatile organic compounds result from the FLEC detected by GC/MS analysis

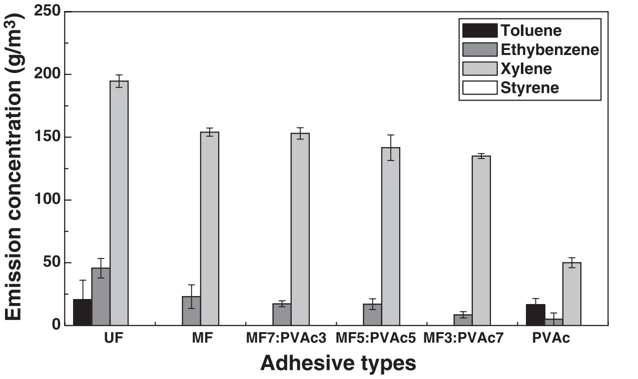

Fig. 12 Volatile organic compounds emission concentrations of (toluene, ethylbenzene, xylene, and styrene) from engineered flooring bonded with all adhesive systems as determined by the VOC analyzer

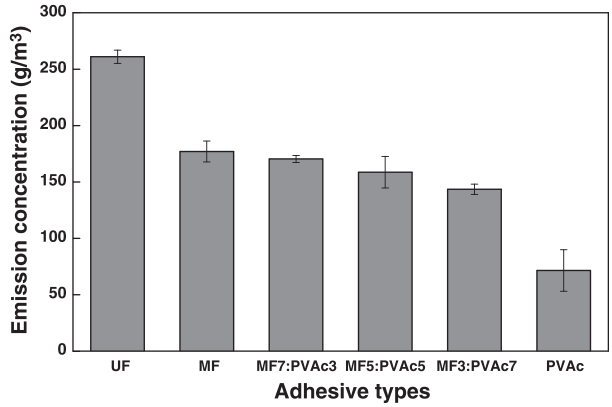

Fig. 13 Total volatile organic compounds emission concentrations from engineered flooring bonded with all adhesive systems as determined by the VOC analyzer

based composites was formaldehyde, it was followed by VOC emission, as proved in the authors' previous study (Kim et al., 2006a). These TVOC EFs were calculated by the same method as the 20-l chamber method.

Figure 12 presents concentrations of the four indicated VOCs from engineered flooring bonded with each adhesive system, as determined by the VOC analyzer. For each substance, the concentrations were measured at 96 h (4 days) after the start of the test. In the figures, three different phases are observed. In the first phase, the concentration in the 3-l polyester bag was increased due to the constant emission of organic compounds and was limited by the given air exchange rate. From all samples, xylene was the highest detected compound, whereas styrene was not detected in any of the systems. The second detected compound was ethylbenzene, followed by toluene. Even from the blends which included MF resin, no toluene was detected. However, UF resin was the highest emission concentration adhesive system, while PVAc was the lowest. In the VOC analyzer test, we defined TVOC as the sum of four detected main aromatic hydrocarbon gases: toluene, ethylbenzene, xylene, and styrene. The results are shown in Figure 13. Although it was hard to compare directly the 20-l chamber and FLEC results because these data were based only on the sum of four VOC compounds, the VOC analyzer was found to be a suitable pre-test method for application as a TVOC emission test. The TVOC emission results were also shown to be similar to those of FLEC.

To compare with the standard desiccator method, we tested TVOC emission with the FLEC and 20-l chamber methods. Although the 20-l chamber method is the standard VOC emission test in Korea, we have developed an easier, faster, and more economical test which is also portable as is the FLEC method. The results of TVOC emission concentration and TVOC EF confirmed the good correlation between the results of the VOC analyzer and the FLEC/20-l chamber method for engineered flooring bonded with all adhesive systems, as shown in Figure 14. TVOC emission concentration as determined by the VOC analyzer was directly proportional to the TVOC EF by the FLEC and 20-l chamber methods, which supports the use of the VOC analyzer in the manufacturing field where a quick and easy test for VOC emission is required. Due to its good correlation with the TVOC emission levels obtained from the standard desiccator, FLEC and 20-l chamber methods, the VOC analyzer can be successfully applied to the measurement of TVOC emissions from adhesives used in building materials. With further refinement, the quantitative analysis of TVOC emission by the VOC analyzer will become an easier, faster and more economical technique than the currently used standard methods.

Conclusion

By desiccator method, the formaldehyde emission, which was the highest for the UF resin, was reduced by exchanging with MF resin and was further decreased with increasing addition of PVAc as the replacement for MF resin. The formaldehyde emission results by the 20-l small-chamber and FLEC methods showed a similar tendency with the results from the desiccator method. After the replacement of UF resin by MF resin, PVAc addition further reduced the formaldehyde emission. With increasing installation time, formaldehyde EFs were decreased. Furthermore, the correlation with the desiccator method was as high as that for the 20-l chamber and FLEC methods. Whereas 7 days are needed for the 20-l small chamber, only a few hours are required for the FLEC. However, HPLC was used to analyze the gases gathered in the 2,4-DNPH cartridge. The emission behavior of other aldehydes showed a similar tendency with formaldehyde emission. VOC emission results by 20-l small-chamber and FLEC

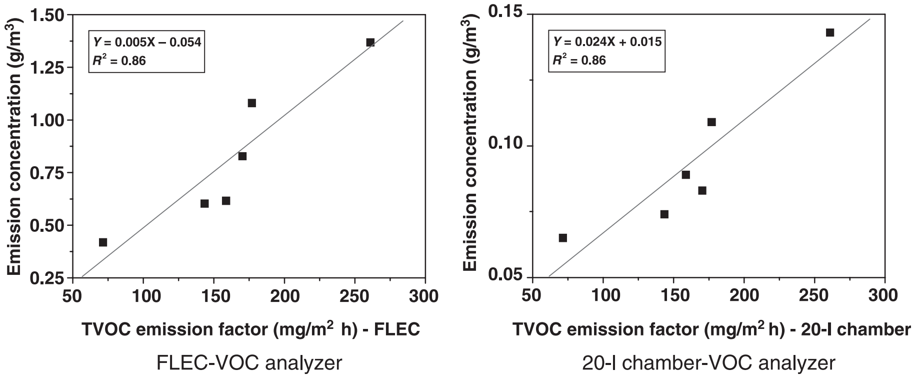

Fig. 14 Correlation of total volatile organic compounds emission between the field and laboratory emission cell/20-l chamber and VOC analyzer

methods were similar to formaldehyde and aldehyde emission results. VOCs were calculated between C_6 and C_{16} as TVOC. TVOC EF results by 20-l small-chamber and FLEC methods showed comparable data with formaldehyde emission by FLEC. Although formaldehyde was the harmful gas emitted at the highest level from wood-based composites, it was followed by VOC emission. In the VOC analyzer test, we defined TVOC as the sum of the four main detected aromatic hydrocarbon gases: toluene, ethylbenzene, xylene, and styrene. Although it was hard to compare directly the 20-l chamber and FLEC results because the data were based only on the sum of four VOC compounds, the VOC analyzer was found to be a suitable pre-test method for application as a TVOC emission test. TVOC emission results were also shown to be similar to those of FLEC. To conclude, MF/PVAc hybrid resins were successfully applied as adhesives for engineered flooring bonding to reduce formaldehyde and VOC emissions.

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