

Comparison of Formaldehyde Emission of Wood-based Panels with Different Adhesive-hardener Combinations by Gas Chromatography and Standard Methods^{*1}

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ABSTRACT

Formaldehyde emissions from wood-based panels bonded with pine and wattle tannin-based adhesives, urea-formaldehyde resin (UF), melamine-formaldehyde resin (MF), and co-polycondensed resin of urea-melamine-formaldehyde (UMF) were measured by the Japanese standard method using a desiccator (JIS A 1460) and the EN 120 (European Committee For Standardization, 1991) method using the perforator value. In formaldehyde emission, all particleboards made using the wattle tannin-based adhesive with three different hardeners, paraformaldehyde, hexamethylenetetramine, and tris(hydroxyl)nitromethan (TN), satisfied the requirements of grade E₁. But only those made using the pine tannin-based adhesive with the hexamine as hardener met the grade E₁ requirements. Hexamine was effective in reducing formaldehyde emission in tannin-based adhesives when used as the hardener. While the UF resin showed a desiccator value of 7.1 mg/ℓ and a perforator value of 12.1 mg/100 g, the MF resin exhibited a desiccator value of 0.6 mg/ℓ and a perforator value of 2.9 mg/100 g. According to the Japanese Industrial Standard and the European Standard, the formaldehyde emission level of the MDF panels made with UF resin in this study came under grade E₂. The formaldehyde emission level was dramatically reduced by the addition of MF resin. The desiccator and perforator methods produced proportionally equivalent results. Gas chromatography, a more sensitive and advanced method, was also used. The samples for gas chromatography were gathered during the experiment involving the perforator method. The formaldehyde contents measured by gas chromatography were directly proportional to the perforator values.

Keywords : formaldehyde emission, tannin-based adhesives, urea-formaldehyde (UF) resin, melamine-formaldehyde (MF) resin, desiccator, perforator, gas chromatography

1. INTRODUCTION

Formaldehyde (HCOH) has been a subject of concern in the formaldehyde resin-bonded wood-

based panel industry for a number of years. Virtually all the wood panel products, such as plywood, particleboard, and medium-density fiberboards are manufactured using either urea

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formaldehyde (UF) or phenol formaldehyde (PF) adhesive. Formaldehyde is gaseous at room temperature, but it can be transformed into paraformaldehyde through polymerization and readily form methyleneglycol through dissolution in water (Meyer *et al.*, 1986). The toxicity of wood-based panels bonded with urea-formaldehyde resin, due to the emission of formaldehyde and the associated possible health hazard, could act as an obstacle to their acceptance by the public, given the prevailing climate of environmental awareness and concern.

To reduce formaldehyde emission, the possibility of using replacement materials for UF and PF adhesives has been studied for a long time. Tannin formaldehyde adhesives are obtained by the hardening of polymeric flavonoids of natural origin, especially of condensed tannin by polycondensation with formaldehyde (Pizzi 1994). Hardeners, however, cause formaldehyde emission even when tannin-based adhesive is used (Trosa and Pizzi 1994; Kim *et al.*, 2002). In the last decade, several approaches of producing wood-based panels with low formaldehyde emission using these wood adhesives have been developed.

Recently, the finding that hardening of melamine-urea-formaldehyde (MUF) resins occurs mostly due to their melamine reactivity has led to the realization of developing a mechanism or system of hardening to improve the performance or the formaldehyde emission of MF. This improvement can be more easily obtained with pure melamine-formaldehyde (MF) resins than with MUF resins (Kim and Kim 2003; Kim and Kim in press). Fast-reacting phenolic novolaks have been found to harden with hexamethylenetetramine via the formation of a majority of stable benzylamine bridges rather than methylene bridges. This process entails the minimal decomposition of hexamethylenetetramine to formaldehyde and hence much reduced

formaldehyde emission from the hardened resin and wood products bonded with it (Pizzi 1994; Pizzi and Tekely 1994; Pizzi *et al.*, 1996; Kim *et al.*, 2003; Kim *et al.*, 2005 in press).

To compare the levels of formaldehyde emission, many different methods have been employed. Roffael (1978) introduced the very simple WKI (Wilhelm-Klauditz-Institut) method and also used a special climate chamber for the measurement of the formaldehyde concentration in the air. In Europe, the perforator method has been used for a long time. For this method, special apparatus is needed (Roffael and Mehlhorn 1980). The European Particleboard Association (EPA) originally developed this test procedure in the late 1970s and called it perforator method, which is a simple method that was established in 1984 as European Standard EN 120. In North America, Australia, and Asia, however, the desiccator method was adopted. The desiccator test was developed in the middle of the 1970s in Japan and standardized in the United States in 1983. The estimation of the formaldehyde level is performed spectrophotometrically in all of the existing methods, including in the flask, perforator, and desiccator methods. In the middle of the 1990s, the emission of formaldehyde and other volatile organic compounds (VOCs) during hot pressing were measured using an enclosed caul plate and gas chromatography-mass spectrometry (GC-MS) (Carlson *et al.*, 1995; Wolcott *et al.*, 1996). With GC-MS, not only the emission level of formaldehyde is determined, but also that of other VOCs. Gas chromatography (GC) is preeminent among analytical separation methods. It offers a rapid and very high-resolutive separation of a very wide range of compounds, with the only restriction that the compound being analyzed should have sufficient volatility (Baugh 1993). The present article reviews the application of GC to the determination of various families of

Table 1. The weight formula for synthesized resins

Unit : g

Resin	MF(60%*)	Copolycondensation of UMF + MF		UF(51%*)		
Formula	Melamine	2175	UMF(55%*)	Urea	12044	
	38.5% Formaldehyde**	2400	Urea	12400	38.5% Formaldehyde**	19600
			Melamine	650		
			38.5% Formaldehyde**	19000		
			MF(60%*)			
			Melamine	2175		
			38.5% Formaldehyde**	2400		

* solids content

** formaldehyde solution

environmental contaminants, which traditionally have been analyzed with this technique. Included are substances such as VOCs, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs), pesticides as well as other organic pollutants, such as PBDEs, PCAs, and toxaphene (Santos and Galceran 2002).

The present investigation focused on three main areas. Firstly, a comparison was made of the traditional desiccator and perforator methods with gas chromatography for the determination of formaldehyde emission levels. Secondly, the effect of adding MF resin on the formaldehyde emission levels of UF resin was studied. Finally, the effect of hardeners on the formaldehyde emission levels of the wattle and pine tannin-based adhesives with three different hardeners (paraformaldehyde, hexamethylenetetramine, and tris(hydroxyl)nitromethane) was discussed.

2. MATERIAL and METHODS

2.1. Resins

Each of the resins used to produce the wood-based panels was synthesized in the laboratory. We synthesized urea-formaldehyde (UF) resin, melamine-formaldehyde (MF) resin, and

the co-polycondensed resin of urea-melamine-formaldehyde (UMF) and MF resins. The formulas for these resins are given in Table 1. The molar ratios of the resins were 1.25 (F/U) for UF resin, 1.75 (F/M) for MF resin, and 0.95 (F/M+U) for the UMF resin intended for co-polycondensation. Before the medium-density fiberboard (MDF) was manufactured, 3 parts (to resin) of 25% ammonium chloride as a hardener and 13 parts of 44% wax solution as a water-repellent were added.

Two types of commercial tannin extracts from wattle and pine were prepared. The wattle (*Acacia mearnsii*, mimosa) was supplied by the Bondtite Co. Ltd. in Australia and the pine (*Pinus radiata*, radiata pine) by DITECO Ltd. in Chile. These tannins consisted of fine dark brown powders with the moisture contents of 4%. Aqueous tannin extracts with a 40% concentration were prepared by dissolving the spray-dried powders of each tannin extract in water. To these solutions, 6.5, 8, and 10% of each hardener system by weight of dry tannin extract were added. The additive concentrations were selected by referring other results (Trosa and Pizzi 1994; Pichelin *et al.*, 1999; Pizzi *et al.* 1994). The pH ranged from 5.5 to 6. While paraformaldehyde and tris(hydroxyl)nitromethane (TN) were used in the pure solid state, hexamethylenetetramine was used in a 35% hexa-

mine solution (Pichelin *et al.*, 1999). For the determination and comparison of the effect of hardener content, paraformaldehyde for wattle and hexamethylenetetramine for pine were selected. By the weight of dry tannin extract, 0, 4, 8, and 12% of paraformaldehyde were applied to the wattle tannin and 0, 3, 6.5, and 10% of hexamethylenetetramine to the pine tannin.

2.2. Manufacturing Wood-based Panel

The wood fibers produced from Korean pine (*Pinus densiflora*) and dried to the moisture content of 4% were obtained from Dongwha Enterprise. The medium-density fiberboard (MDF) was manufactured using the above adhesives at a target specific gravity of 0.8 and dimensions of 270 mm × 270 mm × 8 mm (length × width × thickness). The wood fibers were placed in a rotary drum blender, and the resin, as a composite binder, was sprayed onto the wood fibers while rotating the blender. The amount of adhesive was 14 wt.% of the raw material, based on the oven-dried weight. The mixtures of fibers and adhesives were cold pressed at 2 kgf/cm² for 2 min in order to improve the stability of the mat and to obtain the proper density gradient of the composites before hot pressing. The mixture was then hot pressed, to form composite boards, at a peak pressure of 30 kgf/cm² and a temperature of 160°C. The main pressing time was 5 min and the pressure was then released in two steps of 1 min each.

The recycled wood particles with the moisture content of 3% were obtained from Dongwha Enterprise. Particleboard (PB) was manufactured using both pine and wattle tannin-based adhesives with the 3 different hardeners at a target specific gravity of 0.8 and dimensions of 270 mm × 270 mm × 8 mm (length × width × thickness). The hot pressing temperature was 170°C. The mats were pressed for 5 min by pressure of 30 kgf/cm². The manufactured MDF and PB

were pre-conditioned at 25°C and 65% RH for two weeks before testing.

2.3. Formaldehyde Emission by Desiccator and Perforator Methods

The Japanese standard method using a desiccator (JIS A 1460) and the EN 120 (European Committee For Standardization, 1991) method using the perforator value were employed as the standard test methods for determination of formaldehyde emission.

2.4. Gas Chromatography

During the experimental process of perforator method, samples were gathered following perforator extraction. The water present in the perforator, prior to shaking with acetyl acetone and ammonium acetate solutions, was used as the sample for analysis of formaldehyde and other volatile organic compounds.

In order to transfer the formaldehyde from water to toluene in preparation for the GC-ECD procedure, 2,4-dinitrophenylhydrazine solution was used (Velikonja *et al.*, 1995). Firstly, 1 ml of acetonitrile was prepared by dissolving 10 mg of 2,4-dinitrophenylhydrazine and diluting to 10 ml with HCl-H₂O (1:3, v/v). Secondly, 1 ml of this solution, the test sample (water from the perforator) and toluene were mixed in a 20 ml vial. Formaldehyde rearranged with toluene was injected into the GC. From the original formaldehyde solution (ca. 35%), stock solutions of formaldehyde at concentrations of 0, 0.5, 2, 5, 7, and 10 (ppm) were prepared and standardized with distilled water to calculate the weighing line.

A gas chromatograph (Hewlett-Packard Model 5890; NICEM, Seoul National University) with a ⁶³Ni electron-capture detector (Agilent Technologies, Palo Alto, CA, USA), equipped with a model 7673 auto-injector and a split-splitless

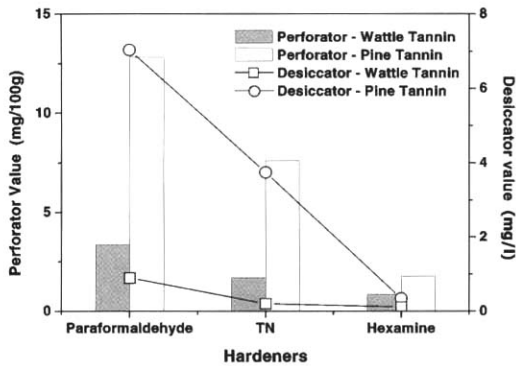


Fig. 1. Perforator and desiccator values of particleboards made with different tannin-based adhesives and different hardeners.

injection port, was used in combination with a Hewlett-Packard HP 3396 Series integrator for gas chromatography analysis. HP ChemStation software (version A.03.21) was used to program and operate the system.

A 30 m × 0.53 mm I.D. fused-silica capillary column coated with DB-5 (J&W Scientific, Folsom, CA, USA) with a 0.25 μm film thickness was used for chromatographic separation, and nitrogen was used as the carrier gas at a flow-rate of 1.5 ml/min. The injection port and detector temperatures were 200°C and 300°C, respectively. The initial column temperature was 75°C. Following injection, the oven temperature was held at 75°C for 3 min, heated at 15°C/min to 150°C and held at 150°C for 1 min, and then heated at 3°C/min to 250°C. The column was re-conditioned at the end of each run by continuing to heat at 15°C/min to 300°C, and holding at 300°C for 5 min before cooling the oven back down to the original conditions (Kim and Kim 2004).

4. RESULTS and DISCUSSION

The formaldehyde emission levels of particleboard (PB) bonded with tannin-based adhesives were measured using the perforator and desic-

cator methods. Fig. 1 shows the formaldehyde emission levels of PB bonded with wattle and pine tannin-based adhesives for 3 different hardeners, paraformaldehyde, hexamethylenetetramine, and tris(hydroxyl)nitromethane (TN). The largest values were obtained from the pine tannin-based adhesive with paraformaldehyde as hardener system, which were 12.8 mg/100 g by perforator and 7.0 mg/l by desiccator. In the case of wattle tannin-based adhesive with paraformaldehyde as hardener, however, the corresponding values were 3.4 mg/100 g. According to EN 120, particleboard of grade E₁ should emit < 8.0 mg/100 g of dry particles. And JIS A 1460 defines emission level of E₁ grade as < 1.5 mg/l. The increasing trend of the formaldehyde emission levels was observed in the PB manufactured using pine tannin-based adhesive.

On the other hand, different results were identified from PB manufactured using pine tannin-based adhesive. Although the pine tannin-based adhesive with hexamine as hardener showed a low perforator value of 1.8 (grade E₀) and desiccator value of 0.3 (grade E₀), the PB bonded by pine tannin-based adhesive with paraformaldehyde and TN as hardeners came under grade E₂. The reason could be due to the curing mechanism of hardener and the reactivity of tannin molecule toward formaldehyde. Trosa and Pizzi (2001) reported that in the case of tannin-based adhesive with hexamine as hardener, di- and tri- benzylamine bridges were formed before the completion of the curing process, which are subsequently converted to methylene bridges, when the tannin-based adhesive reacts with the hardener of hexamine. Another reason is the fast reactivity of pine tannin-based adhesive toward formaldehyde, whose structure includes the phloroglucinolic A-ring. Assuming the reactivity of phenol towards formaldehyde to be 1, and that of resorcinol and phloroglucinol to be 10 and 100, respectively, the flavonoid resorcinolic A-rings have a reac-

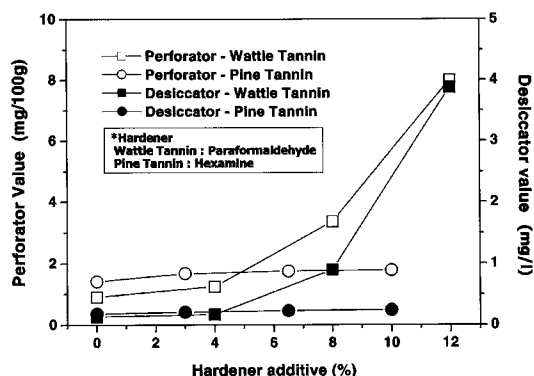


Fig. 2. Comparison of perforator and desiccator values of the formaldehyde emissions from particleboards bonded with the tannin-based adhesives as a function of the percentage of hardener content.

tivity of about 8–9, while the phloroglucinolic A-rings have a reactivity of well over 50 (Pizzi and Tekely 1995). Because this fast reactivity leads to a poor reaction occurrence, adhesive and hardener are not able to be cross-linked, which leads to auto condensation taking place between tannin molecules. Consequently, unreacted formaldehyde is emitted, thus giving rise to high perforator and desiccator values in the case of pine tannin-based adhesive with paraformaldehyde and TN as hardeners. The perforator values by hardener content are shown in Fig. 2. In the case of the wattle tannin-based adhesive with paraformaldehyde as hardener, the perforator and desiccator values increased as the amount of hardener increased. In the case of pine tannin-based adhesive with hexamine as hardener, however, the perforator and desiccator values were not affected by the increase of hardener contents. For low formaldehyde emission, the best performance was obtained when hexamine was used as the hardener.

Fig. 3 compares the formaldehyde emission behavior of MF resin, UF resins, and tannin-based adhesives with hexamine as hardener. While the UF resin showed a desiccator value of 7.1 mg/l and a perforator value of 12.1 mg/

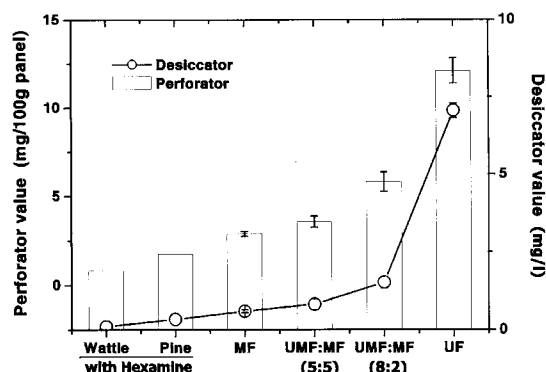


Fig. 3. Comparison of formaldehyde emissions from medium density fiberboards bonded with tannin-based adhesives with hexamine as hardener, UF resin, and MF resin by the perforator and desiccator methods (a part of the data was cited from Kim and Kim 2004).

100 g panel, the MF resin exhibited a desiccator value of 0.6 mg/l and a perforator value of 2.9 mg/100 g panel. According to both standards, the formaldehyde emission level of medium-density fiberboard (MDF) made using the UF resin was E₂ grade. To reduce the formaldehyde emission, MF resin should be added. Fig. 3 also demonstrates a dramatic reduction in formaldehyde emission with the addition of MF resin. In general, the reduction in formaldehyde emission levels from products bonded with UF resin has been achieved by employing several technological methods (Myers 1989). In this study, however, MF resin was used as a low formaldehyde emission adhesive, which contains amino groups like the UF resin. As the MF resin content increased, the formaldehyde emission values measured by the desiccator and perforator methods proportionally decreased.

The condensation reaction of melamine with formaldehyde is similar to that between urea and formaldehyde. However, the reaction of formaldehyde to melamine occurs more easily and completely than does urea. The amino group in melamine easily accepts up to two molecules of formaldehyde. Thus, the complete methylola-

tion of melamine is possible, whereas it is not proved for urea. Up to six molecules of formaldehyde are attached to a molecule of melamine. The methylolation step then leads to a series of methylol compounds with two to six methylol groups. Because melamine is less soluble in water than urea, the hydrophilic stage proceeds more rapidly in MF resin formation than in UF condensation. Therefore, hydrophobic intermediates of the MF condensation appear early in the reaction. Another important difference is that the condensation of MF and their subsequent curing can occur not only under acid conditions but also under neutral or even slightly alkaline conditions. The mechanism of the further reaction of methylolated melamine to form hydrophobic intermediates is the same as for UF resins, involving the splitting off of water and formaldehyde. Methylene and ether bridges are formed and the molecular size of the resin increases rapidly. These intermediate condensation products constitute the bulk of the commercial MF resins. The final curing process transforms the intermediate to the desired MF infusible resins through the reaction of amino and methylol groups, which are still available for reaction (Pizzi 1994). Even though MF resin can be used as an adhesive of producing low formaldehyde emission in wood-based panels, using melamine in wood-based panels is much more expensive than urea. For this reason, MUF resin by the addition of urea is often used in order to make them less expensive. Moreover, the formaldehyde emission of tannin-based adhesives, natural adhesives, with hexamine as hardener was much lower than commercial adhesives for wood panels such as UF and MF resins. In Fig. 4, the desiccator and perforator values are compared. Although perforator value was directly proportional to the desiccator value in the case of E₁ grade level, it increased less steeply than the desiccator value. Whereas the weight (100 g) of wooden board is used in the

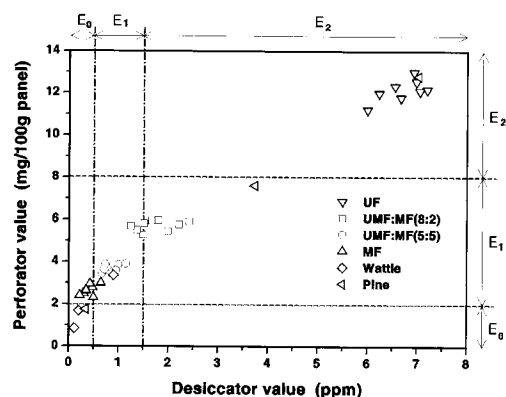


Fig. 4. Correlation of formaldehyde emissions from medium density fiberboards between perforator and GC methods.

*E: Formaldehyde emission grade

perforator method, the dimensions (1800 mm²) of the wooden board are taken into consideration in the desiccator method. In spite of slightly different emission values of formaldehyde from the same boards because of the difference in measuring method, these two methods produce proportionally equivalent results.

To accomplish a more sensitive separation of the sample, the optimal volatile solvent is needed in gas chromatography (GC). Because the formaldehyde to be analyzed was dissolved in water, it was not suitable for use with the DB-5 fused-silica capillary column, and therefore water was replaced with toluene. However, formaldehyde exhibits a greater chemical attraction with water than toluene. 2,4-dinitrophenylhydrazine solution acetonitrile and 25% HCl solution was used for metathesis as a catalyst (Lipari and Swarin 1982). To draw the calibration curve, formaldehyde solutions of various consistencies, 0, 0.5, 2, 5, 7, and 10 ppm, were tested. The peaks at 25 min of retention time are presumed to correspond to formaldehyde. The peak areas were automatically calculated with HP ChemStation software and the calibration curve for gas chromatography was obtained. The numerical formula linking the peak area and the retention

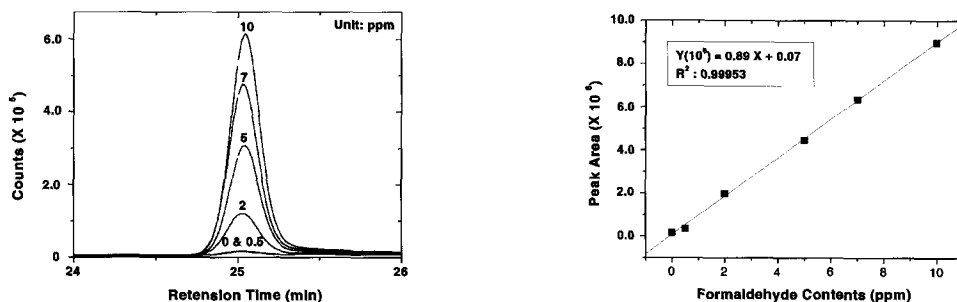


Fig. 5. Formaldehyde peaks at 25 min and the calibration curve by gas chromatography (Kim and Kim 2004).

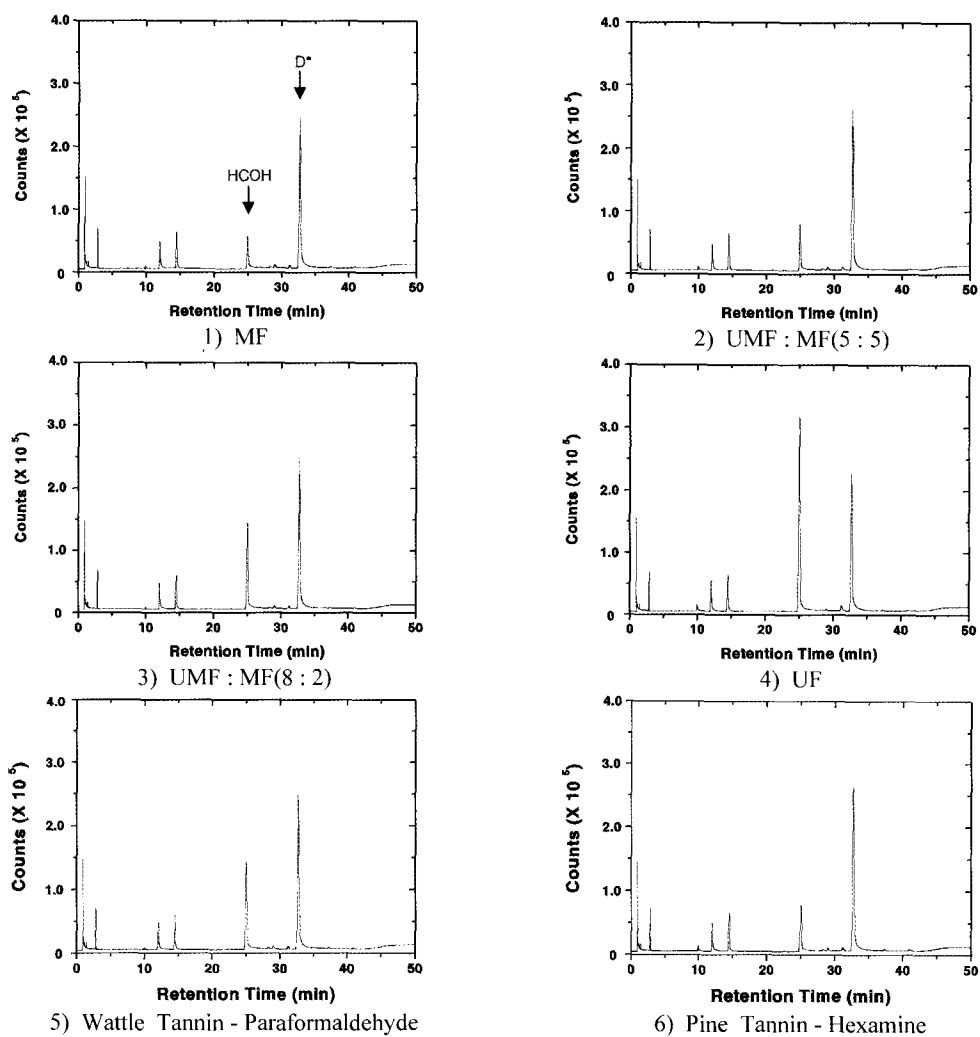


Fig. 6. Chromatograms of various resins: MF resin, co-polycondensed resin of UMF and MF (UMF : MF = 8 : 2 and 5 : 5), UF resin, and tannin-based resins (a part of the data was cited from Kim and Kim 2004). D*: 2,4-dinitrophenylhydrazine solution with acetonitrile and HCL solution.

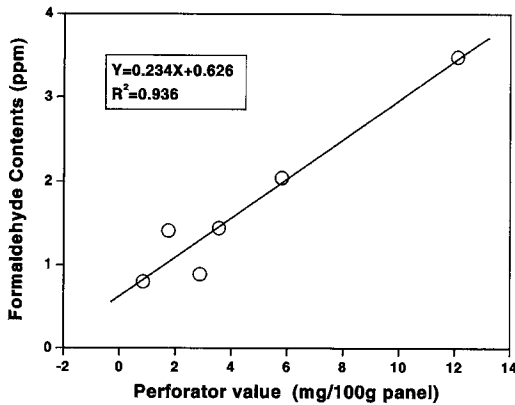


Fig. 7. Correlation of formaldehyde emissions from wood-based panels between perforator and GC methods.

time was $Y(\times 10^6) = 0.89X + 0.07$, where Y is the formaldehyde content (mg/ℓ) and X is the calculated peak area, as shown in Fig. 5. Characteristic chromatograms of six resins, one MF resin, two mixture types of UMF and MF (UMF:MF = 8:2 and 5:5) resins, one UF resin, one tannin-paraformaldehyde system, and one pine tannin-hexamine system, are shown in Fig. 6. The solvent peaks appeared early and have the same shape and height. The only difference between the two chromatograms occurs in the height of formaldehyde peaks, at 25 min. From this original chromatogram, the peak areas were obtained and the formaldehyde contents were calculated.

We found that there was a good correlation between the results of the perforator and GC methods for these different resins, as shown in Fig. 7. The formaldehyde concentrations measured by the GC were directly proportional to the perforator values. From the report of Marutzky (1989), wood-based panels appeared to show sufficient correlation between the emission values determined in large-chamber tests. Based on the correlation between the large-chamber and perforator values, the perforator method was the second to become accepted for

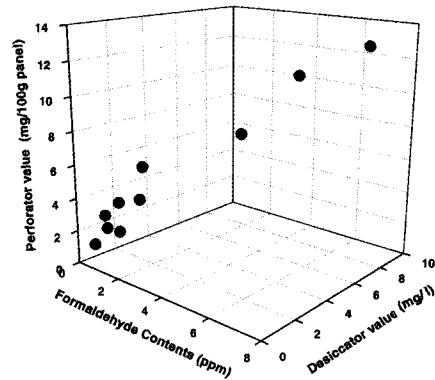


Fig. 8. Correlation of formaldehyde emissions from wood-based panels between perforator, desiccator, and GC methods.

the determination of emission class of particleboards in Germany. For this reason, the perforator method is deemed to be a satisfactory method of determining formaldehyde emission, and therefore the GC method, which produced results that were well correlated with the perforator and desiccator values, can also be successfully applied for the measurement of formaldehyde emission. These results from three different methods were shown together in Fig. 8. With further refinement, the quantitative analysis of formaldehyde emission by GC will become more precise and provide a more advanced technique than the current typically used methods.

5. CONCLUSION

Generally, the formaldehyde emission levels of wood particleboards bonded with tannin-based adhesives was low and satisfied the requirements of grade E₁, except in the case of pine tannin-based adhesive with paraformaldehyde and and tris(hydroxyl)nitromethan (TN) as hardeners when measured by the perforator and desiccator methods. When hexamine was used as a hardener, the lowest emission levels were observed. This result can be attributed to the

reaction mechanism of hexamine, which leads to the formation of benzylamine bridges between tannins molecules.

In the formaldehyde emission behavior of the MF and UF resins, the UF resin showed a desiccator value of 7.1 mg/ℓ and a perforator value of 12.1 mg/100 g panel but the MF resin exhibited a desiccator value of 0.6 mg/ℓ and a perforator value of 2.9 mg/100 g panel. The formaldehyde emission level of the medium density fiberboards made with the UF resin in this study came under E₂ grade. In order to reduce the formaldehyde emission level, MF resin was added. The formaldehyde emission behavior was dramatically reduced by the addition of MF resin. The desiccator and perforator values were compared. Although the perforator value was directly proportional to the desiccator value within the E₁ grade level, its magnitude was much greater than that of desiccator method. In spite of the slightly differences between the sampling methods, the desiccator and perforator methods produced proportionally equivalent results.

The formaldehyde emission levels obtained by GC were similar to those by the perforator and desiccator methods. We found a good correlation between the results of the perforator method, desiccator method, and the measurement made by the GC for different resins. The formaldehyde contents measured by GC were directly proportional to the perforator values. With further refinement, the quantitative analysis of formaldehyde emission by GC will become more precise and provide a more advanced technique than the current typically used methods.

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