

WETTABILITY OF FIRE RETARDANT TREATED LAMINATED VENEER LUMBER (LVL) MANUFACTURED FROM VENEERS DRIED AT DIFFERENT TEMPERATURES

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Wettability of the fire retardant treated (FRT) laminated veneer lumber (LVL) manufactured from wood veneers dried at different temperatures was investigated. Commercially manufactured veneer of beech wood (*Fagus orientalis* L.) was treated with borax-boric acid (BX/BA, 1:1 by weight), monoammonium phosphate (MAP), and diammonium phosphate (DAP) using a full-cell pressure process. The veneers were then dried at different temperatures (120, 140, 160, and 180°C), and experimental LVLs were made from these veneer sheets. The wettability of LVL was characterized by contact angle analysis. The lowest contact angle was obtained from LVL made from BX/BA-treated veneers, while the highest value was found for the control LVL. The CA values of these samples at each re-drying level were lower than LVLs made from untreated veneers. Re-drying of the treated veneers decreased the CA values of the LVL, while it was found higher for the LVL made from untreated veneer.

Key words: Wettability; Contact angle; Fire retardant chemical; Drying temperature; Laminated veneer lumber

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INTRODUCTION

Fire-retardant-treated (FRT) wood products such as solid wood, plywood, and laminated veneer lumber (LVL) provide a viable alternative to traditional noncombustible materials where a higher level of fire safety is desirable. Wood products treated with waterborne preservatives are being used for various exterior applications such as structural and nonstructural assemblies. The most common fire-retarding chemicals used for wood and wood-based panels are: inorganic salts, such as monoammonium phosphate (MAP), diammonium phosphate (DAP), ammonium sulfate; and boron compounds, such as borax (BX) and boric acid (BA). Boron compounds can be used to increase the resistance of composites to fire and biodegradation. Boron compounds are one of the safest in current use, and no fatalities or other harmful effects have occurred due to this or other industrial uses. The fire-retardant chemicals most used for wood products contain phosphorus, especially MAP and DAP. These phosphates are among the oldest known fire-retardant systems, and they are included in most proprietary systems used for wood.

In general, rotary-peeling of wood veneers used for LVL manufacture are dried between 120-180°C in an industrial jet dryer. However, wood drying at temperatures between 160 and 180°C can cause modifications in surface composition (Sernek et al. 2004). Several known changes, especially oxidation, occur to the wood surface over time during exposure to high temperature. An inactivated wood surface can cause adhesion problems because of the interference with wetting, flow, and penetration of adhesive, and also interfere with the cure and resulting cohesive strength of the adhesive. Wettability is

crucial for good adhesion in wood bonding. The wettability of wood can be characterized by various methods (Gray 1962; Casilla et al. 1981; Gardner 1996; Gardner et al. 1991). Recently, contact angle method has been commonly used to determine surface characteristics of wood and wood based composites (Sernek 2002; Aydin 2004; Ayrilmis and Winandy 2009). This method is important to determine the adhesive and coating properties of wood and wood-based composite surfaces (Petrisans et al. 2003). When the contact angle is zero, perfect wetting of a surface occurs.

Problems can be encountered with adding fire-retardant chemicals to wood during manufacture. For example, several mechanisms have been proposed to correct the generally adverse effects of inorganic fire retardants on the bonding of the resin, including pH effects, incompatibility between resins and fire retardants, adverse effects on resin viscosity, reduction in the number of hydroxyl groups available for hydrogen bonding, and mechanical interference by fire-retardant salts, resulting in the reduced bonding (Boggio and Gertjeansen 1982). Although previous studies reported that waterborne fire retardants decreased the adhesive bonding performance of the LVLs (Ozciftci et al. 2007; Colakoglu et al. 2003), their effects on the wettability of the LVL were not extensively investigated. The objective of this study was to investigate the effect of various fire retardants, boron compounds and phosphates, and re-drying temperatures of the treated veneers on wettability of LVL.

EXPERIMENTAL

Materials

Commercial rotary cut veneers obtained from Beech (*Fagus orientalis* Lipsky) logs were used to make LVL under laboratory conditions. Beech is naturally grown in northeast Turkey. Air-dry density of beech wood averages 0.63 g/cm³ (Berkel 1970), and its wood is convenient for veneer, plywood, and LVL manufacturing. Each veneer sheet was 500 mm × 500 mm × 2.7 mm thick. The veneers were almost defect-free. The sheets were kept in a conditioning chamber with temperature of 25°C and relative humidity (RH) of 37% until they were equilibrated at 7% MC. Three different fire-retardant chemical formulations were used in treatments: a mixture of boric acid (BA) (H₃BO₃) and borax (BX) (Na₂B₄O₇·10H₂O) (BA/BX, 1:1 by weight); monoammonium phosphate (MAP) (NH₄H₂PO₄); and diammonium phosphate (DAP) (NH₄)₂HPO₄. The typical chemical compositions of BX/BA (1:1 by weight), MAP, and DAP are shown in Table 1.

Table 1. Typical Composition of Borax, Boric Acid, Monoammonium Phosphate, and Diammonium Phosphate

| Chemical | Component | Amount (%) |
|---------------------------------|-------------------------------|------------|
| Borax-boric acid (BX/BA) | B ₂ O ₃ | 46.3 |
| | Na ₂ O | 8.2 |
| | Purity | 99.9 |
| Monoammonium phosphate (MAP) | P ₂ O ₅ | 61.0 |
| | N | 12.0 |
| | Purity | 99.9 |
| Diammonium phosphate (DAP) | P ₂ O ₅ | 53.0 |
| | NH ₃ | 25.0 |
| | N | 20.8 |
| | Purity | 99.9 |

Fire Retardant Treatments

Prior to LVL manufacture, the veneers were pressure-treated with the fire-retardant chemicals using a full-cell pressure process. A vacuum of 0.086 MPa was pulled for 30 min, chemicals were added, and pressure of 1.1 MPa was then applied for 60 min. Concentration of the chemical solutions was adjusted to provide 56 kg of chemical retention on 1 m³ oven-dry wood weight. The control veneers were pressure impregnated but only with distilled water under the same conditions as treated veneers.

LVL Manufacture

Following the impregnation, the treated veneer sheets were dried in an industrial jet dryer of four different temperatures for 15 min., 120°C, 140°C, 160°C, and 180°C, respectively. The sheets were then kept in a conditioning chamber until they were equilibrated at 7% moisture content before LVL panels were manufactured. A total of thirty-six 5-ply, 13-mm thick experimental panels were manufactured from veneer sheets with the dimension of 500 mm × 500 mm × 2.7- mm. An exterior phenol-formaldehyde (PF) resin with 47% solid content was applied on single bonding surfaces of the veneers at a rate of 200 g/m². The individual veneers were then assembled, with the grain of all veneers running along the length-wise direction of the billet, and hot-pressed using a pressure of 1.5 MPa and press temperature of 140°C for 15 minutes in a laboratory-type hot press. The resulting LVL panels were allowed to cool for 48 hours in the climate room having 65% RH and 20±2°C before they were cut into test samples.

Determination of Wettability

Contact angle (CA) analysis was used to evaluate the wettability characteristics of the panels in this study. The contact angle was defined as the angle through the liquid phase formed between the surface of a solid and the line tangent to the droplet radius from the point of contact with the solid. A sessile drop method was used to measure a contact angle (θ) of a 5 μ L distilled water drop, which was applied to the surface by means of a pipette. The sample size for the wettability test was 13 mm x 50 mm x 50 mm. Before evaluating of wettability tests, the samples were conditioned at 65% relative humidity at 20°C in a climate chamber until they reached about 12% moisture content. Determination of contact angle was performed using the conic section method. An imaging system was used to measure contact angle and shape and size of water droplets for the tested surfaces of the LVL samples.

CA measurements were obtained by using a goniometer system connected with a digital camera and computer system. The liquid employed for the measurements was distilled water at 20°C with a surface tension of 72.80 mN/m. The CA was determined for each image by digital image analysis software. The image was captured immediately after the the droplet of distilled water was placed on the LVL sample surface, and then every 1 second for a duration of 20 sec. The mean CA value and the standard deviation for each sample were calculated from twenty photo images. A total of sixty testing samples, fifteen samples for each treatment, were used for the CA measurements. For the CA tests, all multiple comparisons were first subjected to analysis of variance (ANOVA), and significant differences between mean values of the untreated and treated LVL test samples were determined using Duncan's multiple range test.

RESULTS AND DISCUSSION

Table 2 displays CA values of the LVL samples manufactured from the untreated and treated veneers dried at different temperatures. Statistical analysis showed some noticeable differences ($p < 0.001$) between CA mean-values of the LVLs. Duncan's multiple comparison tests were used to determine the differences between the treatment groups and the test results are shown in Table 2 as letters. The control group showed a significant difference compared to all the treatment groups at each re-drying level. The interactions between fire-retardant chemicals and re-drying temperature of the treated veneers were also found to be significant ($p < 0.001$) by two-way ANOVA test. The LVLs made from untreated veneers dried at 180°C had the highest contact angle value of 122.1° while the lowest contact angle was found for the LVLs made from BX/BA treated veneers dried at 180°C had a value of 55.7°.

Table 2. Average Contact Angle Values of the Treatment Groups

| Treatment chemical | Retention (kg/m ³) | Veneer re-drying temperature | Contact angle values |
|--------------------|-----------------------------------|------------------------------|----------------------------|
| | | (°C) | (°) |
| Untreated | - | 120 | 101.2 (4.9) A ^a |
| | | 140 | 106.7 (3.9) B |
| | | 160 | 112.2 (3.6) C |
| | | 180 | 122.1 (3.7) D |
| MAP | 56.2 | 120 | 91.6 (9.62) E |
| | | 140 | 85.6 (8.5) F |
| | | 160 | 78.6 (7.5) G |
| | | 180 | 71.9 (10.9) HL |
| DAP | 56.6 | 120 | 84.3 (9.1) F |
| | | 140 | 81.2 (10.2) FG |
| | | 160 | 73.8 (7.1) M |
| | | 180 | 67.4 (8.7) L |
| BX/BA | 57.8 | 120 | 73.1 (12.2) HM |
| | | 140 | 68.4 (9.6) L |
| | | 160 | 62.3 (10.7) N |
| | | 180 | 55.7 (10.1) O |

^a Groups with same letters in column indicate that there was no statistical difference ($p < 0.001$) between the samples according to the Duncan's multiply range test. Numbers in parentheses are standard deviations.

Typical graphs showing the mean CA values of LVLs made from untreated- and BX/BA treated-veneers group versus time are presented in Figs. 1 and 2.

The CA values of the LVLs made from the untreated veneers were significantly increased with increasing veneer re-drying temperature (lower wettability). However, the CA values of the LVLs made from FRT veneers were decreased with increasing veneer re-drying temperatures (Fig. 3). The CA values of LVLs made from treated veneers at each re-drying level were lower than the LVLs made from untreated veneers.

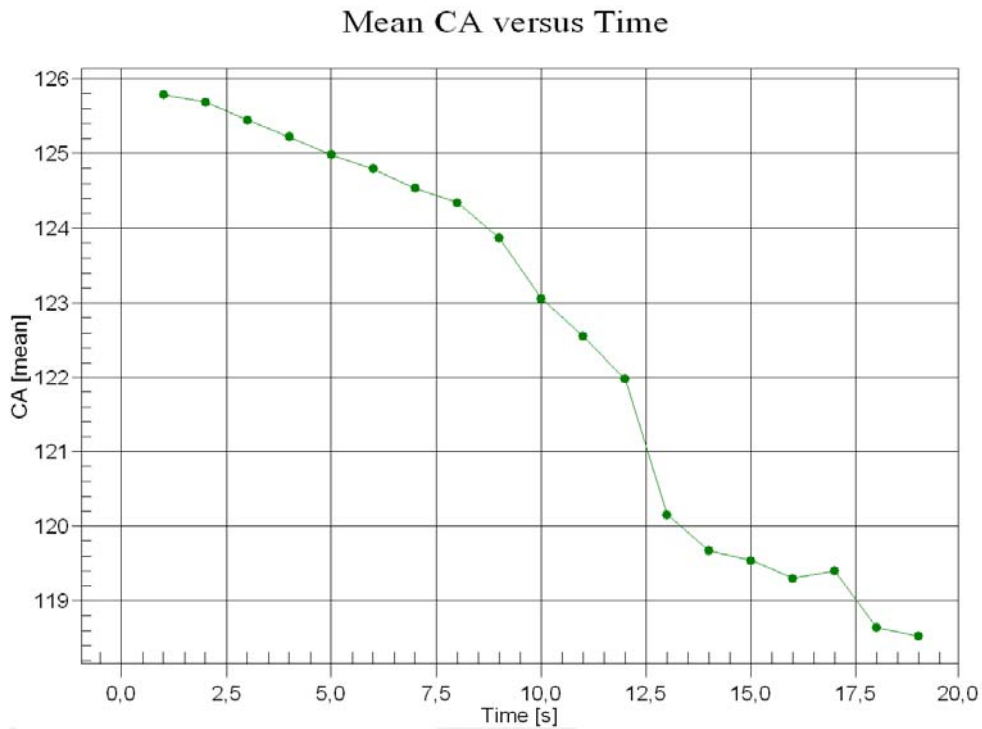


Fig. 1. Mean CA values of control LVLs made from re-dried veneers at 180°C vs. time

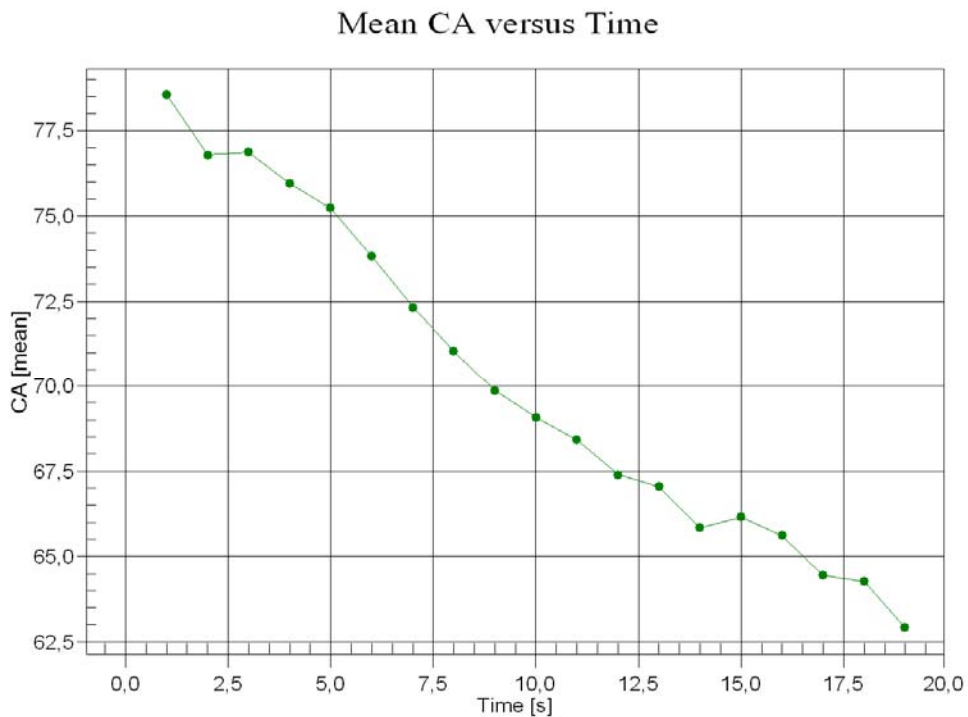


Fig. 2. Mean CA values of the LVLs from BX/BA treated and re-dried veneers at 180°C vs. time

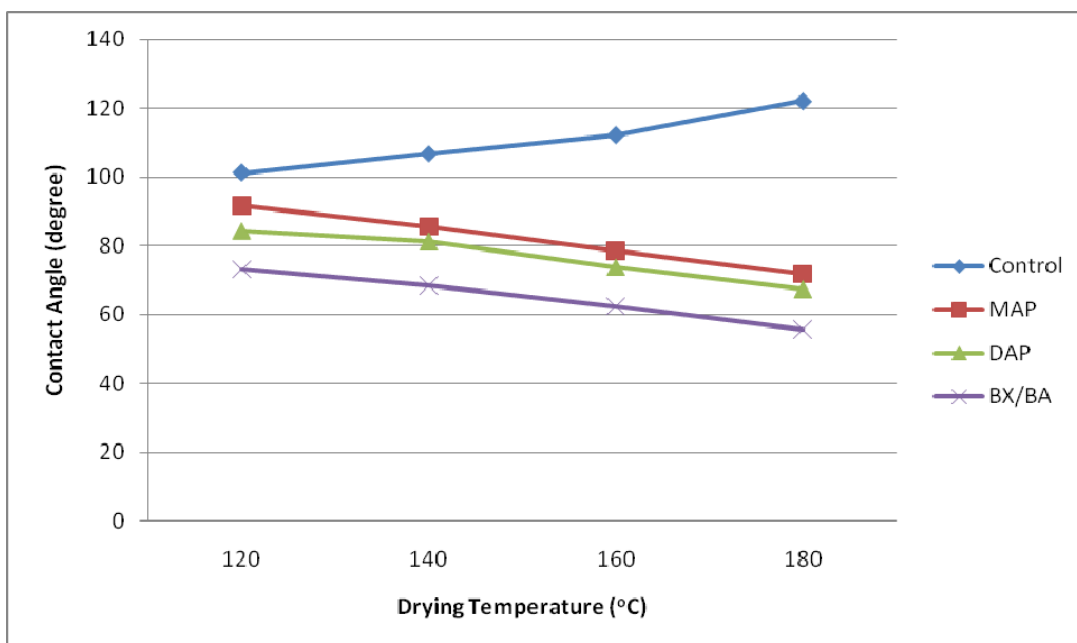


Fig. 3. CA values of the LVL groups as functions re-drying temperature and the chemical type

More interesting results were obtained in the samples treated with the boron compounds. Although the LVLs made from MAP- and DAP-treated veneer had similar CA values, the CA values of BX/BA treated-LVLs were considerably lower. These results suggest that boron compounds may affect the wettability of the LVLs made from re-dried veneers even though thermal treatments result in hydrophobication, and, in turn, decreased water absorption. This effect is probably related to BA-water interaction, which is a typical Lewis-acid-base reaction, to form hydrated BA molecules. Because water itself acts in some reactions as a base and in others as an acid, it is therefore referred to as amphoteric. Hence, BA can form a coordinate covalent bond with Lewis base (e.g., OH⁻ from water), to form hydrated BA molecules that have high bond energies (Frihart 2005). But water cannot react with other FRT chemicals as BA reacted. Having this information, it is reasonable to summarize that the BA-water reaction is more easily accomplished, hence there is a higher water uptake than other fire retardant chemicals. The changes (%) in the CA values of the treated LVL groups as compared to the control group are presented in Fig. 4.

Wood treated with inorganic flame-retardant salts is usually more hygroscopic than untreated wood. In particular, boron compounds and phosphates may have diverse effects on the hygroscopicity of wood (Shi and Walker 2006; Levan and Winandy 1990; Alexiou et al. 1986; Hashim et al. 1994). In addition, variations in chemical composition of wood can influence sorption properties. In general, hemicellulose is the most hygroscopic, followed by cellulose and lignin (Zhang and Datta 2004). Structural and chemical modifications of wood cell-wall constituents may lead to the formation of additional hydrogen-bonding sites for water. The water absorption increase, in other words wettability can be attributed to the new adsorption sites that were formed from the chemical treatments. A number of studies also verified a definite correlation between chemical treatments and water-uptake properties of wood (Levan and Winandy 1990; Alexiou et al. 1986; Hashim et al. 1994).

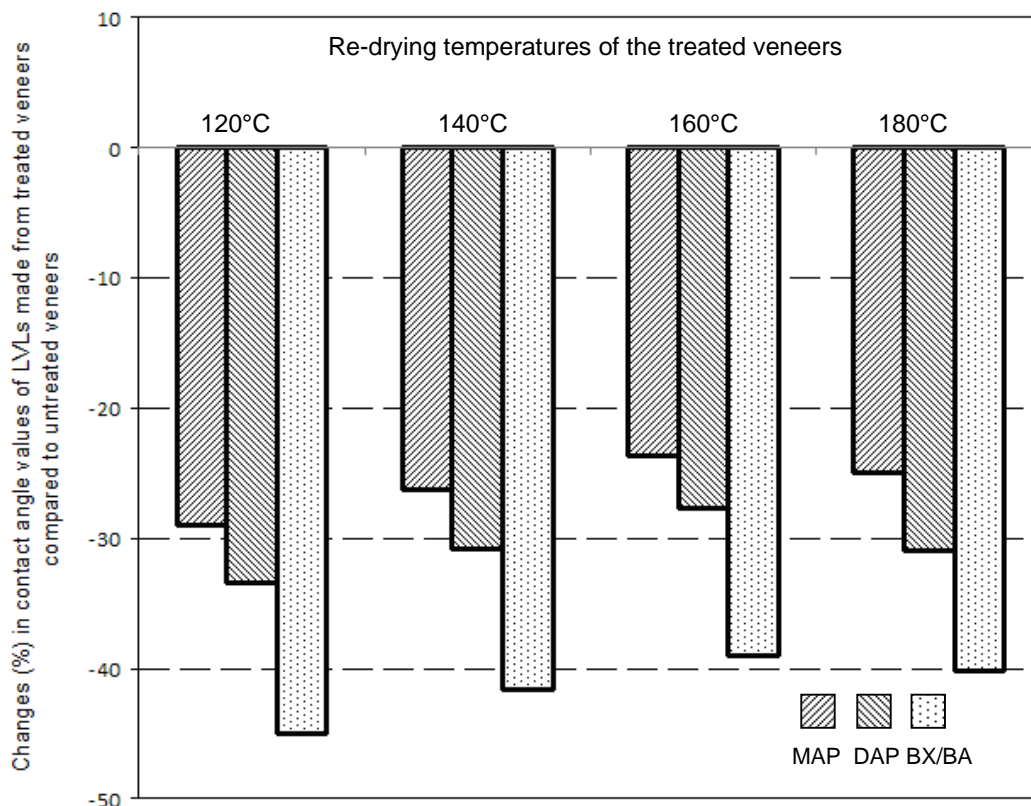


Fig. 4. Changes (%) in CA values of the LVL groups as functions of the chemical type and re-drying temperature of the veneers

The increase in contact angle for the LVLs made from untreated veneers dried at increasing temperatures may be interpreted as a decrease in hydrophilicity (Sernek 2002). The surface of wood exposed to high temperatures is less polar and thus repels water, resulting in a lower wettability than in the case of untreated wood (Christiansen 1990, 1994, 1997). Kollmann and Schneider (1963) reported that sorption capacity of beech wood exposed to various temperatures ranging from 100°C to 180°C was decreased. In the same study, it was stated that sorption capacity decreased with thermal treatment temperature and duration. Peculiar behavior of the wettability in relation to re-drying of the untreated veneers may be explained at the cellular level. Hemicelluloses are hydrolyzed during thermal-treatment, and this decreases the hygroscopicity of thermally treated-wood (Winandy and Smith 2006). Exposure duration and temperature are two important factors affecting hemicelluloses degradation (Levan and Winandy 1990). Due to a decrease of hydroxyl groups on carbohydrate chains, the cell wall of wood exposed to high temperatures absorbs less water. When wood is exposed to high temperatures, many extractives move towards the surface of the wood. Decrease of wettability can also be due to extractive migration resulted from low-molecular wood extractives, fatty and resin acids and their esters, terpenes, phenols, etc.

CONCLUSIONS AND FURTHER WORK

The waterborne fire retardants, boron compounds and phosphates, decreased the CA values of the LVL surfaces due to their hygroscopic characteristics. The lowest contact angle was obtained from LVLs made from BX/BA-treated veneers, while the highest values were found for the control LVLs. The CA values of these samples at each re-drying level were lower than LVLs made from untreated veneers. Although LVL samples made from MAP- and DAP-treated veneer showed similar CA values, the CA values of BX/BA treated-LVL samples were considerably lower. Based on the findings obtained from the CA measurements, it can be stated that boron and phosphates crystals on the LVL surface could tend to accelerate the reaction, which lessened penetration and mechanical interlocking of the adhesive into the porous structure of the wood. These preliminary findings indicated that the wettability of the LVLs was significantly affected by the fire retardant treated veneers dried at different temperatures. Further studies should monitor the contact angles for longer time periods to attain a better understanding of the effect of the treatment variables on the surface quality of the LVLs.

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