Proceedings of the International Convention of Society of Wood Science and Technology and United Nations Economic Commission for Europe – Timber Committee
October 11-14, 2010, Geneva, Switzerland

Evaluation of Test Methods for Determination of Formaldehyde Emission from Composite Wood Products

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Abstract

Formaldehyde (HCHO) is mainly used to produce synthetic resins and adhesives by reaction with phenols, urea, and melamine. Urea-formaldehyde (UF) resin is a major commercial adhesive, especially within the forest products industry. Composite wood products (CWPs) are usually used for building furniture, cabinets, flooring, and wall panels for use in commercial and residential structures. However, CWPs bonded with formaldehyde-based resins can be toxic due to the emission of formaldehyde. Formaldehyde has been a major concern in the forest products industry in recent years, and its emission is an important factor in evaluating the environmental and health effects of CWPs. Formaldehyde is a potential risk factor for human health. A number of CWPs (primarily particleboard, medium-density fiberboard and plywood), laminated and without lamination, of different thicknesses (2.5, 3.2 , 8, 12, 15, 16, 18, 19, 21 and 22 mm) and moisture contents, were collected from different Czech producers. The formaldehyde emissions of CWPs were evaluated by the most frequently used European test methods: the gas analysis method (EN 717-2) and the perforator method (EN 120). Standard values of formaldehyde emission were measured. This article gives a comparison of two different analytical methods by determining the correlation coefficient (r) among different parameters. The coefficient of determination (R^2) by extracting equations was applied for regression analysis. The main findings of the study clearly show that the two methods produce proportional results, and the variation between the two methods can be explained by differences in test conditions such as loading factor, temperature, RH, duration of test and air exchange rate. Another important factor is the variation in treatment of the sample; for example, sealing of the edges, sealing of the back, and conditioning before measurement.

Keywords formaldehyde emission, EN 717-2, EN 120, composite wood products.

Introduction

Formaldehyde emissions have been an important issue for many years, and numerous standards have been issued to reduce the emissions from composite panel wood products. Occupational exposure limits for formaldehyde concentration were first issued in several European countries in an attempt to handle possible problems. Residential standards were also imposed in the U.S. and other countries. The basis of all regulations had been the recommendation of the German Federal Health Agency in 1977 of a maximum formaldehyde concentration in the air of 0.1 ppm. Considerable efforts in research and development in the chemical industry, along with harmonious cooperation with the wood-based panels industry, made it possible to overcome the problem of formaldehyde emissions. It is apparent that formaldehyde concentration limits in most industrialized countries have been dramatically reduced over the last 20 years in order to keep the air clean and protect the health of humans. Moreover, it is notable that the formaldehyde contents of wood-based panels today are 10 to 15 times lower than those of 15 years before (Markessini 1994).

In 1992, the California Air Resources Board (CARB) identified formaldehyde as a toxic air contaminant, based primarily on the determination that it was a human carcinogen with no known safe level of exposure (CARB 1992). Exposure to formaldehyde has both non-cancer and cancer health effects. The non-cancer health effects of formaldehyde are eye, nose, and/or throat irritation. The International Agency for Research on Cancer (IARC 2004) conducted an evaluation of formaldehyde and concluded that there is sufficient evidence that formaldehyde causes nasopharyngeal cancer in humans. Formaldehyde has also been found to produce nasal carcinomas after long-term chronic exposure to 14.1 ppm and 5.6 ppm of formaldehyde in rats and mice, respectively (Kim and Kim 2005).

Wood-based panels such as particleboard (PB), oriented strand board (OSB), medium density fiberboard (MDF) and hardwood plywood are most commonly manufactured using either urea-formaldehyde (UF) or phenol-formaldehyde (PF) adhesives. According to the EN 312 (2003), PB is classified as E_1 for formaldehyde contents up to 8 mg HCHO/100 g dry board and as E_2 for concentrations between 8 and 30 mg HCHO/100 g dry board, respectively.

Formaldehyde test methods were developed along two tracks: large test chambers designed to imitate a room in a home, and smaller, quicker tests suitable for a lab bench and plant quality control (Yu and Crump 1999, Risholm-Sundmana et al. 2007, Salem et al. 2009). The large chambers such as EN 717-1 (2004) and ASTM E1333-96 (ASTM 2002), due to the perceived accuracy with which they simulate human environments, became known as reference tests and were frequently cited in government regulations and standards. The smaller tests became known in Europe as derived test methods, such as the gas analysis method (EN 717-2 1994), flask method (EN 717-3 1996) and perforator method (EN 120 1992). In industrial practice, the perforator method is the most widespread test procedure for measuring formaldehyde content from PB and MDF in Europe. The national and international formaldehyde emissions regulations and the test methods used to quantify formaldehyde emissions from CWPs were reviewed by Ruffing et al. (2010).

In this work, the formaldehyde emissions from PB, MDF and plywood (PW) were measured with the gas analysis and perforator methods. The relationships between the concentrations obtained by the gas analysis and perforator values are discussed in this study.

Materials and Methods

Formaldehyde Measurements Included In This Study

Boards Loading

Approximately 111 different commercial boards shown in Table 1 were obtained from a commercial wood manufacturing plant in the Czech Republic. All specimens were conditioned to equilibrium at a temperature of 20 °C and 65% relative humidity (RH). These boards were examined for their formaldehyde emission. The majority were UF-bonded PB and plywood. Also included were several UF-bonded MDF. They are divided into three groups on the basis of their types.

Table 1: Number of specimens used for the gas analysis and perforator tests according to the thickness of the boards.

	PB					MDF		PW	
Board type	**P_2**			**PL**		**MDF**	**MDFL**	**PLY**	**PLYs**
Thickness (mm)	12-18	8-10	19	8-22	19	3.2-18	2.5-19	15-21	15-21
N° of Samples	23	17	2	15	2	14	6	13	19

P_2: boards for interior fitments (including furniture) for use in dry conditions (EN 312-2, 2003), PL: laminated particleboard, MDF: general purpose boards for use in dry conditions, MDFL: laminated MDF, PLY: non-structural plywood, PLYs: structural plywood.

To determine the reproducibility within one lab (tests made at different times), we took the following three measurements for the gas analysis and perforator methods. The first measurement was done from a total of 23 P_2 samples with thickness 12-18 mm. Moreover, the formaldehyde emission from 17 P_2 specimens with 8-10 mm and 2 specimens of 19 mm were done using only the gas analysis method. For more comparison, a total of 15 PL samples with 8-22 mm were measured for their formaldehyde emissions, as well as 2 samples of 19 mm measured only by gas analysis. For the second measurement, fourteen test pieces were randomly cut from 3.2-18 mm MDF boards and wrapped in plastic; then the formaldehyde emission was done. A duplicate measurement was run separately from MDFL with 2.5, 18 and 19 mm. The third measurement was done using 32 specimens of 15-21 mm plywood (13 samples from PLY and 19 samples From PLYs).

Statistical Design and Analysis

Data were analyzed separately for each test method and type of wood product used in this study to measure formaldehyde emission. Correlation coefficients (r) between gas analysis and perforator values were estimated using the CORR option of SAS (1999). On the other hand, the formaldehyde emission measured by the gas analysis method from the two types of PB with 12-19 mm were statistically analyzed using the general linear model (GLM) procedure in the SAS software package (SAS 1999), for a completely randomized design (CRD) with 2 types of PB × 5 thicknesses in a factorial arrangement with different repetitions (Steel and Torrie, 1989). Means were tested for their significance using a least square means test (LSMEANS) with the statistical model: $y = \mu + \alpha i + \beta j + \alpha\beta ij + \varepsilon k(ij)$, corresponding to a factorial design of two factors with i and j levels for each factor. Duncan's multiple-range test (Duncan, 1955) was used to determine differences between LSMEANS values with a significance level of $p<0.05$.

Formaldehyde Test Methods
Determination of formaldehyde emission in this work was carried out by two approved methods for determining formaldehyde, used at the international level, and a further comparison between them: the gas analysis method and the perforator method. Some main characteristics of these methods are given and are also discussed in articles by Yu and Crump (1999) and Salem et al. (2009).

Gas Analysis Method, EN 717-2
This method describes determination of the accelerated release of formaldehyde from wood-based panels. A test piece of 400 x 50 mm is placed in a 4-litre cylindrical chamber with controlled temperature (60 °C), RH (≤ 3%), airflow and pressure. Air is continuously passed through the chamber at 1L/min over the test piece, whose edge is sealed with self-adhesive aluminium tape before testing. The gas analysis value ($mg/m^2.h$) depends on the gaseous resistance, density, moisture content, board thickness and airflow rate. The high temperature can cause reactions in the material to affect the result, and although higher emitting materials usually give a consistent value after 2-4 h of testing, inconsistent values can be attained with some other materials (Yu and Crump 1999). Formaldehyde released from the test piece mixes with the air in the chamber. This air is continually drawn from the chamber and passes through gas wash bottles, containing water, which absorbs the released formaldehyde. The emission E_1 is ≤ 3.5 mg $HCHO/m^2.h$.

Perforator Method, EN 120
This is a well-established test method widely used in industry; the total operation and analysis time is approximately 3 h. A sample board of 110 g total, in 25 x 25-mm pieces, is boiled for 2 h using 600 ml toluene under reflux. The formaldehyde is absorbed in the water. After analysis of the extract, the formaldehyde content of the boards is expressed in milligrams per 100 g of dry board and is corrected for moisture content of 6.5%. Density, board thickness, porosity and moisture distribution affect the perforator value and correlation with the emission concentration. The test is very sensitive to the moisture content in the material and in the toluene during the extraction of the free formaldehyde. Storage conditions and the species of wood can also affect the perforator value (Yu and Crump 1999). The emission E_1 is ≤ 8 mg HCHO/100 g dry coated board and ≤ 12 mg HCHO/100 g dry uncoated board.

The formaldehyde concentration in the water from the two methods was determined photometrically by acetylacetone spectrophotometric analysis. This technique, as described by Nash (1953), is widely applied and is a standard procedure for the specific analysis of formaldehyde. The determination is based on the Hantzsch reaction, in which aqueous formaldehyde reacts with ammonium ions and acetylacetone to yield diacetyldihydrolutidine (DDL); DDL has an absorption maximum at 412 nm.

Results and Discussion

Gas Analysis and Perforator Values

The gas analysis and perforator values that were obtained for almost all of the boards examined from PB, MDF and plywood are shown in Table 2. Each value is the mean value from the tested boards. For PB, the gas analysis values ranged from 0.24-1.68 and from 0.23-1.38 mg/m^2.h for P_2 and PL, respectively. In comparison, the perforator values were 3.83-7.53 and from 4.19 to 8.3 mg/100 g dry board for P_2 and PL, respectively. Most of the values met the E_1 requirements. The emission for 22 mm PL was 8.3 mg/100 g dry board by the perforator method. These results were slightly over the E_1 ($\leq$ 8 mg/100 g dry board) grade. The sample used for this study emitted a lot of free formaldehyde.

The gas analysis and perforator values were 0.38-0.71 mg/m^2.h and 5.03-7.36 mg/100 g dry board for the MDF and 0.3-0.61 mg/m^2.h and 4.25-6.83 g/100 g dry board for the MDFL, respectively. According to both standards, the formaldehyde emission level for MDF and MDFL was at the E_1 grade. The formaldehyde emission values for the two types of plywood measured by the gas analysis ranged from 0.13 to 0.31 mg/m^2.h, below the E_1 grade. Although the weight (100 g) of the wooden board is used in the perforator method, the dimensions of the wooden board are taken into consideration in the gas analysis method. In spite of the formaldehyde emission values from the same boards being slightly different because of the difference in measuring methods, these two methods produced proportionally equivalent results.

Table 2: Values of formaldehyde content from PB, MDF and PW boards of different types and thicknesses.

Boards	Type	Thickness (mm)											
		2.5	3.2	8	10	12	13	15	16	18	19	21	22
PB	P_2	-	-	0.46[a]	0.24	0.30	0.65	0.35	0.43	0.63	1.68	-	-
		-	-	(na)[b]	(na)	(3.83)	(na)	(4.55)	(5.21)	(7.53)	(na)	-	-
	PL	-	-	0.23	0.28	-	-	-	0.33	0.50	0.84	-	1.38
		-	-	(4.19)	(5.23)	-	-	-	(5.75)	(7.41)	(na)	-	(8.30)
MDF	MDF	-	0.38	-	-	-	-	-	0.47	0.71	-	-	-
		-	(5.03)	-	-	-	-	-	(6.38)	(7.36)	-	-	-
	MDFL	0.31	-	-	-	-	-	-	-	0.61	0.30	-	-
		(4.68)	-	-	-	-	-	-	-	(6.83)	(4.25)	-	-
PW	PLY	-	-	-	-	-	-	0.23	-	0.21	-	0.15	-
	PLYs	-	-	-	-	-	-	0.13	-	0.22	-	0.31	-

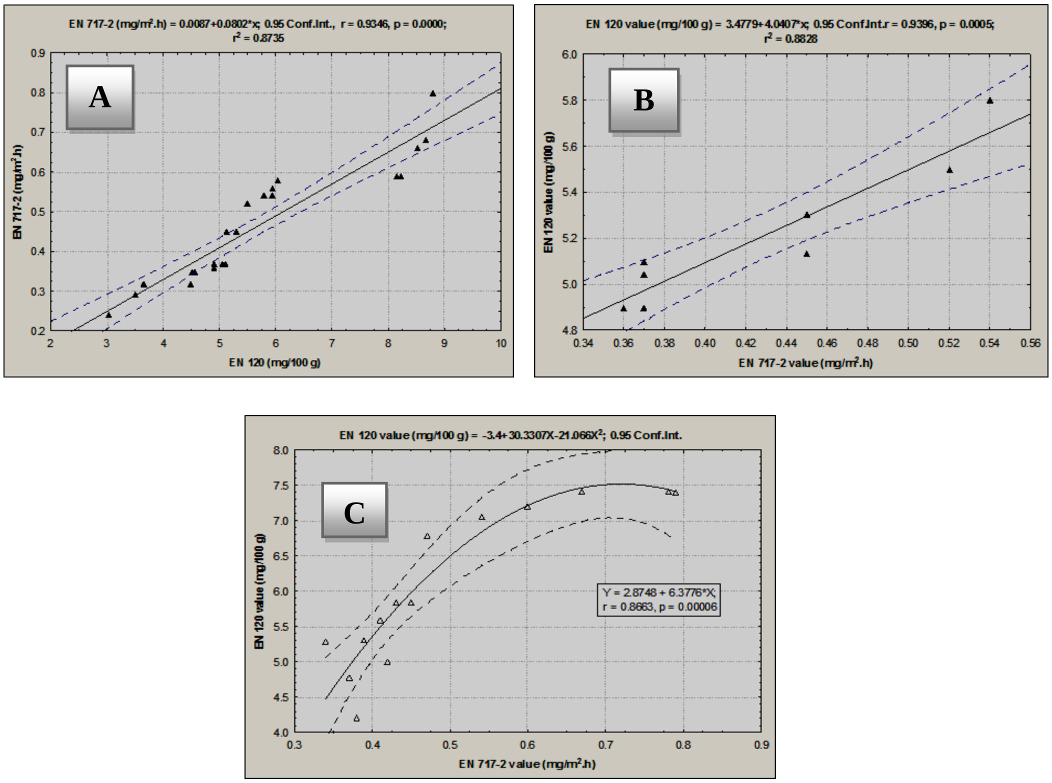
a: calculated gas analysis value (mg/m^2.h).
b: values in parenthesis are the corrected perforator value (mg/100 g) at a moisture content of 6.5 % (EN 312, 2003).
na: data not available.

The Relationship between Gas Analysis and Perforator Values

A linear regression analysis was made from the P_2 12-18 mm on the gas analysis concentrations and the corresponding average perforator values (Fig. 1A), producing a good correlation coefficient of 0.93 with the perforator method. Furthermore, there was a good correlation (0.93) between the gas analysis and the perforator when they were used to measure the formaldehyde concentration from the P_2 with 18 mm (Fig. 1B). The polynomial regression in Figure 1C for

MDF 3.2-18 mm shows a correlation coefficient of 0.86 between the gas analysis and perforator tests.

Figure 1: Correlation between EN 717-2 and EN 120 for particleboards P_2, thickness 12-18 mm (A)and thickness 18 mm (B), and for MDF, thickness 3.2-18 mm (C).



The Effect of Board Type and Thickness on Formaldehyde Emission

The GLM results related to the influences of PB type (P_2, PL), thickness (12-19 mm) and the interaction between them on the formaldehyde emission values, determined by the gas analysis method, showed a highly significant effect. It was statistically proven that the application of surface coatings helps to significantly decrease the formaldehyde emission of the panels (Table 3). Covering the PB surfaces helps to bring about low porosity and reduces the formaldehyde released from the surface of the panels (Nemli and Çolakoğlu 2005).

Table 3: The gas analysis values from the different types of particleboard and thicknesses.

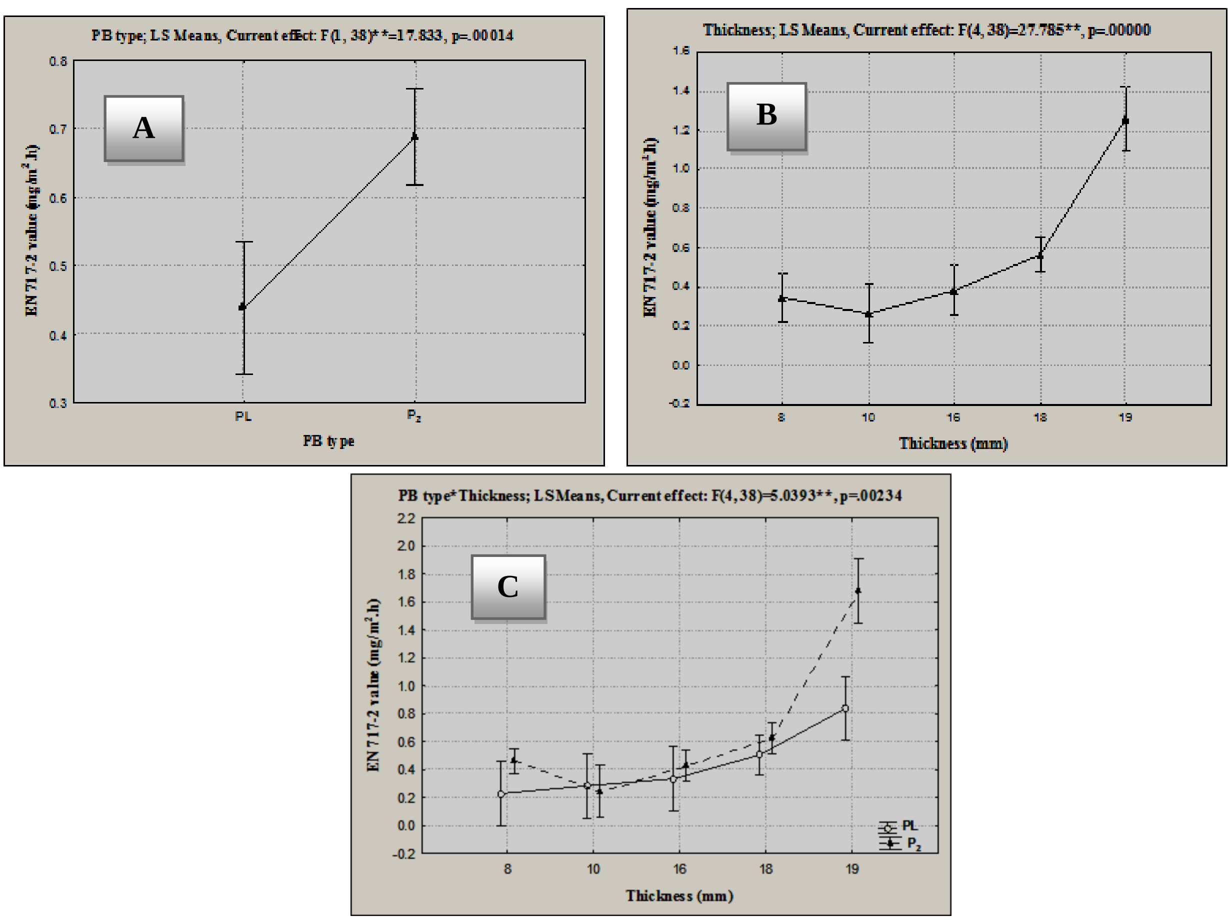
Board type	**Thickness (mm)**					**PB type Mean**
	8	10	16	18	19	
P_2	0.460^{aBC}	0.243^{aC}	0.428^{aBC}	0.625^{aB}	1.680^{aA}	0.687^{a}
PL	0.230^{bD}	0.285^{aD}	0.335^{bC}	0.506^{bB}	0.840^{bA}	0.439^{b}
Thickness Mean	0.345^{BC}	0.264^{C}	0.381^{BC}	0.565^{B}	1.260^{A}	
***P* value**	**PB type**	**Thickness**	**PB type*Thickness**			
	0.0001	<0.0001	0.0023			

Note: Different letters represent statistical differences between the averages of the values.

Means with the same letter are not significantly different ($P<0.05$).
The small letters on the same column are used to compare between board types of the same thickness, and the capital letters in the same row to compare between thicknesses for the same type of board.

Board type (Fig. 2A) and thickness (Fig. 2B) had a highly significant effect on the formaldehyde emission, according to LSMeans. Clearly, the laminated boards emitted formaldehyde less than the uncoated boards, and an increase in thickness resulted in more emission of formaldehyde. Moreover, the interaction between the board type and thickness had a highly significant effect on the emission of formaldehyde (Fig. 2C). As a general rule, an increase in the thickness of uncoated boards leads to an increase in formaldehyde emission.

Figure 2: The mean effect of PB types (A), thicknesses (B) and the interaction between them (C) on the formaldehyde emission measured by EN 717-2.



Conclusion

In this study, the formaldehyde emission from particleboard, MDF and plywood are measured well using either the gas analysis or perforator methods. The correlation between the gas analysis and perforator methods was good. Based on the preliminary results, most of the board types tested has to fulfill the same emission limit of E_1. On the other hand, the laminating of particleboard surfaces and the thickness had a great influence on formaldehyde emission. For the production of E_1 grade boards, all of the process parameters should be taken into account together.

Acknowledgements
This work was supported by grants from the Internal Grant Agency (IGA, Faculty of Forestry and Wood Sciences, Czech University of Life Sciences, Prague).
The authors also wish to thank the staff of the Research Timber Institute, Prague, Czech Republic for their valuable contributions to our research.

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