Comparison of standard methods and gas chromatography method in determination of formaldehyde emission from MDF bonded with formaldehyde-based resins

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Abstract

Formaldehyde emissions from MDF bonded with urea–formaldehyde resin (UF), melamine–formaldehyde resin (MF) and the co-polycondensation resin of urea–melamine–formaldehyde (UMF) and melamine–formaldehyde, measured by the Japanese standard method of determining formaldehyde emission with a desiccator (JIS A 5908) and the DIN EN 120 (European Committee For Standardization, 1991) method using the perforator value, were used as the typical standard methods. While the UF resin showed a desiccator value of 7.05 ppm and a perforator value of 12.1 mg/100 g panel, the MF resin exhibited a desiccator value of 0.6 ppm and a perforator value of 2.88 mg/100 g panel. 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 was E_2 grade. The formaldehyde emission level was dramatically reduced by the addition of MF resin. This is because the addition of formaldehyde to melamine occurs more easily and completely than its addition to urea, even though the condensation reaction of melamine with formaldehyde is similar to that between urea and formaldehyde. These two methods, the desiccator method and the perforator method, produced proportionally equivalent results. Gas chromatography, a more sensitive and advanced method, was also used. The samples used for gas chromatography were gathered during the experiment involving the perforator method. The formaldehyde emission levels obtained from gas chromatography were similar to those obtained from the perforator method. The formaldehyde contents measured by gas chromatography were directly proportional to the perforator values.
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1. Introduction

Formaldehyde (HCOH) is a suspected human carcinogen that is known to be released from pressed-wood products used in home construction, including products made with urea–formaldehyde (UF) resins (e.g., particleboard, hardwood plywood, medium density fiberboard (MDF), and paneling) and those made with phenol–formaldehyde (PF) resin (e.g., softwood plywood, oriented strandboard) (Otson and Fellin, 1992; Kelly et al., 1999). 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. As a result, the European and Northern American governments have already or are about to impose regulations limiting the emission of

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formaldehyde from building materials and from the materials used for the manufacture of furniture and fitments (Kavvouras et al., 1998). Many consumer products containing formaldehyde-based resins release formaldehyde vapor, leading to consumer dissatisfaction and health-related complaints. These emissions have resulted in various symptoms, the most common of which is irritation of the eyes and the upper respiratory tract. Formaldehyde has also been found to produce nasal carcinomas in mice and rats after exposure to 14.1 and 5.6 ppm of formaldehyde, respectively, over a long period of time. These findings have led to an intensified interest in the indoor environment. Consumer products, specifically construction materials, are a major source of formaldehyde in the indoor environment (Pickrell et al., 1986).

These days, melamine–formaldehyde (MF) and melamine–urea–formaldehyde (MUF) resins are mainly used as thermosetting wood adhesives for wood panels. Both resins give excellent adhesive performance, good moisture resistance and tend to produce lower formaldehyde emission than urea formaldehyde resins. Recently, the finding, that the hardening of MUF resins occurs mostly due to their melamine reactivity, has led to the realization that the development of a mechanism or system of hardening, in order to improve the performance or the formaldehyde emission of MF, can be more easily obtained with pure MF resins than with MUF resins.

Equally recently, fast-reacting phenolic novolaks have been found to harden with hexamethylenetetra-mine 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 and Kim, 2003).

The reactions which occur during the synthesis of MF resin can be roughly divided into two different stages; methylolation and condensation. At the start of the resin synthesis, melamine reacts with formaldehyde leading to the formation of a series of nine different methylolmelamines. In reaction 1, the first addition reaction of formaldehyde to melamine is shown. The second reaction step involves condensation, i.e., bridge formation, between the various (methylol)melamines leading to the formation of a large number of different oligomers. In principle, two different types of bridge may form during the condensation step, the ratio of which depends strongly on the pH. At relatively low pH (7–8), methylene bridges are formed (reaction 2a), whereas at pH values above 9, the formation of ether bridges is favored (reaction 2b). Then a large number of oligomeric derivatives are formed and crosslinked networking occurs during baking (Jahromi, 1999), and shown in Fig. 1.

Many building materials emit volatile organic compounds (VOC) which have the potential to affect health and comfort. The formaldehyde emission from wood

Reaction I : Addition of formaldehyde to melamine

$$M\text{-}NH_2 + CH_2O \Leftrightarrow M\text{-}NHCH_2OH$$
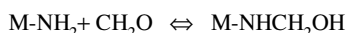
Reaction II : Condensation reaction between methylolmelamines

(a) $M\text{-}NHCH_2OH + HOCH_2HN\text{-}M \Leftrightarrow M\text{-}NHCH_2OCH_2NH\text{-}M + H_2O$

(b) $M\text{-}NHCH_2OH + H_2N\text{-}M \Leftrightarrow M\text{-}NHCH_2NH\text{-}M + H_2O$
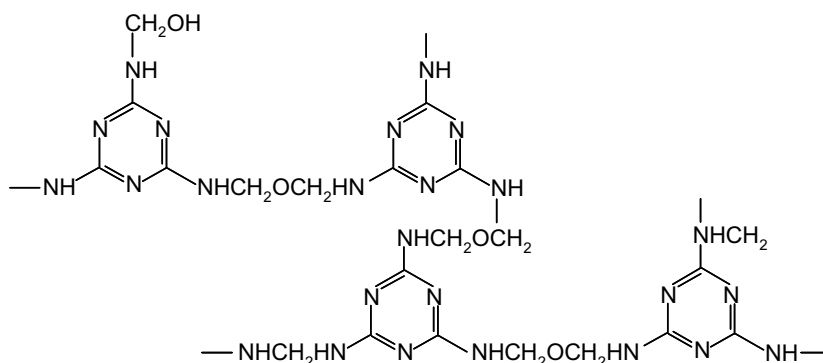
Cross-linking : MF cross-linked network

Fig. 1. Steps involved in the MF synthesis and MF chemical structure (Rishole-Sundman and Wallin, 1999).

based materials is usually determined in a reaction chamber at a predefined temperature, humidity and ventilation rate. The concentration of formaldehyde in the air within the chamber is measured until a constant concentration is reached. This is a time consuming method and it also requires special equipment (Coullerez et al., 2000; Rishole-Sundman and Wallin, 1999).

To measure the levels of formaldehyde emission, many different methods have been used. Roffael introduced the very simple WKI method. He also used a special climate chamber for the measurement of the formaldehyde concentration in the air (Roffael, 1978).

In Europe, the perforator method has long been used. For this method, special apparatus is needed (Roffael and Mehlhorn, 1980). The European particleboard association originally developed this test procedure in the late 1970s and called it the 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 WKI, perforator and desiccator methods. In the middle of the 1990s, Carlson and Wolcott measured formaldehyde emission and that of other VOCs during pressing, 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 formaldehyde emission level is determined, but also that of other VOCs. Gas chromatography (GC) is pre-eminent among analytical separation methods. It offers the rapid and very high resolution separation of a very wide range of compounds, with the only restriction being that the compound being analyzed should have sufficient volatility. The GC instrument constructed by James and Martin 50 years ago contained most of the features of a modern day gas chromatograph: a means of controlling the flow of the mobile-phase carrier gas, stabilization of the temperature of the column, and a sensitive detector to determine and record the concentrations of the separated

constituents at the end of the column. These pioneers also introduced the concept of separation efficiency, and discussed the influence of such parameters as the gas flow rate and diffusion of the sample in the mobile phase (Baugh, 1993).

The present article reviews the application of GC to the determination of various families of environmental contaminants, which traditionally have been analyzed with this technique. Included are substances such as volatile organic compounds (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; Kim and Kim, 2004).

The present investigation focused on two 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.

2. Methods

2.1. Resin and manufacturing of MDF

Each of the resins used to produce the MDF, was synthesized in the laboratory. We synthesized urea–formaldehyde resin (UF), melamine–formaldehyde resin (MF) and the co-polycondensation resin of urea–melamine–formaldehyde (UMF) and melamine–formaldehyde. These formulas for these resins are given in Table 1. The molar ratios of the resins were 1.25 (F/U) for urea–formaldehyde resin, 1.75 (F/M) for melamine–formaldehyde resin and 0.95 (F/M and U) for the urea–melamine–formaldehyde resin used for co-polycondensation. Before the MDF was manufactured, three parts (to resin) of 25% ammonium chloride as a hardener and 13 parts of 44% wax solution for waterproofing were added.

The wood fiber distributed from Dongwha Enterprise was made from Korean pine (*Pinus densiflora*) with a

Table 1
The weight formula for synthesized resins (unit: g)

Resin	MF (60%[a])		Copolycondensation of UMF + MF		UF (51%[a])	
Formula	Melamine	2175	UMF (55%[a])		Urea	12,044
	38.5% Formaldehyde[b]	2400	Urea	12,400	38.5% Formaldehyde[b]	19,600
			Melamine	650		
			38.5% Formaldehyde[b]	19,000		
			MF (60%[a])			
			Melamine	2175		
			38.5% Formaldehyde[b]	12,400		

[a] Solid content.
[b] Formaldehyde solution.

moisture content of 4%. The MDF was manufactured using the above adhesives, in order to have a specific gravity of 0.8 and dimensions of 270 mm × 270 mm × 8 mm.

The wood fiber was placed in a rotary drum mixer, and the resin, used as a composite binder, was sprayed onto the wood fiber while rotating the mixer. The amount of adhesive was based on 14 wt% of the raw material, as determined using the oven-dried weight. The mixture of fiber and adhesives was 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. We manufactured 15 MDF panels for each adhesive system. The manufactured boards were pre-conditioned at 25 °C and 65% RH for two weeks before testing.

2.2. Formaldehyde emission by desiccator and perforator method

The Japanese standard method of determining the formaldehyde emission with a desiccator (JIS A 5908) and the DIN EN 120 (European Committee For Standardization, 1991) method using the perforator value were used as the typical standard methods.

The 2-h desiccator method uses a common glass desiccator with a volume of 10.5 l. Eight test specimens, with dimensions of 7.0 mm × 12.7 mm, which were cut from a board and conditioned for 7 days at 23 °C and 50% relative humidity, are positioned in the desiccator. The emission test lasts 24 h in the covered desiccator at a temperature of 23 °C. The emitted formaldehyde is absorbed in a water-filled Petri dish and is analyzed by means of the chromotropic acid method. The perforator method involves the extraction of small particle-board samples with toluene in a perforator apparatus. The extracted formaldehyde is sampled in water and determined by the iodine method. The formaldehyde content is expressed in milligrams of formaldehyde per 100 g of dry board. It is a simple test, and the total time required to perform it is about 3 h (Marutzky, 1989).

2.3. Gas chromatography

During the process of carrying out the perforator method experiment, samples were gathered following perforator extraction. The water present in the perforator, prior to shaking with acetyl acetone and ammonium acetate solutions, contained 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 (Lipari and Swarin, 1982; 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 metathesized 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 Hewlett–Packard Model 5890 A gas chromatograph (NICEM, Seoul National University) with a ^{63}Ni electron-capture detector (Agilent Technologies, Palo Alto, CA, USA), equipped with a model 7673 auto-injector and a split–splitless injection port, was used in combination with a Hewlett–Packard HP 3396 Series II 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, with a flow rate of 1.5 ml/min, was used as the carrier gas. 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–150 °C and held at 150 °C for 1 min, and then heated at 3 °C/min–250 °C. The column was re-conditioned at the end of each run by continuing to heat at 15 °C/min–300 °C, and holding at 300 °C for 5 min before cooling the oven back down to the original conditions (Kim and Kim, 2004).

3. Results and discussion

The evolution of formaldehyde from urea–formaldehyde materials is incontrovertible. Over the past 40 years, investigators have examined extensively the structure of the components of urea–formaldehyde resin systems and the physical chemistry of their formation and degradation in aqueous solutions. Classical kinetic, chromatographic, and NMR techniques have been applied to the study of this process (Tomita, 1980; Kumar and Sood, 1990). We can conclude from these studies that the reactions leading to the formation of the urea–formaldehyde products formed during UF resin synthesis and curing are reversible. In the forward direction, water is eliminated; therefore, the reverse reactions can be viewed as hydrolysis, which leads to the release of formaldehyde. Because most, if not all, of these reactions are catalyzed by acid, the use of an acid catalyst

to hasten bond curing unfortunately also increases the rate of hydrolysis and formaldehyde liberation.

Fig. 2 compares the formaldehyde emission behavior of the MF and UF resins used in this study. While the UF resin showed a desiccator value of 7.05 ppm and a perforator value of 12.1 mg/100 g panel, the MF resin exhibited a desiccator value of 0.6 ppm and a perforator value of 2.88 mg/100 g panel. According to both the Japanese industrial standard and the European standard, the formaldehyde emission level of the MDF panels made using the UF resin was E_2 grade. To reduce the formaldehyde emission, MF resin was added. Fig. 2 demonstrates the dramatic reduction in formaldehyde emission obtained through the addition of MF resin. In general, the reduction in formaldehyde emission levels from products bonded with urea–formaldehyde adhesive resins has been achieved by employing one or more of several technological methods (Myers, 1989).

These methods include:

- Changing the formulation of the urea–formaldehyde adhesive resin (e.g., lowering the F/U ratio); urea–formaldehyde resins were modified by:
- Adding formaldehyde-scavenging materials directly to the urea–formaldehyde adhesive resin
- Separately adding formaldehyde-scavenging materials to the wood finish
- Treating panels after their manufacture either with a formaldehyde scavenger or by the application of coatings or laminates
- Switching to an entirely different adhesive resin system.

However, in this study, MF resin was used as a low formaldehyde emission adhesive containing amino groups, as in the case of the UF resin. As the MF resin content increased, the formaldehyde emission values, as measured by the desiccator and perforator methods, decreased to the same extent.
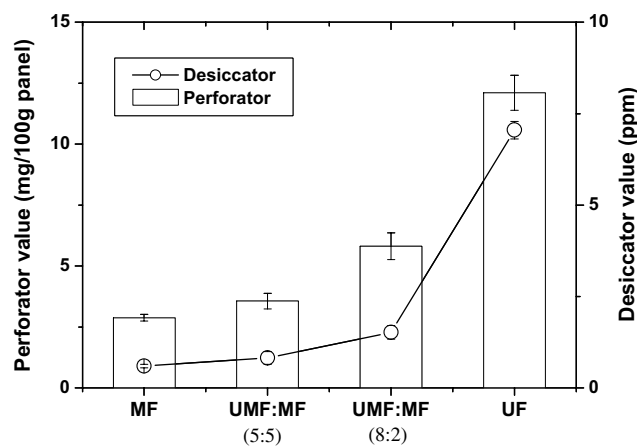
The condensation reaction of melamine with formaldehyde is similar to that between urea and formaldehyde. However, the addition of formaldehyde to melamine occurs more easily and completely than its addition to urea. As explained in Fig. 1, the amino group in melamine easily accepts up to two molecules of formaldehyde. Thus, the complete methylolation of melamine is possible, whereas it is not possible with 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. Therefore, hydrophobic intermediates of the MF condensation appear early in the reaction. Another important difference is that the condensation of MF to give resins, 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 methylol 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 soluble and 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 producing low formaldehyde emission in wood-based panels, using melamine in wood-based panels is much more expensive than urea.

Fig. 2. Comparison of formaldehyde emission evaluated by desiccator and perforator method of UF and MF resin.
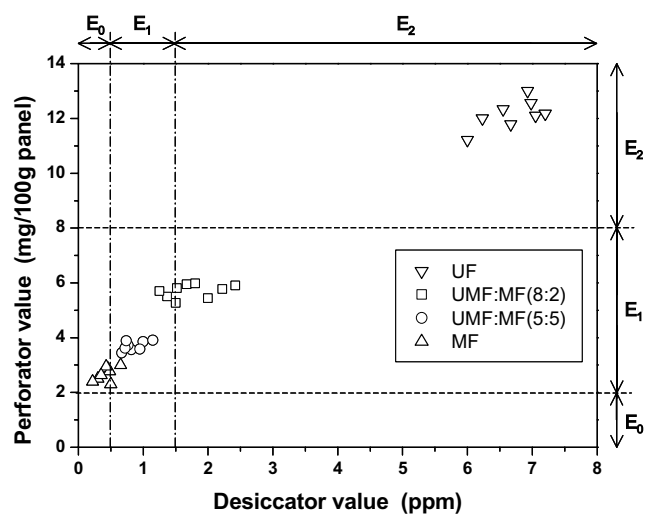

Fig. 3. Correlation between formaldehyde emission from MDF determined by the desiccator method and the perforator method. *E: formaldehyde emission grade.

For this reason, MF or MUF resins which have been diluted by the addition of urea, in order to make them less expensive, are often used.

In Fig. 3, the desiccator value and the perforator value are compared. Although the perforator value was directly proportional to the desiccator value in the case of the E_1 grade level, it increased less than the desiccator value. Whereas a precise correct amount (100 g) of wooden board used in the perforator method, only the dimensions of the wooden board are considered taken into consideration in the desiccator method. In spite

of the formaldehyde emission values from the same boards being slightly different because of the difference in between the two sampling methods, 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. Because water dissolved the formaldehyde we wanted to analyze, 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 for water
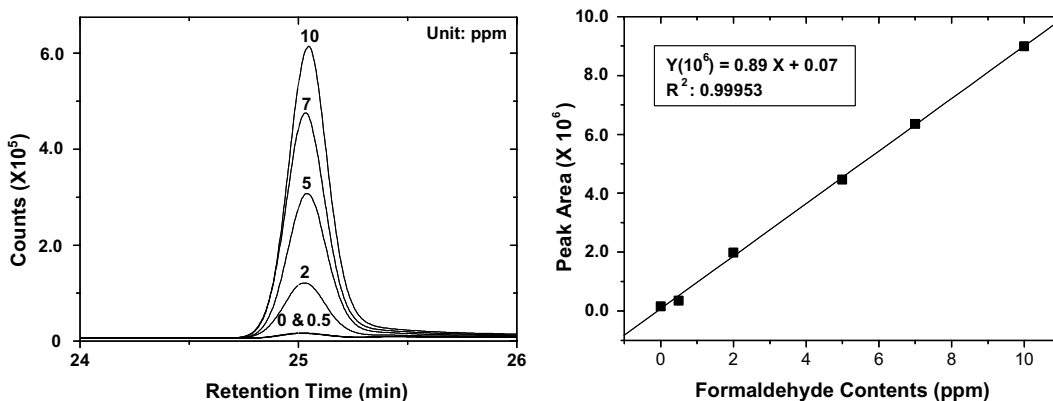

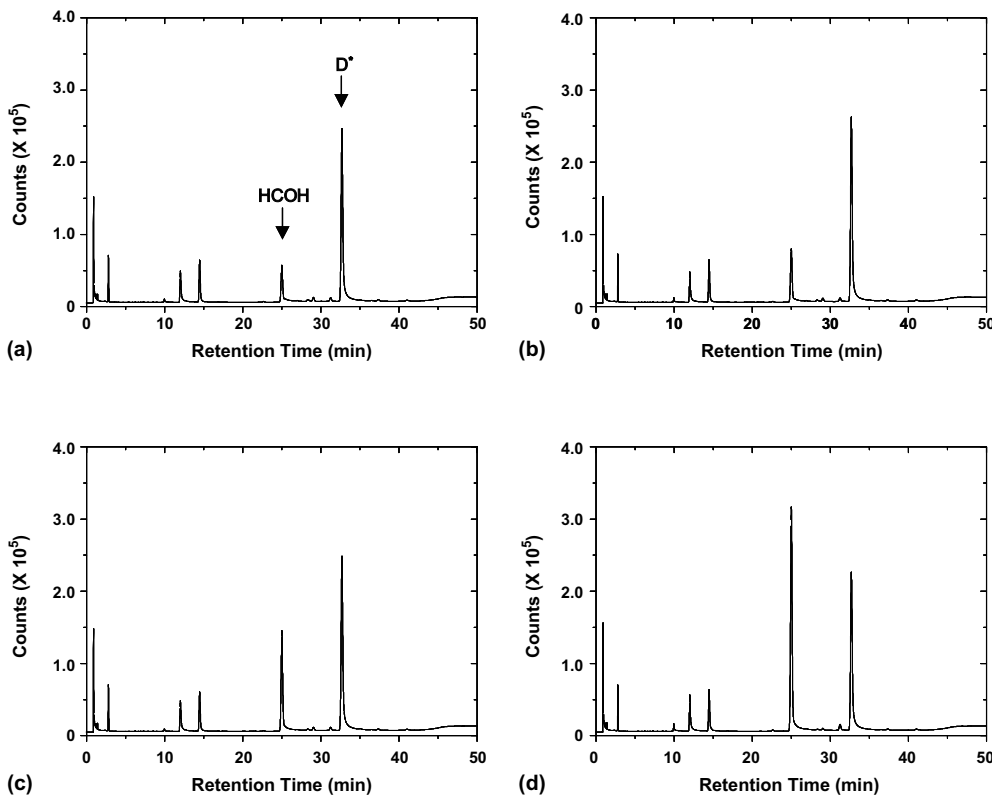Fig. 4. Formaldehyde peaks at 25 min and the calibration curve by gas chromatography.

Fig. 5. Chromatograms of four resins: MF resin, co-polycondensation resin of UMF and MF (UMF:MF = 8:2 and 5:5) and UF resin. D*: 2,4-dinitrophenylhydrazine solution with acetonitrile and HCL solution. (a) MF, (b) UMF:MF (5:5), (c) UMF:MF (8:2) (d) UF.

than for toluene. 2,4-dinitrophenylhydrazine solution with acetonitrile and 25% HCl solution was used as a catalyst for metathesis. In order 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 time was $Y(\times 10^6) = 0.89X + 0.07$, where Y is the formaldehyde content (ppm) and X is the calculated peak area, as shown in Fig. 4. Characteristic chromatograms of four resins, MF resin, two versions of the co-polycondensation resin of UMF and MF(UMF: MF = 8:2 and 5:5) and UF resin, are shown in Fig. 5. The solvent peaks appeared early and have the same shape and height. The only difference between the two chromatograms is the difference in height of the 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 good correlation between the results of the perforator method and the measurements made by gas chromatography for these four different resins, as shown in Fig. 6. The formaldehyde contents measured by gas chromatography were directly proportional to the perforator values. 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 values and the perforator

values, the perforator method was the second method to become accepted for the determination of the 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 gas chromatography method, which produced results which were well correlated with the perforator values, can also be successfully applied to the measurement of formaldehyde emission. With further refinement, the quantitative analysis of formaldehyde emission by gas chromatography will become more precise and provide a more advanced technique than the current typically used methods.

4. Conclusion

In the formaldehyde emission behavior of the MF and UF resins, while the UF resin showed a desiccator value of 7.05 ppm and a perforator value of 12.1 mg/100 g panel, while the MF resin exhibited a desiccator value of 0.6 ppm and a perforator value of 2.88 mg/100 g panel. According to the Japanese industrial standard and the European standard, the formaldehyde emission level of the MDF panels made with the UF resin in this study was E_2 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. This is because the addition of formaldehyde to melamine occurs more easily and completely than its addition to urea, even though the condensation reaction of melamine with formaldehyde is similar to that between urea and formaldehyde.

The desiccator value and perforator value were compared. Although the perforator value was directly proportional to the desiccator value within the E_1 grade level, it increased less than the desiccator value. In spite of the formaldehyde emission values from same boards being only slightly different because of the differences between the sampling methods, these two methods, the desiccator method and perforator method, produced proportionally equivalent results.

The formaldehyde emission levels obtained using gas chromatography were similar to those obtained using the perforator method, which is the method typically used. We found that there was a good correlation between the results of the perforator method and the measurement made by gas chromatography for four different resins, as shown in Fig. 6. The formaldehyde contents measured by gas chromatography were directly proportional to the perforator values. With further refinement, the quantitative analysis of formaldehyde emission by gas chromatography will become more precise and provide a more advanced technique than the current typically used methods.
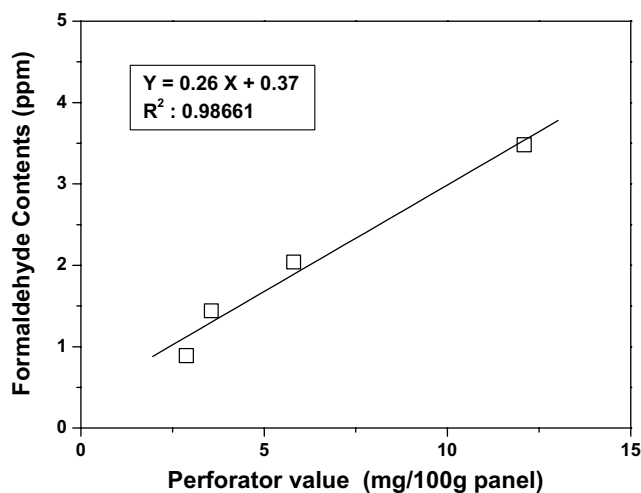

Fig. 6. Correlation between formaldehyde emission from MDF determined by the perforator and the GC method.

Acknowledgements

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