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Formaldehyde and TVOC emission behaviors according to finishing treatment with surface materials using 20 L chamber and FLEC

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ABSTRACT

Formaldehyde and TVOC are emitted from wood-based panels that are made using wood particles, wood fiber, wood chips and formaldehyde-based resins. This study examined the formaldehyde and TVOC emission behavior of medium density fiberboard (MDF) overlaid with three types of uncoated lignocellulosic surface materials (oak decorative veneer, low pressure melamine impregnated paper and high pressure melamine impregnated paper) and four types of coated surface materials (coated paper, two types of finishing foils, and PVC) using the Field and Laboratory Emission Cell (FLEC) method and a 20 L small chamber method. The uncoated lignocellulosic surface materials exhibited lower formaldehyde and TVOC emission levels. The coated surface materials did not show reduced TVOC emissions but the formaldehyde emission was reduced in the 20 L small chamber test. In the FLEC test, both the uncoated lignocellulosic surface materials and coated surface materials showed lower TVOC and formaldehyde emissions from MDF.

1. Introduction

Wood-based panels, such as particleboard (PB), medium density fiberboard (MDF) and veneer, are used widely in the manufacture of furniture, flooring, housing and other industrial products. These consumer products contain formaldehyde-based resins on account of the latter's superb bonding properties and low cost. However, wood-based panels bonded with urea-formaldehyde resin emit formaldehyde, which is toxic and is associated with possible health hazards, such as irritation of the eyes and the upper respiratory tract. This can act as an obstacle to their acceptance by the public, given the prevailing climate of environmental awareness and concern. As a result, the European and Northern American governments have imposed regulations limiting the emission of formaldehyde from building materials and from the materials used in the manufacture of furniture and fittings [1].

Building and furnishing materials may emit many volatile organic compounds (VOCs) into the indoor air. Due to their toxicity and adverse effect on human health, it is essential to use low level polluting materials instead. Indoor air pollutants mainly include nitrogen oxides (NO_x) and VOCs, which can have adverse health impacts on the occupants [2]. Even though the carpet is made by wool, VOCs and carbonyl are emitted. Especially, 4-phenylcyclohexene and 2,2-butoxyethoxy-ethanol were the main VOCs emitted and aromatic compounds and carbonyls (formaldehyde, acetaldehyde, acetone and propanal) are found at lower concentrations which tend to substantially decrease during the 3 days exposure period [3].

VOCs are composed primarily of BTEX (benzene, toluene, ethylbenzene and xylene) and halogenated hydrocarbons [4]. Among the many VOC compounds, toluene, ethylbenzene, xylene and styrene were chosen for this study, because they are the major VOCs found in indoor environments in different countries [5]. Wolkoff [6] reported that it is important to know the nature of primary and secondary emissions from building products. The primary emissions are free (non-bound) VOCs with generally low molecular weight, such as solvent residues, additives and non-reacted raw products, e.g. monomers. Secondary emissions are chemically or physically bound VOCs. Several of these are emitted or formed by a variety of processes under special chemical or physical conditions. Many building products based on natural raw materials, as opposed to synthetic building products, behave as a secondary emission sources and generally emit VOCs continuously. These emission sources appear to be caused partly by oxidative degradation to lower molecular weight VOCs with low odor thresholds, such as (unsaturated) aldehydes and fatty acids from C_1 to C_{10}, and alcohols such as 2-ethylhexanol [7].

Before they can be used as furnishing materials, wood-based panels need to be treated to match the specific requirements of

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their final use. Therefore, finishing treatment methods that produce an over layer or coating, such as paints, prints, varnishes, veneers, laminates, impregnated papers, and finishing foils, are used to reduce the absorption of water and humidity, as well as eliminate the release of harmful gases [8]. These surface materials, such as decorative vinyl films and melamine impregnated paper, can reduce the emission of formaldehyde from wood-based panels [9]. Nemli [10] examined the effects of the coating materials process parameters on the technological properties of PB, and stated that the surface coating decreased the level of formaldehyde emission.

A variety of methods are used to measure the level of formaldehyde emission from wood-based panels, including perforator, flask, gas analysis, desiccator, and large-scale chamber methods [11]. The 20 L small chamber and Field and Laboratory Emission Cell methods were designed to measure the emission of formaldehyde and VOCs from planar surface building materials and paints [12,13].

The Korean government began controlling the indoor air quality in 2004. The guidelines prepared by the Ministry of Environment regulate the use of building materials that emit pollutants. The regulations prohibit the use of materials with a Total VOC (TVOC) emission level >4.0 mg/m^2 h (JIS A 1901, small chamber method) [14]. Therefore, a comparison of formaldehyde emissions from building finishing materials used in underfloor heating systems traditionally used in Korea was carried out [15]. In addition, environmental-friendly hybrid resins were developed for flooring materials [16,17], and the level of VOC emission from building finishing materials was evaluated at various temperatures using a 20 L small chamber and VOC Analyzer [13].

This study examined the level of formaldehyde and TVOC emissions from wood-based panels overlaid with a surface material to confirm the ability of each surface material to reduce these emissions using a 20 L small chamber and FLEC.

2. Experimental

2.1. Materials

The MDF materials used in this study were 3 mm-thick furniture materials obtained from Dongwha Enterprise Co., Ltd. The MDF raw materials were Korean pine (*Pinus densiflora* Siebold et Zucc.), and urea-formaldehyde resin was used as the adhesive. This study employed three types of lignocellulosic surface materials, oak decorative veneer, low pressure melamine (LPM) impregnated paper and high pressure melamine (HPM) impregnated paper. The decorative veneer was manufactured by dry pressing in an oven after slicing logs with moisture contents of 12 wt%. The LPM was made from paper impregnated with melamine and urea-formaldehyde resin (6:4 ratio). The HPM consisted of four types of paper, which were overlay paper and pattern paper impregnated with 65 wt% and 45 wt% of melamine resin, respectively, and core paper and balancing paper impregnated with 45 wt% phenol resin. These papers were obtained from Dongwha Enterprise Co., Ltd. (South Korea). The coated paper was approximately 25 g/m^2 and coated with 4 g of urethane resin. There were two types of finishing foils, pre-impregnated finishing foil and post-impregnated finishing foil as shown in Fig. 1. PVC is used as a general finishing surface material for furniture, papered floors, etc., and was kindly provided by Dongwha Enterprise Co., Ltd. (South Korea).

2.2. Sample preparation

All the surface materials were overlaid on MDF as resins according to the hot press conditions listed in Table 1. These resins are applied in various industries according to the characteristics of each surface material. Two types of resins were used to overlay the surface materials on the MDF by a hot press instrument. The LPM exhibits auto-adhesion properties under heat treatment conditions at 90–120 °C.

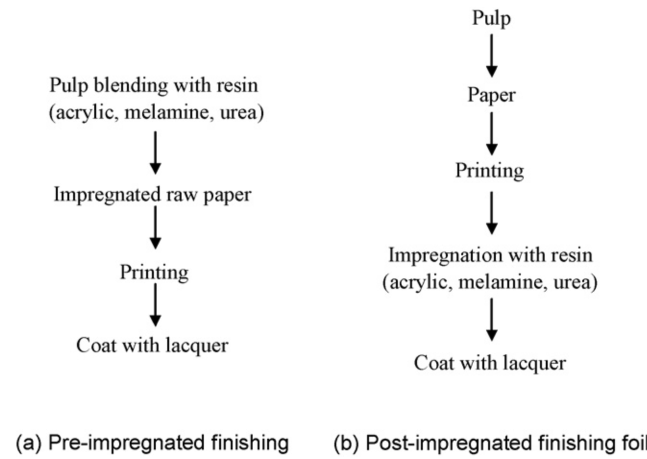

Fig. 1. Pre-impregnated and post-impregnated finishing manufacture flow diagrams.

2.3. Test method

2.3.1. Evaluation of formaldehyde and TVOC emission by 20 L small chamber test

A 20 L small chamber was developed in Japan to determine the emission levels of formaldehyde and VOCs from construction materials, paints, whose performance is in compliance with the ASTM (D5116-97 and D6007-96) [18,19] and ECA (Nos. 2, 8, 13, and 16) [20–23]. Before the samples were installed in the 20 L small chamber, they were washed with distilled water to eliminate any pollutants and baked in an oven at 270 °C. The 20 L small chamber was supplied with purified air with 50 ± 5% humidity (RH) at a ventilation rate of 0.5 h^{-1} and an air-flow of 0.01 m^3 h^{-1}. Table 2 lists the test conditions. The test pieces, all sealed with seal boxes, were set in the chamber, and the air inside the chamber was sampled after 12 h. During the experiments to measure the emission of formaldehyde and TVOC, the inner chamber temperature was kept at a constant 25 ± 1 °C. The air in the chamber was sampled after 1, 3, 5 and 7 days using TENAX TA tubes and DNPH cartridges. The TVOC concentrations were analyzed by gas chromatography with a mass spectrum detector (GC–MSD), and the formaldehyde concentration was analyzed by high pressure liquid chromatography (HPLC). The 20 L small chamber test was carried out according to the guidelines of the Ministry of the Environment, Korea.

Table 1
Resin types and hot pressing conditions for the surface material overlay.

	Resin	Hot press condition Pressure (kg f/cm^2)
Uncoated surface materials		
Decorative veneer	PVAc	30
LPM	–	30
HPM	PVAc	60
Coated surface materials		
Coated paper	EVA[c]	30
FF (pre-type)[a]	EVA	30
FF (post-type)[b]	EVA	30
PVC	EVA	30

–: no resin applied.
[a] Pre-impregnated finishing foil.
[b] Post-impregnated finishing foil.
[c] Ethyl vinyl acetate resin.

Table 2
Test conditions in the 20 L small chamber and FLEC method.

Test condition	20 L small chamber	FLEC
Sample area (m^2)	0.0392	0.0177
Volume (L)	20	0.035
Loading factor (area of sample/volume, m^2/m^3)	1.96	507.64
Air change rate (h^{-1})	0.5 ± 0.05	428.58
Air supply (ml/min)	167	250
Equilibration time	Sampling after 7 days	Sampling after 15–30 min
Temperature, humidity	25 ± 1.0 °C, 50 ± 5%	23 ± 2.0 °C, 50 ± 5%
Compounds, sampling flow and total sampling	VOC: 167 ml/min, 3.2 L Formaldehyde: 167 ml/min, 10 L	VOC: 50 ml/min, 1.5 L Formaldehyde: 150 ml/min, 4.5 L
Inlet air	Room air	High purity air
Background concentration	VOC: 2 μg/m^3, TVOC: 10 μg/m^3	VOC: 2 μg/m^3, TVOC: 20 μg/m^3
Cleaning process	Cleaning with pure water then placed in an oven for 15 min at 260 °C	Vacuum oven or cleaning with methylene followed by high purity air for 1 day
Analysis method	VOC: GC/MS Formaldehyde: HPLC	VOC: GC/MS Formaldehyde: HPLC

2.3.2. Measurement of formaldehyde and TVOC emission concentrations by FLEC test

The TVOC and formaldehyde emissions of the surface materials were measured using FLEC techniques. Table 2 lists the test conditions. Dry air (with a moisture content < 5 ppmv) from a gas cylinder was passed through a water bubbler in an air supply instrument to obtain a moisture content of 50%. The air was introduced into the inlet of the FLEC and formed laminar flow in the slit of the FLEC [24]. After the convective mass transfer of the air into the surface material, the air was discharged out of the FLEC. The rate of air exchange was controlled using an air pump. The pressure, temperature and RH of the air were monitored using a sensor fitted to the air supply pump.

3. Results and discussion

3.1. Measurement of TVOC emission from surface materials using 20 L chamber and FLEC

Fig. 2 shows the TVOC emission factors from the lignocellulosic surface materials measured by 20 L chamber. Koontz and Hoag [25] reported that unfinished PB and MDF from North America emitted a large amount of VOCs in addition to formaldehyde, often at greater levels than that of formaldehyde. The MDF emitted 0.38 mg/m^2 h of TVOC after 7 days. However, the TVOC emission factors from the MDF coated with lignocellulosic surface materials ranged from 0.09 to 0.15 mg/m^2 h, which was lower than that of the uncoated MDF during the same period. The LPM and HPM were manufactured in a paper treated containing a mixture of urea-formaldehyde resin and melamine formaldehyde resin with a small amount of solvents. The surface materials that coated the surface of the MDF interrupted the emission of the VOCs from the MDF. Therefore, the thickness of the HPM was increased due to the additional thickness of the four different types of paper mentioned above. However, the resulting HPM showed a lower level of TVOC emission from the MDF. The veneer exhibited a lower level of emission of VOCs than the uncoated surface materials. The veneer has lower air tightness than the other materials because it is made from logs that contain unevenness surfaces and minute cracks. Consequently, VOCs can be emitted easily from the MDF. The major VOCs from the non-overlaid MDF were harmful VOCs, such as acetone, benzene, styrene, toluene, ethylbenzene and xylene.

Fig. 3 shows that the TVOC emission factors of the MDF overlaid with coated surface materials generally increased. With the exception of the coated paper (after 7 days), the TVOC values of all specimens were higher than those of the control MDF. There was a rapid decrease in the level of VOC emission from the coated urethane paint on the upper surface of the coated paper. After 7 days, the TVOC emission factor of the pre-impregnated finishing-foil-overlaid MDF was approximately 0.87 mg/m^2 h, which was higher than that of the other materials during the same period. The post-impregnated finishing foil and PVC showed similar TVOC emission factors of 0.72 and 0.70 mg/m^2 h, respectively. The TVOC emission factors of MDF coated with surface materials were generally higher than those of the control MDF.

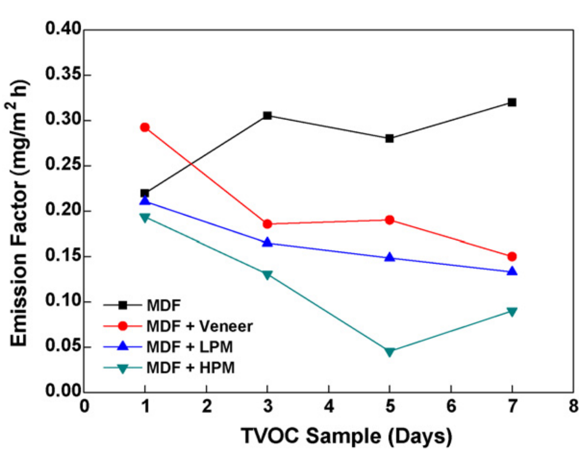

Fig. 2. TVOC emission factors from uncoated lignocellulosic surface materials.

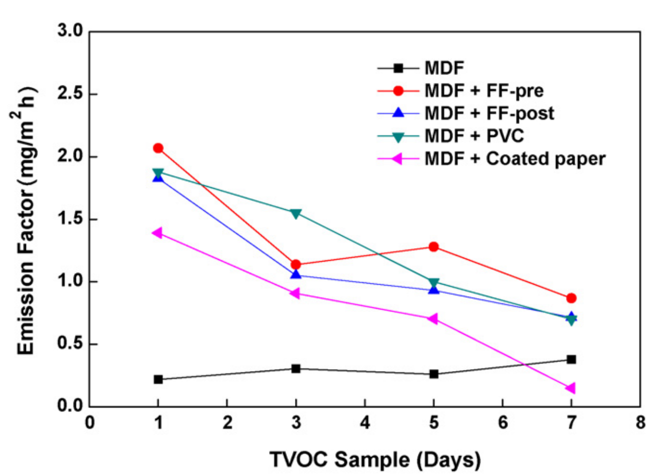

Fig. 3. TVOC emission factors from the coated surface materials.

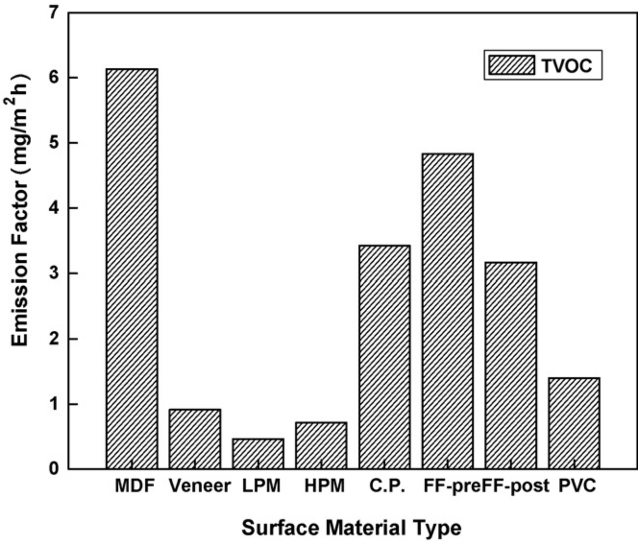

Fig. 4. Results of TVOC emission factors using the FLEC.

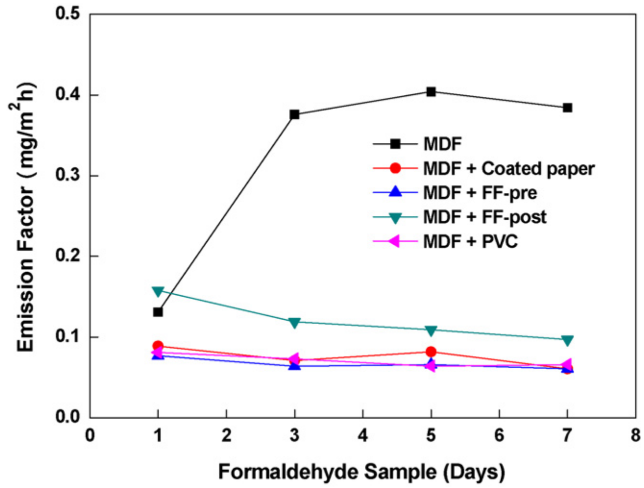

Fig. 6. Formaldehyde emission factors from the coated surface materials.

Fig. 4 shows the TVOC emission factors of the MDF overlaid with surface materials determined using a FLEC. The TVOC from the control MDF was approximately 6.1 mg/m^2 h. All surface material specimens showed lower TVOC emission factors from MDF due to the difference between the 20 L small chamber and FLEC methods. However, the MDF overlaid with the uncoated lignocellulosic surface material showed a approximately 2–10 times lower TVOC emission factor than that of the MDF overlaid with the coated surface material. The TVOC emission factor showed a similar tendency in both the 20 L small chamber and FLEC methods.

3.2. Measurement of formaldehyde emission from the surface materials using 20 L chamber and FLEC

Formaldehyde is released from hot pressed-wood products made from urea-formaldehyde (UF) resin or phenol-formaldehyde (PF) resin (e.g., plywood, PB, MDF, and oriented strand board) [26]. For this reason, formaldehyde is the main aldehyde emitted from the wood-based products. Formaldehyde was emitted at approximately 0.13–0.40 mg/m^2 h from the non-overlaid MDF during the experimental period, as shown in Fig. 5. All the specimens showed lower formaldehyde emission factors than the control except for the first value of the veneer, which was high because it included a small amount of formaldehyde to prevent putrefaction. However, after approximately 2 days, the veneer showed lower formaldehyde emission. The HPM showed similar TVOC emission to that reported above. After 7 days, the formaldehyde emission factor of HPM was 0.06 mg/m^2 h, which is approximately 5.7 times lower than that of the uncoated MDF during the same period, indicating a significant reduction of the formaldehyde emission. The amount of formaldehyde emitted from LPM was stable, but even the formaldehyde factor of LPM was approximately 0.22 mg/m^2 h, which is 3 times higher than for impregnated urea-formaldehyde resin and HPM, but showed a similar tendency to HPM. Fig. 6 shows the formaldehyde emission factors of the MDF overlaid with coated surface materials that had been lowered during the experiment. After 7 days, the formaldehyde factor from the MDF overlaid with the coated surface material was approximately 0.06–0.09 mg/m^2 h. Because the coated surface materials contained barely any formaldehyde, the amount of formaldehyde emitted from the coated MDF was less than one fifth of that emitted from the uncoated MDF. However, the formaldehyde emission factors from these surface materials were relatively higher than those of the other coated surface materials because the manufacturing process of finishing foils involves their impregnation with formaldehyde resin and coated lacquer. The formaldehyde factor of the post-impregnated finishing foil was 0.09 mg/m^2 h, which was higher than that of the pre-impregnated finishing foil. The membrane on the paper, which was obtained from the printing treatment and urethane coating process, exhibited lower formaldehyde emission levels because the pre-impregnated finishing foil was coated with urethane after the impregnation process with formaldehyde-based resins and printing treatment. This is similar to the formaldehyde emission factor from the MDF overlaid with surface materials using FLEC shown in Fig. 7. From the author's result [27], the 20 L small chamber and FLEC methods on TVOC and formaldehyde emission was compared. The TVOC emission concentration and TVOC EF confirmed the good correlation between the results of the FLEC and 20 L chamber methods for wood-based composite systems.

In the case of the uncoated surface materials, HPM showed the lowest level of formaldehyde emission (approximately 0.04 mg/m^2 h), while the formaldehyde value of PVC (approximately 0.03 mg/m^2 h) was the lowest among the coated surface materials, representing an almost 30–50-fold reduction compared to the control MDF.

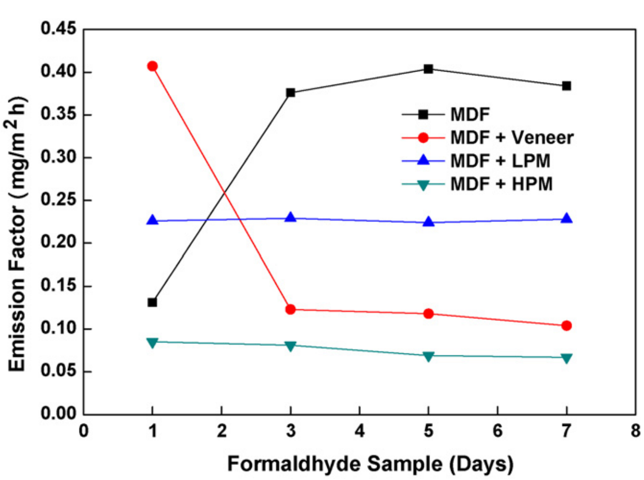

Fig. 5. Formaldehyde emission factors from the uncoated lignocellulosic surface materials.

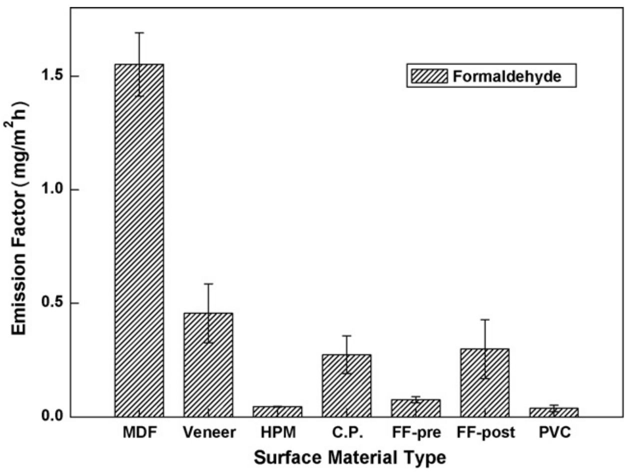

Fig. 7. Results of the formaldehyde emission factor using the FLEC.

4. Conclusion

The uncoated lignocellulosic surface materials showed reduced TVOC and formaldehyde emissions. HPM showed the lowest TVOC and formaldehyde emissions using the 20 L small chamber. In the case of the uncoated lignocellulosic surface materials, the veneer reduced the TVOC emissions, and LPM showed a lower formaldehyde factor than the others. The coated surface materials effectively reduced the level of formaldehyde emission from the MDF in the measurements using the 20 L small chamber. However, in the case of TVOC, the TVOC emission factors of the coated surface materials were generally higher than those of the control MDF because the finishing matters (e.g., urethane and lacquer) of the upper surface of the coated surface materials emitted VOCs. The greatest reduction in the emission of both TVOC and formaldehyde from the MDF in the case of the coated surface materials using the 20 L small chamber was obtained with PVC. In the FLEC test, the uncoated lignocellulosic materials showed significantly lower TVOC emissions from the MDF, approximately 2–10 times lower than those of the MDF overlaid with coated surface material. PVC, HPM and pre-impregnated finishing foil showed lower formaldehyde factors of 0.03, 0.04 and 0.07 mg/m^2 h, respectively, in the FLEC method.

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