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Volatile acetic acid and formaldehyde emission from plywood treated with boron compound

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Abstract

The effects of plywood on formaldehyde and volatile acetic acid emissions treated with borax and boric acid were investigated. The treated plywood samples were manufactured by using two different methods; each veneer was first impregnated by a dipping method before the first group of plywood was manufactured. The second group of plywood panels was produced by adding preservatives (borax, boric acid) into the glue mixture. Two types of urea formaldehyde resin and phenol formaldehyde resin were used as adhesives. The formaldehyde emissions of the plywood were measured by using desiccator method (JIS-A-5908). The amount of acetic acid in distilled water taken from the desiccator was determined by using high performance liquid chromatography. The results revealed that boron compounds affected the emission values of panels differently. Borax showed decreasing effect on the formaldehyde emission, whereas boric acid showed increasing effect.

Keywords: Volatile acetic acid; Formaldehyde emission; Borax; Boric acid; Plywood

1. Introduction

Over the past several decades, air pollution in homes and office buildings has become a matter of increasing concern. Formaldehyde emission has been the major concern associated with bonded wood products. Recently, interest has turned to other volatile organic chemicals (VOCs) [1]. Composite wood products such as particleboard, plywood and MDF are widely used in indoor products such as subflooring, door cores and furniture [2]. Emissions of VOCs potentially can arise from any of the materials that compose a panel; until recently attention has been on emissions of formaldehyde from UF adhesive [3]. It was concluded that the wood products were responsible for the elevated levels of terpenes, aldehydes, and acetic acid. Along with the air pollutant, volatile acids in woods are of great technical importance because of their corrosion of metals, iron–tannin discoloration of woods, influence on curing time of synthetic lacquers and glues and fixation of wood-preserving salts [4]. Air pollution is different from other contaminations in that air is freely exchanged among regions. Therefore, global solutions are required. Also, these chemicals have adverse health effects such as eye and respiratory irritation, irritability, inability to concentrate and sleepiness [5]. Because of increased emphasis on indoor air quality, accurate information is needed regarding the amounts and types of VOCs emitted from building materials or used in the indoor environment. On the other hand, many methods and chemicals have been devised to reduce some troublesome inherent properties (degradable by insect and fungi attack, flammable) of wood-based panel products. Boron compounds may be the most investigated preservatives for wood based panel products because of their beneficial effects such as preservative effectiveness, a broad spectrum of activity against insects and fungi and less impact on mechanical properties compared to other flame-retardant chemicals [6]. However, previous studies have not shown how formaldehyde and volatile acetic acid emissions of wood products are affected by these chemicals and preservation methods. Especially acetic acid emissions of treated plywood panels were investigated because of technological significance besides the other necessity mentioned above.

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2. Material and method

In this experimental study, 2 mm-thick rotary cut veneers were obtained from beech (steamed) and alder (non-steamed) logs at laboratory conditions. The veneers were then dried to 6–8% moisture content and weighed after dipping into 5% aqueous solution of preservative for 20 min. After impregnation, the veneers were subjected to a second drying process at industrial conditions, and then conditioned to 7% moisture content again and re-weighed. The net uptake of borax and boric acid was calculated from the difference between the last weights and the initial weights of veneers. The other group of samples was produced with untreated veneers by adding borax ($Na_2B_4O_7 10H_2O$) and boric acid (H_3BO_3) into the glue mixture. Four, 5-ply and 10 mm-thick plywood panels for each group were produced. Two types of urea formaldehyde resin (U/F mol ratio: 1/1.32 and 1/1.74) and phenol formaldehyde were used as adhesives. The adhesive mixtures were applied on single bonding surfaces of veneers at approximately 160 g/m^2 by using a roller-gluing machine. Press pressure, temperature and duration were applied at 1.2 N/mm^2, 110°C and 10 min, respectively. The formaldehyde emissions of the plywood were measured by using desiccator method (JIS-A-5908). The amount of acetic acid in distilled water taken from the desiccator was determined by using high-performance liquid chromatography (HPLC) (C 18, CIC-ODS column, 214 nm, flow rate 1 ml/min, 1% $HClO_4$ as mobile phase).

3. Results and discussion

The mean retentions of veneers were found for borax as 12.8 kg/m^3 (min. 11.4; max. 17.1) and 11.8 kg/m^3 (min. 8.8; max. 13.3), for boric acid as 13.3 kg/m^3 (min. 10.1; max. 18.3) and 12.8 kg/m^3 (min. 10.4; max. 14.7), beech and alder, respectively.

3.1. Formaldehyde emission

The effect of borax and boric acid on the formaldehyde emission of plywood is shown in Fig. 1. The formaldehyde emission values of the alder plywood panels were found to be higher than those of the beech plywood panels. The large differences reported for the emission behaviour of various wood products are due to their differing structures. The differences between wood products can be explained by the different structures of the materials that determines the emission path of a formaldehyde molecule [7]. This situation has more influence on the formaldehyde emissions of panels determined by dessicator or chamber methods than the perforator method in which the formaldehyde content of wood products is determined by extraction with toluene. In plywood, the inner layers are encircled by the outer layers and the glue line film acts as an inner barrier comparable to a coated surface. Therefore, permeability of the veneers which consisted of plywood panels is a very important factor which affects the emission rate for dessiccator method. That the formaldehyde emissions of beech panels are higher may be related to the higher density of the beech wood. That the beech logs were steamed might also increase the permeability of veneers obtained from them. The treatment processes with boron compounds evidently affected the formaldehyde emissions of the panels. Borax showed a decreasing effect on the formaldehyde emissions, whereas boric acid showed an increasing effect. Treatment with borax decreased the formaldehyde emission values of the panels produced from treated veneers by 8.97%, 3.65%, and 36.36% for beech and 14.94%, 9.93% and 20.57% for alder panels bonded with UF1, UF2 and PF, respectively. The decreases in formaldehyde emission values of the panels produced by adding borax into the glue mixtures of UF1 and UF2 were found to be 20.32% and 11.58% for beech, 21.33% and 17.94% for alder, respectively. The panels manufactured by two different methods with boric acid emitted higher amounts of formaldehyde than those of the untreated panels for both beech and alder. The amount of formaldehyde release from the beech panels produced by boric acid-treated veneers increased from 5.46 to 6.47 mg/l for UF1, from 3.28 to 4.92 mg/l for UF2 and from 0.55 to 0.60 for PF adhesive. Adding boric acid into the glue mixture also increased the formaldehyde emissions of the panels. Especially, adding boric acid into the mixture of the UF glue with high formaldehyde mol ratio led to significant increase in the formaldehyde emissions of both beech and alder plywood panels compared to the panels produced from boric acid-treated veneers (2.52 mg/l for beech, 1.45 mg/l for alder). This situation is not evident for plywood panels bonded by using UF resin with lower formaldehyde mol ratio. It is known that acetyl groups combined as esters of noncellulosic polysaccharides hydrolyse in alkaline condition [8,9]. Because of alkaline properties, borax may have caused hydrolyse of acetyl groups with the existence of the thermal effects like drying or press temperature in panel production. The acetic acid that arises from these conditions reacted with free formaldehyde in resin. In addition, it may have decreased the ability of hydrolyse of UF resins by increasing the pH values of veneers. UF resins, as already known, undergo hydrolyses excessively in acidic ambience [7]. The higher formaldehyde emission values of the plywood panels produced from the boric acid-treated veneers support to this knowledge. When treatment methods were compared, the least emission values were determined for the panels produced by adding borax into the glue mixture. On the contrary, the formaldehyde emissions of the panels produced in the same way with boric acid were the highest.

3.2. Acetic acid emission

As seen in Fig. 2, when untreated panels (control) were compared, the acetic acid emissions of the alder plywood

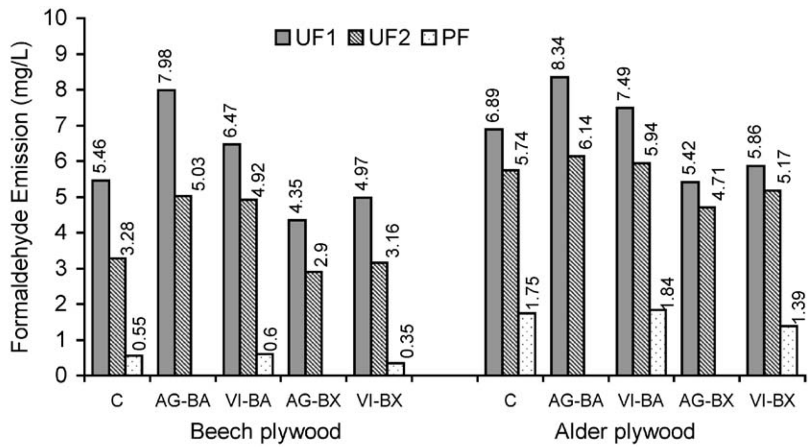

Fig. 1. Effects of boric acid and borax on the formaldehyde emission of plywood. UF1 = urea formaldehyde (U/F mol ratio: 1/1.74), UF2 = urea formaldehyde (U/F mol ratio: 1/1.32), PF = phenol formaldehyde, AG-BA = boric acid into the glue mixture (not added PF glue), VI-BA = veneer imp. with boric acid, AG-BX = borax into the glue mixture (not added PF glue), VI-BX = Veneer imp. with borax.

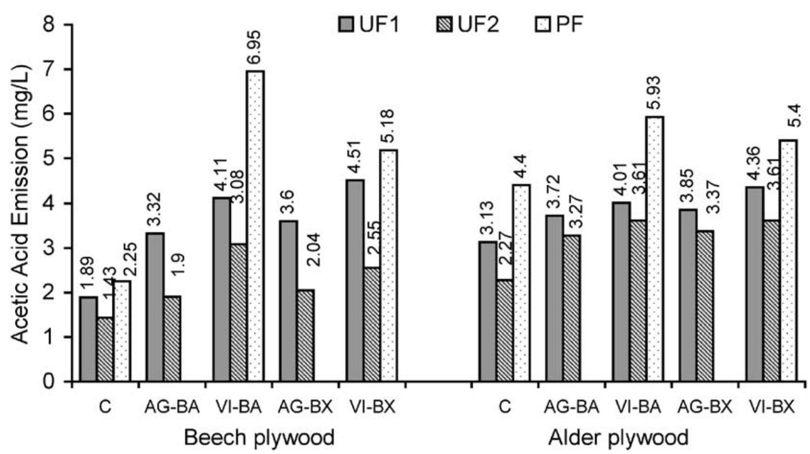

Fig. 2. Effects of boric acid and borax on the volatile acetic acid emission of plywood.

panels were found to be higher than those of the beech panels. The acetic acid measurements were made using absorption solution taken from the dessicator in room condition. Therefore, the density and diffusion properties of wood from which veneers were obtained should be taken into consideration in the evaluation of the emission test results in addition to the chemical reactions between the impregnation matter and resins or wood materials in panel production steps, because the reactions that are important for formaldehyde and acid emissions occur in glue line during the hot pressing. When compared with other wood-based panel products like particle board or MDF, the emission ratio of plywood panels mostly depend on the properties of outer layer since the glue lines of plywood panels are covered with that veneer. Diffusion properties of the veneers can be ascribed to the differences in formaldehyde and acetic acid emissions between alder and beech panels. It was stated in a previous work [10] that diffusion strength of the surface coating materials affect formaldehyde emissions of the wood-based panel products. Volatile acid released from wood also depend on the chemical content of wood and the processes applied to it. Each wood species has different emission potential from the other one due to different chemical contents. Acetic acid, and to a lesser degree, formic acid are the main volatile acids normally encountered in wood. The major source of acetic acid has been traced to acetyl groups which are bound to carbohydrates in the wood [11]. Several studies have established the relationship between the evolutions of acetic acid with the corresponding decrease in the acetyl content of the wood indicating that the acid arises from the hydrolysis of the acetyl groups [9]. That the acetic acid emissions of panels (particleboard and plywood) varied from one species to another from which panels were produced was based on the acetyl group contents of woods in some earlier publications [12,13]. Although, having high amounts of acetyl group content, some wood species released less volatile acid than others with low acetyl group content and this was stated in some other works [14]. It can be concluded from this explanation that both the acetyl group content and the thermal stability of this group have an important role in the acetic acid emission of panels. When all groups were compared, the highest acid emission value was determined from the panels bonded with phenol formaldehyde resin. During panel production with this resin, the splitting reaction of alkaline-sensitive-acetyl group is accelerated due to alkaline-curing reaction. In addition, the temperature applied for curing is higher for PF resins than UF resins. Therefore, thermal processes effective in the splitting of acetyl group may be more severe. It was also stated that acetyl groups split from wood in particle board production with urea formaldehyde adhesive under acidic condition [12]. In addition, when treated plywood panels were compared, the effect of formaldehyde mol ratio on the acid emissions was more evident for beech panels than for alder panels. The acetic acid emissions of the panels produced from treated veneers were found to be higher than those of the panels produced by adding preservatives into the glue mixture (seen in Fig. 2). For instance, the increases in the amount of acetic acid emissions from beech panels produced by preservatives added UF1 glue mixture were 1.71 mg/l for borax, 1.43 mg/l for boric acid, while those of the beech panels produced from impregnated veneers were 2.62 and 2.22 mg/l. Application of the second drying process may have increased the chemical changes which occur in treated veneers. The reactions between treated matter used and wood components speeded up with the effects of drying temperature may have caused to split more acetyl groups from hemicelluloses which are less stable than cellulose and lignin. However, thermal effects occur only in the glue line for the panels produced by adding preservatives into the glue mixture.

4. Conclusion

The formaldehyde emissions of plywood panels treated with boric acid increase. On the contrary, treatment with borax has a small decreasing effect for formaldehyde emission. The difference between formaldehyde emission values of the beech panels treated with boric acid and untreated beech panels was higher than that of the alder plywood panels. The increases in the amount of formaldehyde release from the panels produced by adding boric acid into the glue mixtures of UF1 and UF2 were 2.52 and 1.75 mg/l for beech and 1.45 and 0.40 for alder, respectively. The values calculated for the panels produced from impregnated veneers were 1.01, 1.64 and 0.05 for beech and 0.60, 0.20 and 0.09 for alder, UF1, UF2, and PF, respectively. Although treatment of the veneers with boron compounds had an increasing effect on the acetic acid emission of the plywood panels bonded with PF adhesive, boric acid had a greater effect (4.7 mg/l for beech, 1.53 mg/l for alder). When UF adhesive was used, the increase in acetic acid emission value was not as much as in the PF adhesive being used. The acetic acid emissions of the plywood panels bonded with UF adhesive having low U/F mol ratio were less than those of the panels bonded with high U/F mol ratio-UF adhesive. For example, the increases in the amount of acetic acid emissions from beech panels produced by adding preservatives into the UF1 glue mixture were 1.71 mg/l for borax, 1.43 mg/l for boric acid, while those of the beech panels bonded with UF2 were 0.61 and 0.47 mg/l. The amount of the volatile acetic acid emission was found to be higher for plywood panels produced from treated veneers than those of the panels produced by adding boron compounds into the UF glue mixtures.

Acknowledgements

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