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Effect of various fire retardant chemicals in different concentrations on formaldehyde emission of plywood

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Abstract

Aim of study: Although treated panels make up a large portion of the plywood market, treatment with some wood preservatives has been known to cause some problems such as bonding failures besides the environmental pollution related to the disposal of chemicals after treatment. Formaldehyde release from wood based panels is also another problem regarding the indoor air quality. In the present study, it was aimed to investigate the formaldehyde emission contents of plywood panels treated with fire retardant chemicals.

Area of study: This study was conducted at the Pilot Facility of Department of Forest Industry Engineering, Karadeniz Technical University in Trabzon, Turkey.

Material and Methods: Poplar, alder and Scots pine veneers were used to produce plywood. Zinc borate, monoammonium phosphate and ammonium sulfate were used as fire retardant chemicals. The veneer sheets were treated with immersion method and chosen three different concentrations as 5%, 7% and 10% aqueous solutions. Urea formaldehyde (UF) glue resin was used as adhesive. Formaldehyde emission contents of plywood panels were determined according to flask method described in DIN EN 717-3 standard.

Main results: It was found that formaldehyde release from panels produced with the veneers treated with zinc borate were higher than those of control panels and the emission values increased when the concentration increased. The lower formaldehyde emission values were obtained for monoammonium phosphate and ammonium sulfate treated panels and the emission values decreased when the concentration increased.

Research highlights: In some usage areas where high strength properties are not expected, plywood panels manufactured from veneers treated with the fire retardant chemicals (monoammonium phosphate and ammonium sulfate) may be used for reducing formaldehyde release.

Keywords: Formaldehyde emission, Plywood, Concentration, Fire retardant, UF

Farklı konsantrasyonlardaki çeşitli yangın geciktirici kimyasalların kontrplakların formaldehit emisyonu üzerine etkisi

Özet

Çalışmanın amacı: Emprenyeli levhalar, kontrplak piyasasında geniş bir yer edinmelerine rağmen, bazı ahşap koruyucularla emprenye işlemi, yapışma kusurları, emprenye sonrası kimyasal atıklarından dolayı oluşan çevre kirliliği gibi bazı problemlere sebep olduğu bilinmektedir. Ahşap esaslı levhalardan açığa çıkan formaldehit, iç mekanların hava kalitesinde etkili olan başka bir problemdir. Bu çalışmada, yangın geciktirici kimyasallar ile emprenye edilmiş kontrplak levhalarının formaldehit emisyonu miktarlarının araştırılması amaçlanmıştır.

Çalışma alanı: Bu çalışma, Trabzon'daki Karadeniz Teknik Üniversitesi Orman Endüstri Mühendisliği Bölümü Pilot tesisinde yapılmıştır.

Materyal ve Yöntem: Kavak, kızılağaç ve sarıçam (*Pinus sylvestris* L.) kaplamalar, kontrplak için kullanılmıştır. Çinko borat, monoamonyum fosfat ve amonyum sülfat, yangın geciktirici olarak kullanılmıştır. Kaplama levhaları, %5, 7 ve 10 olmak üzere üç farklı çözelti konsantrasyonu seçilmiş ve daldırma yöntemi kullanılarak emprenye edilmiştir. Kontrplak levhalarının formaldehit emisyonu miktarları, DIN EN 717-3 standardında belirlenen şişe yöntemine göre belirlenmiştir.

Sonuçlar: Çinko borat ile emprenye edilmiş kaplamalardan üretilen kontrplak levhalardan açığa çıkan formaldehit kontrol gruplarından daha yüksek bulunmuştur ve emisyon değerlerinin, konsantrasyon arttıkça arttığı belirlenmiştir. En düşük formaldehit emisyon değerleri, monoamonyum fosfat ve amonyum sülfat ile emprenye edilmiş levhalardan elde edilmiştir ve emisyon değerlerinin, konsantrasyon arttıkça azaldığı belirlenmiştir.

Araştırma vurguları: Yüksek direnç özelliklerinin aranmadığı bazı kullanım yerlerinde, formaldehit emisyonunu azaltmak için yangın geciktirici kimyasallarla (monoamonyum fosfat ve amonyum sülfat) emprenye edilen kaplamalardan üretilen kontrplak levhaları kullanılabilir.

Anahtar Kelimeler: Formaldehit emisyonu, Kontrplak, Konsantrasyon, Yangın geciktirici, ÜF

Introduction

Plywood is one of the main products that can be used as structural material and has traditionally played an important role in light frame construction. Plywood and other wood-based products are widely used in the manufacture of furniture, engineered flooring, housing, and other industrial products (Bohm, Salem Srba., 2012, p. 221). However, the usage and application areas of plywood are limited since the plywood is a flammable material. Therefore, there has been much interest in the fire-retardant-treatment of wood-based panels (Cheng & Wang, 2011, p. 1715). The use of plywood treated with fire retardants is becoming popular. They are very important for specialized construction applications and furniture industry (Tanritanir & Akbulut, 1999, p. 122; Winandy, 2001, p. 47; Ayrilmis, Korkut, Tanritanir, Winandy & Hiziroglu, 2006, p. 888).

Fire retardant-treated wood products provide a viable alternative to traditional non-combustible materials where a higher level of fire safety is desirable or necessary (White & Mitchell, 1992, p. 250). Boron compounds are often considered good fire retardants because of their beneficial effects such as preservative effectiveness, neutral pH, and less impact on mechanical properties than some other fire retardant chemicals (Levan & Tran, 1990, p. 39). Phosphorus-containing chemicals such as mono- and di-ammonium phosphates are also known as strong fire retardants, and they have been used for wood and wood-based materials for many years (Grexa, Horvathova, Besinova & Lehocky, 1999, p. 529).

Formaldehyde is a potential human carcinogen and, due to its high risk level, it is classified differently than most other pollutants (Salem, Zeidler, Böhm, & Srba, 2013, p. 1200). Also, this chemical has adverse health effects such as eye and respiratory irritation, irritability, inability to concentrate and sleepiness (Milota, 2000, p. 10-9; Colak & Colakoglu, 2004, p. 533). The most important man-made source of formaldehyde is automotive exhaust that are not fitted with catalytic converters. Formaldehyde is also produced industrially in large quantities and used in many applications. The major anthropogenic sources affecting humans in the indoor environment are products containing formaldehyde such as resins, glues, insulating materials, oriented strand board (OSB), plywood, and fabrics (Uchiyama, Matsushima, Kitao, Tokunaga, Andoc & Otsuboa, 2007, p. 8825). As wood-based panels are possible sources of formaldehyde emissions, during recent years, a lot of work has evaluated the effects of press conditions (press temperature and time), mat moisture content lower-molecular-weight UF resins, and the addition of formaldehyde scavengers on formaldehyde emissions, and investigated the manufacture of various wood-based panels using low-formaldehyde and non-formaldehyde resins (Minemura, 1976, p. 8; Hao & Liu, 1993, p. 2; Grigoriou, 2000, p. 34; Wiglusz, Nikei, Igielska & Sitko, 2002, p. 108; Wang, Gardner & Baummann 2003, p. 65; Aydin, Colakoglu, Colak & Demirkir, 2006, p. 1311; Wang, Yang, Lin, Lin & Tsai, 2007, p. 2472; Wang, Zhao, Gao & Guo, 2012, p. 1972). Moreover, it was reported that plywood made by adding borax ($Na_2B_4O_710\text{-}H_2O$) (Colak & Colakoglu, 2004, p. 533) and polyvinyl acetate (Kim & Kim, 2005, p. 456) to the glue mixture exhibited reduced formaldehyde emission. It has also been reported that laminating wood-based composite panel surfaces with decorative vinyl film and melamine-impregnated paper reduces formaldehyde emissions (Groah, Gramp & Trant, 1984, p. 27; Nemli & Colakoglu, 2005, p. 83). Also, studies have been made with tannin extracted from the bark of wattle (Vazquez, Freire, Gonzalez & Antorrena, 2000, p. 57; Kim, Lee, Hyun-Joong & Hyoung, 2003, p. 1863; Santana, Baumann & Conner, 1995, p. 146; Pizzi & Scharfetter, 1978, p. 1745), acacia (Pizzi, 2000, p. 277; Jahanshahee, Tabarsa, Asghari & Resalati, 2010, p. 27; Jahanshahee, Tabarsa & Asghari 2012, p. 296) and starch (Farag, 1995, p. 192; Yoshida, Okabe, Yao, Shiraishi & Oya 2005, p. 335; Turunen, Alvila, Pakkanen & Rainio, 2003, p. 582; Basta, El-saied, Gobran & Sultan, 2006, p. 325), mangrove (Sowunmi, Ebewele, Peters & Conner, 2000, p. 574) in co-condensed resins with phenol and formaldehyde.

In the past, the important criteria for assessing a wood adhesive for a specific application were its technical properties, gluing behaviour, and cost. During recent years, a new set of criteria has attained more and more importance: the environmental and health aspects of the adhesive itself (Aydin et. al., 2006, p. 1312).

However, few published papers describing techniques for reducing formaldehyde emissions as an environmental pollutant from wood-based panels such as plywood are available. In this study, the effect of various fire retardant chemicals in different concentrations on formaldehyde emission of plywood panels was investigated.

Material and Methods

In this experimental study, 2 mm-thick rotary cut veneers with the dimensions of 500 mm by 500 mm were obtained from poplar (*Populus deltoides* I-77/51 clone), alder (*Alnus glutinosa* subsp. *barbata*) and Scots pine (*Pinus sylvestris* L.) logs. While the alder and poplar veneers were manufactured from freshly cut logs, Scots pine logs were steamed for 12 h before veneer production. The horizontal opening between knife and nosebar was 85% of the veneer thickness, and the vertical opening was 0.5 mm in rotary cutting process. The veneers were then dried to 6–8% moisture content with a veneer dryer. After drying, veneer sheets were treated with some fire retardant chemicals. For this aim, 5, 7 and 10% aqueous solutions of zinc borate, monoammonium phosphate (MAP) and ammonium sulfate were used. The veneers were subjected to re-drying process at 110°C after they immersed in the fire retardant solutions for 20 min. The retention level for each treatment solution was calculated with the following equation, and they were presented in Table 1.

$$R = \frac{G \text{ x } C}{V} \text{ x } 10 \text{ kg/m}^3$$

where

R = Retention level (kg/m^3)

G = treatment solution absorbed by the sample

C = preservative or preservative solution in 100 g treatment solution.

V = volume of sample in cm^3

Table 1. Retention levels of fire retardant chemicals (kg/m^3)

Fire Retardant Chemicals	Aqueous Solutions (%)	Poplar	Alder	Scots pine
Zinc Borate	5	17.118	16.324	13.800
	7	20.854	20.107	19.915
	10	30.243	29.053	26.420
MAP	5	11.233	10.233	12.689
	7	14.219	14.595	18.033
	10	19.514	18.601	23.402
Ammonium Sulfate	5	9.705	9.781	11.578
	7	11.594	11.350	17.553
	10	14.660	15.254	24.993

Three-ply-plywood panels with 6 mm thick were manufactured by using urea formaldehyde resin. The formulations of adhesive mixtures used for plywood manufacturing are given in Table 2. Veneers sheets were conditioned to approximately 5–7% moisture content in a climatization chamber before gluing. The glue mixture was applied at a rate of 160 g/m^2 to the single surface of veneer by using a four-roller glue spreader. Hot press pressure was 12 kg/cm^2 for alder and 8 kg/cm^2 for scots pine and poplar panels while hot pressing time and temperature were 6 min and 110ºC, respectively. Two replicate panels were manufactured for each test groups.

Table 2. The formulations of UF glue mixture used for the manufacturing of plywood

Glue Type	Ingredients of Glue Mixture	Parts by weight
UF	UF resin (with 55% solid content)	100
	Wheat flour	30
	Hardener - NH_4Cl (with 15% concentration)	10

Formaldehyde emission contents of plywood panels were determined according to flask method described in DIN EN 717-3 standard. This is a simple and inexpensive method for testing formaldehyde release and suitable for testing of uncoated boards (Aydin et. al., 2006, p. 1313). In this method; test pieces of known mass is suspended over water in a closed container at constant temperature. The formaldehyde released from the test pieces is absorbed by the water and determined photometrically (Sundman, Larsen, Vestin & Weibull, 2007, p. 3195). The temperature and time were applied as 40°C and 3 h, respectively in determining the formaldehyde emission. The test apparatus shown in Figure 1 was used for the determination of formaldehyde release from plywood panels.

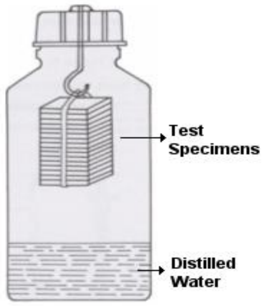

Figure 1. Test apparatus used for the determination of formaldehyde emission content of plywood panels.

Results and Discussion

Formaldehyde emission test results according to wood species were presented in Table 3.

Table 3. Formaldehyde emission contents of plywood panels (mg/100g oven dry panel)

Fire Retardant Chemicals	Aqueous Solutions (%)	Poplar	Alder	Scots pine
Zinc Borate	Control	1.020	0.697	1.158
	5	1.404	1.121	1.600
	7	1.523	1.249	1.620
	10	1.614	1.251	1.796
MAP	5	0.516	0.392	0.571
	7	0.498	0.273	0.533
	10	0.434	0.249	0.532
Ammonium Sulfate	5	0.759	0.484	1.094
	7	0.724	0.449	1.042
	10	0.598	0.394	0.927

As can be seen from Table 3, Scots pine plywood panels had the highest formaldehyde release whereas the lowest formaldehyde emission content was found alder. The treatment processes with fire retardant chemicals evidently affected the formaldehyde emissions of the panels. Monoammonium phosphate and ammonium sulfate showed a decreasing effect on the formaldehyde emissions, whereas zinc borate showed an increasing effect. The formaldehyde emission of panels treated with zinc borate increased while its of panels treated with monoammonium phosphate and ammonium sulfate decreased with increasing concentration. The lowest formaldehyde emission values were obtained for plywood treated with monoammonium phosphate. Treatment with monoammonium phosphate decreased the formaldehyde emission values of the panels produced from treated veneers by 49, 51 and 57% for poplar, 44, 61 and 64% for alder, 51, 54 and 54% for Scots pine panels treated 5, 7 and 10% in aqueous solutions, respectively.

In this study, the ammonia released from monoamonium phosphate and ammonium sulfate could produce N-H functional groups on the surface of the veneer sheets which help to reduce the formaldehyde emission (Zhang, Liu & Lu, 2013, p. 607; Schroder Meyer-Plath, Keller, Besch, Babucke & Ohl 2001, p. 562; Wen, Yang, Ou, Wu, Chou, Luo & Chang, 2006, p. 3166). Zhang et al. (2013) found for plywood panels that formaldehyde emission values decreased with cold-ammonia plasma pretreated veneer sheets. Some studies have also indicated that when wood treated with ammonium acetate solution, the formaldehyde emission from the wood composites reduced (Colak, Colakoglu, Testereci & Aydin, 2002; Myers, 1986, p. 41). Aydin (2004) stated that the ammonium acetate behaves as a formaldehyde scavenger especially when urea-formaldehyde glue was used as adhesive in the manufacturing of wood composites. In addition, Junyou and Shengyou (2010) found the formaldehyde emission from poplar plywood was significantly decreased with addition of ammonia. Wang et al. (2012) stated that combinations of ammonia and sodium sulfite as formaldehyde scavengers had positive effects on the formaldehyde emission of plywood panels. The zinc borate used in this study increased the formaldehyde emission of the all wood species. Colak and Colakoglu (2004) found the boric acid increased the formaldehyde emissions of the panels. In previous study, it was also found that zinc borate had an increasing effect on formaldehyde emission of plywood (Demir, Aydin & Ozturk, 2014, p. 63).

Conclusion

This study investigated effect of fire retardant chemicals on the formaldehyde emission of plywood panels. As a result of this study; formaldehyde emission contents of the panels produced from veneers treated with zinc borate were found to be higher than those of the control panels while the lower formaldehyde emission values were obtained for monoammonium phosphate and ammonium sulfate treated panels when compared to the control panels. The formaldehyde emission of panels treated with zinc borate increased while its of panels treated with monoammonium phosphate and ammonium sulfate decreased with increasing concentration. Treatment of monoammonium phosphate and ammonium sulfate caused considerable reduction in formaldehyde emission from manufactured plywood panels. In some usage areas where high strength properties are not expected, plywood panels manufactured from veneers treated with them may be used for reducing formaldehyde release.

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