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Evaluation of formaldehyde emission of pine and wattle tannin-based adhesives by gas chromatography

Abstract Formaldehyde emissions from wood particleboards bonded with pine and wattle tannin-based adhesives, using hardeners paraformaldehyde, hexamethylenetetramine and TN (tris(hydroxyl)nitromethan), were measured by the perforator method (DIN EN 120—European Committee For Standardization 1991). All particleboards made using the wattle tannin systems with the three different hardeners were satisfied grade E_1, while in the case of pine tannin only the use of the hexamine hardener led to grade E_1 being satisfied. This tendency was attributed to the curing mechanism of the hardener, the reactivity of the tannin molecule toward formaldehyde and the fast reactivity toward formaldehyde of pine tannin, due to the inclusion of phloroglucinolic A-rings within its molecular structure. Hexamine was effective at reducing formaldehyde emission in tannin-based adhesives when used as the hardener. Being a more sensitive and advanced method, it was also used. The samples used for gas chromatography were gathered during the perforator method. The formaldehyde emission levels obtained from gas chromatography were similar to those obtained from the perforator method.

Schätzung der Formaldehydabgabe von Klebern auf Basis von Kiefern- und Akazientannin mittels Gas-Chromatographie

Zusammenfassung Die Formaldehydabgabe von Spanplatten, die mit Klebern aus Kiefern- und Akazientannin gebunden waren, wurden mittels der Perforatormethode gemessen (DIN EN 120 1991). Als Härter wurden Paraformaldehyd, Hexamethylentetramin and TN (Tris(hydroxyl)nitromethan verwendet. Alle Spanplatten, die unter Gebrauch des Akazientannin-Systems mit drei verschiedenen Härtern hergestellt wurden, genügten Grad E_1, während bei Kieferntannin nur der Gebrauch von Hexaminhärter zu Grad E_1 führte. Diese Tendenz war dem Mechanismus des Aushärtens des Härters zuzuschreiben und zwar der Reaktivität der Tanninmoleküle gegenüber Formaldehyd und der schnellen Reaktivität des Kiefertannins gegenüber Formaldehyd, aufgrund der Einschlüsse von Phloroglucin-A-Ringen innerhalb der molekularen Struktur. Hexamin war wirksam, um die Formaldehydabgabe bei Tanninklebern zu reduzieren, wenn es als Härter verwendet wurde. Da es eine empfindlichere und fortgeschrittenere Methode war, wurde sie ebenfalls angewendet. Die Proben, die für die Gaschromatographie verwendet wurden, wurden während der Perforatormethode gesammelt. Die Werte der Formaldehydabgaben, die durch Einsatz der Gaschromatographie erhalten wurden, waren denjenigen ähnlich, die man mittels der Perforatormethode erhielt.

1 Introduction

One of the main concerns of the 21st century is the environment. The environment has become a subject of constant attention, and it has become a focal point of our life and welfare. After having ignored—and even spurned concerns about—the environment during the industrial revolution and the periods of economic development that followed, we are presently more inclined to respect nature (Meyer et al. 1986a, b, c).

Formaldehyde has been a subject of concern in the formaldehyde resin-bonded wood-base panel industry for a number of years. Virtually all wood panel products, such as plywood, wood particleboard and MDF are manufactured using either urea formaldehyde or phenol formaldehyde adhesive. Formaldehyde is gaseous at room temperature, but it can polymerize forming para-formaldehyde, and it readily dissolves in water forming methyleneglycol (Meyer et al. 1986a, b, c).

Many consumer products containing formaldehyde-based resins release formaldehyde vapor, leading to

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consumer dissatisfaction and health-related complaints. These emissions have resulted in various symptoms, the most common of which are irritation of the eyes and of 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 (Meyer et al. 1986a, b, c).

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). In the last decade several approaches to the problem of producing low formaldehyde emission wood panels using these wood adhesives have been developed. Moreover, hardeners cause formaldehyde emission even when tannin adhesive is used (Trosa and Pizzi 1994).

To measure the levels of formaldehyde emission, many methods have been used. Roffael introduced the very simple WKI method. He also used a special climate chamber for the measurement of formaldehyde concentration in the air (Roffael 1978). Myers developed a method wherein he applied a thin film of cured resin and sulfuric acid (Myers 1990). In Europe, the perforator method has been used. For this method, special apparatus is needed (Roffael and Mehlhorn 1980). The Japanese desiccator method has been used in Asian countries (Kim 1994). The estimation of the formaldehyde level is conducted spectrophotometrically in all of the existing methods, including the WKI, perforator and desiccator methods. In the middle of the 1990s, Carlson and Wolcott measured a formaldehyde emission and that of other volatile organic compounds (VOC) during pressing, using an enclosed caul plate and a 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 rapid and very high resolution separations of a very wide range of compounds, with the only restriction 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 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 de- termine and record the concentrations of separated con- stituents at the end of the column. These pioneers also in- troduced the concept of separation efficiency, and dis- cus- sed the influence of parameters such as 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).

The present investigation focused on two main areas. Firstly, a comparison of the traditional perforator method and gas chromatography for the determination of formaldehyde emission levels. Secondly, the effect of hardeners on the formaldehyde emission levels of the tannin-based adhesives, wattle and pine, with three different hardeners (paraformaldehyde, hexamethylenetetramine and tris(hydroxyl)nitromethane).

2 Experimental procedures

2.1 Materials

2.1.1 Wood particle

The wood particles used for manufacturing the particleboard, which were donated by the Donghwa Enterprise Co., Ltd. in South Korea, consisted of recycling chips used for core, which had a moisture content of 3%.

2.1.2 Tannin extracts

Two types of commercial tannin extracts, 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) was supplied by DITECO Ltd. in Chile. These tannins consisted of a fine dark brown powder with a moisture content of 4%.

2.1.3 Hardeners

The three hardeners, paraformaldehyde, hexamethylenetetramine and TN (tris(hydroxyl)nitromethan), were purchased from the Aldrich Chemical Company, Inc. Their chemical structures are shown in Fig. 1.

2.2 Methods

2.2.1 Tannin-based Adhesives

Aqueous tannin extracts with a 40% concentration were prepared by dissolving the spray-dried powder 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. Each additive concentration measurement was based on several results (Trosa and Pizzi 1994; Pichelin et al. 1999; Pizzi et al. 1994). The pH ranged from 5.5 to 6. While paraformaldehyde and TN (tris(hydroxyl)nitromethan) were used in the pure solid

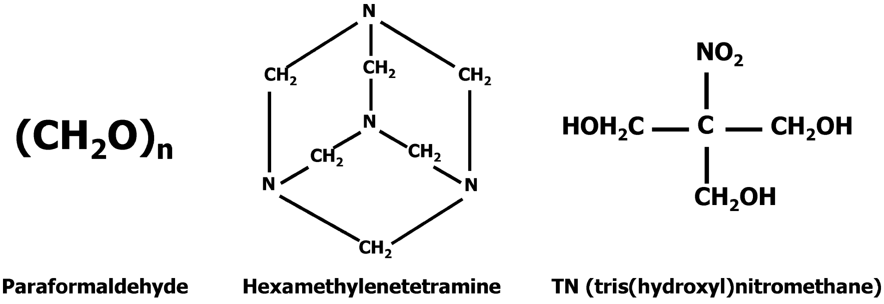


Fig. 1 Chemical structures of the three hardeners
Abb. 1 Chemische Strukturen der drei Härter

Table 1 Total adhesive systems showing the additive contents of the hardeners
Tabelle 1 Gesamtklebersysteme, die die Härterzusätze zeigen

Hardeners		Wattle Tannin	Pine Tannin
Additive Contents	Paraformaldehyde	0% (wattle only)	8%
		4%	
		8%	
		12%	
	Hexamethylenetetramine	6.5%	0% (pine only)
			3%
			6.5%
			10%
	TN (Tris(hydroxymethyl) nitromethane)	10%	10%

state, hexamethylenetetramine was used as a 35% hexamine solution (Pichelin et al. 1999).

For the determination and comparison of the effect of hardener additive content, paraformaldehyde for wattle and hexamethylenetetramine for pine were selected. 0, 4, 8 and 12% of paraformaldehyde, by weight of dry tannin extract, was applied to the wattle tannin, and 0, 3, 6.5 and 10% of hexamethylenetetramine to the pine tannin. The total adhesive system is shown in Table 1.

2.2.2 Manufacturing of particleboard

Particleboards were manufactured using both pine and wattle tannin-based adhesives and with the 3 different hardeners, in order to obtain a specific gravity of 0.8 and dimensions of 270mm×270mm×8 mm (length×width× thickness).

The wood particles were placed in the rotary drum mixer and the tannin-based adhesive, used as a composite binder, was sprayed onto them while rotating in the mixer. The amount of adhesive was based on 14 wt.% of the oven-dried raw material. The mixture of particles and adhesives was cold pressed at 2 kgf/cm^2 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/cm^2 and a temperature of 170°C. The main pressing time was 5 min and the pressure was released in two steps of 1 min each. The manufactured particleboards were pre-conditioned at 25% and at 65% RH for two weeks before testing.

2.2.3 Formaldehyde emission by perforator method

The perforator value of the formaldehyde emission was determined using the DIN EN 120 (European Committee For Standardization 1991) method.

2.2.4 Gas chromatography

2.2.5 Preparation of samples

During the process of carrying out the perforator method experiment, samples were gathered following the 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 (Velikonja 1995). Firstly, 1 ml of acetonitrile was prepared by dissolving 10 mg of 2,4-dinitrophenylhydrazine and diluting with HCl-H_2O(1:3, v/v) to 10 ml. 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.

2.2.6 Apparatus and analytical procedures

A Hewlett-Packard Model 5890 A gas chromatography (NICEM, Seoul National University) with a ^{63}Ni electroncapture 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 α integrator for gas chromatography analysis. HP ChemStation software (version A.03.21) was used to program and operate the system.

2.2.7 Gas chromatography conditions

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. Injection port and detector temperatures were 200 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, then heated at 3°C/min to 250°C. The column was then 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.

3 Results and discussion

3.1 The effect of the hardeners on formaldehyde emission

First, the formaldehyde emission levels of the wood particleboards bonded with tannin-based adhesives were measured using the perforator method. This method is more sensitive than the desiccator method, because this latter method only measures a certain area of the boards. Figure 2 shows the formaldehyde emission levels (hereafter referred to as perforator values) of the wood particleboards bonded with wattle and pine tannin for the 3 different hardeners, paraformaldehyde, hexamethylenetetramine and TN (tris(hydroxyl)nitromethane). The largest perforator value was obtained for the pine tannin paraformaldehyde system, and this value was 12.8. However, in the case of wattle tannin with paraformaldehyde the corresponding value was 3.4, whereas according to DIN EN 120, particleboard of quality E_1 should emit <6.5 mg/100 g of dry particles as determined by the perforator method. This tendency toward increased formaldehyde emission levels was observed for all of the particleboards manufactured using pine tannin.

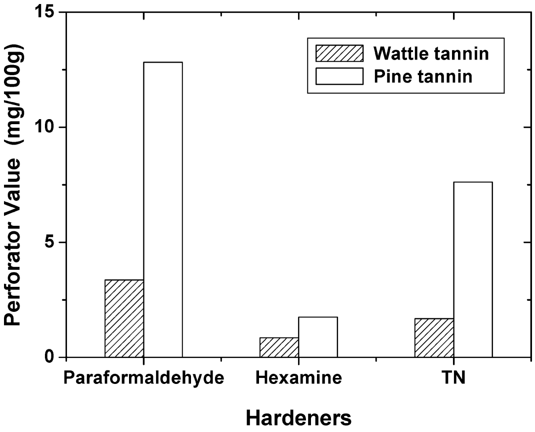


Fig. 2 Perforator values of particleboards made with different tannin-based adhesives and with different hardeners
Abb. 2 Perforatorwerte von Spanplatten, die mit verschiedenen Tannin-Klebern und verschiedenen Härtern hergestellt wurden

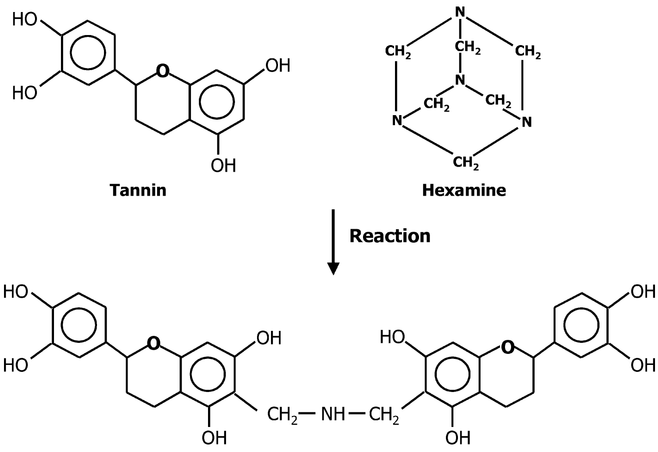


Fig. 3 Schematic diagram of the reaction between tannin and hexamine
Abb. 3 Schematisches Diagramm der Reaktion zwischen Tannin und Hexamin

On the other hand, different results were observed for the particleboards manufactured using pine tannin. Although the pine-hexamine system showed a low perforator value of 1.8 (grade E_1), those particleboards bonded using pine tannins with paraformaldehyde and TN were in grade E_2. Why is this result so different? The answer to this question can be found by examining the curing mechanism of the hardener and the reactivity of the tannin molecule toward formaldehyde. Pizzi reported that in the case of hexamine hardener with tannin, di- and tribenzylamine bridges were formed before the completion of the curing process, which are subsequently converted to methylene bridges, when the tannin reacts with the hexamine [14]. Figure 3 shows this mechanism. Another reason is the fast reactivity toward formaldehyde of pine tannin, 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 reactivity 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 taking place, tannin 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 the high perforator values observed in the

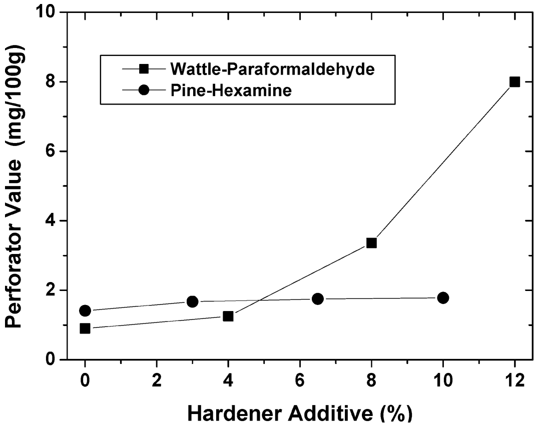


Fig. 4 Comparison of the perforator values of particleboards with the tannin-based adhesives as a function of the percentage of hardener additive
Abb. 4 Vergleich der Perforatorwerte von Spanplatten mit Tanninklebern als Funktion des Prozentsatzes von Härterzusatz

case of pine tannin bonded with paraformaldehyde and TN. The perforator values according to hardener additive are shown in Fig. 4. In the case of the wattle tannin-based adhesive with paraformaldehyde, the perforator value increased as the amount of additive was increased. However, in the case of pine tannin bonded with hexamine the perforator value was not affected by increasing the amount of additive contents. For low formaldehyde emission, the best performance was obtained using hexamine as the hardener.

3.2 Gas chromatography

For more sensitive separation of the sample, the optimal volatile solvent is needed in gas chromatography. Because water dissolved the formaldehyde we want 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 than for toluene. 2,4-dinitrophenylhydrazine solution acetonitrile and 25% HCl solution was used for metathesis as a catalyst.

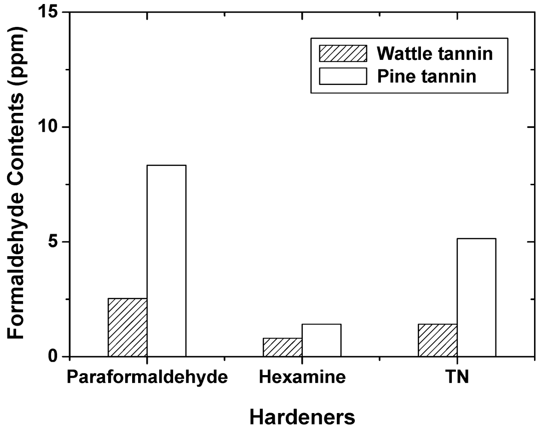
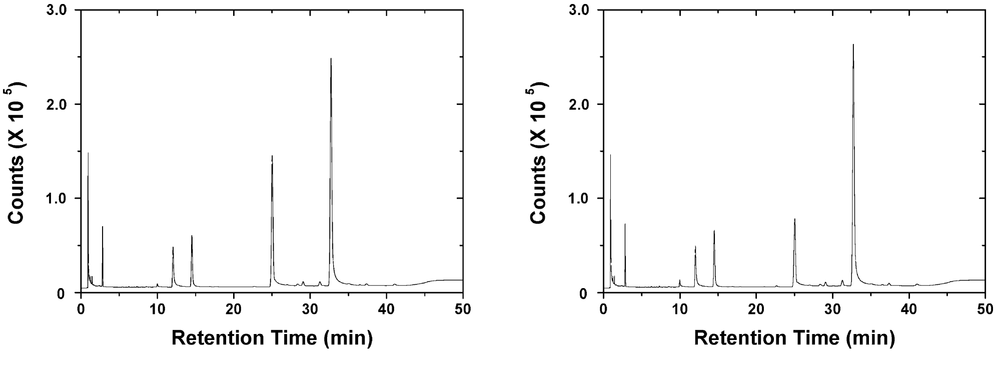


Fig. 6 Formaldehyde contents of wood particleboards made with different tannin-based adhesives and with different hardeners from gas chromatography
Abb. 6 Gaschromatographisch bestimmter Formaldehydgehalt von Holzspanplatten, aus verschiedenen Tanninklebern sowie mit verschiedenen Härtern hergestellt

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=892903.23 X+66191.13, where Y is the formaldehyde content (ppm) and X was is the calculated peak area. Characteristic chromatograms of wattle tannin-paraformaldehyde system and pine tannin-hexamine system 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. Through Figs. 6 to 7, the results obtained from gas chromatography were comparable to those obtained using the perforator method. Even though these results do not comply with any standard, their tendency was very similar to that observed in Figs. 3 and

Fig. 5 Chromatograms of the wattle tannin-paraformaldehyde system and the pine tannin-hexamine system
Abb. 5 Chromatogramme des Akazientannin-Paraformaldehyd-Systems und des Kiefertannin-Hexamin-Systems



1) Wattle Tannin - Paraformaldehyde

2) Pine Tannin - Hexamine

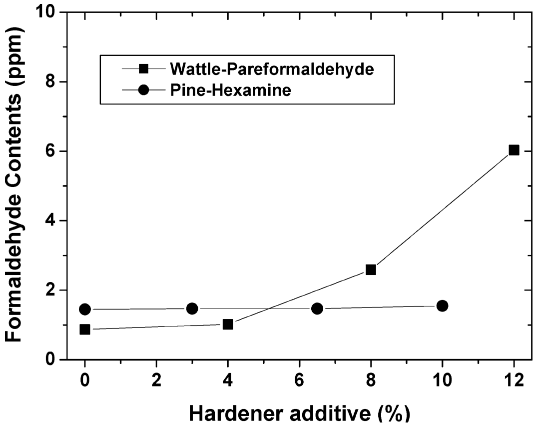


Fig. 7 Comparison of formaldehyde contents of wood particleboards made with tannin-based adhesives as a function of the percentage of hardeners additive from gas chromatography
Abb. 7 Vergleich des gaschromatographisch bestimmten Formaldehydgehalts von Holzspanplatten, hergestellt mit Tanninklebern als eine Funktion des Prozentsatzes von Kleberzusätzen

4. The application of quantitative analysis by gas chromatography to the measurement of formaldehyde emission levels can therefore be considered to be quite successful. Gas chromatography could therefore be used to replace typical formaldehyde emission tests, such as the desiccator and perforator methods.

4 Conclusion

Generally, the formaldehyde emission levels of wood particleboards bonded with tannin-based adhesives were low and satisfied grade E_1, except in the case of pine tannin with paraformaldehyde and TN hardeners as measured by the perforator method. When hexamine was used as a hardener, the lowest emission levels were observed. This tendency can be attributed to the reaction mechanism of hexamine, which leads to the formation of benzylamine bridges between tannins molecules. Furthermore, pine tannin exhibits fast reactivity toward formaldehyde, because it includes phloroglucinolic A-rings in its structure, which react with formaldehyde 50 times faster than does phenol, which results in unreacted formaldehyde remaining in this process. Tannin-based adhesives give rise to low formaldehyde emission levels and therefore represent an environmentally friendly wood adhesive. Gas chromatography was successfully applied to the determination of formaldehyde emission levels. The formaldehyde emission levels obtained using gas chromatography were similar to those obtained using the perforator method, which is the method typically used. 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.

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