PhD Theses

Improving the Fire Resistance of Cement Bonded Particle Board made of poplar and Scots pine particles pre-treated with Boron and Phosphorus Compounds

by

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Under the supervision of

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in

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Problem Area

Cement bonded particleboard (CBPB) has a growing market in central Europe. Requirements and regulations on both the global and national levels are forcing continuous developments. Most of Researchers focused on improving the hygroscopic and mechanical properties of CBPB or shortening the manufacturing time via pre-treatments and binders. However, fire resistance properties were kept on the side. Only few researches have studied the fire resistance of CBPB, it was mainly focused on additives' effect on the thermal stability of CBPB or that it is non-combustible material. The fire resistance of CBPB needs improvement, especially that CBPB is a construction material where fire protection is becoming more and more Substantial in the case of a construction materials like CBPB [1], [2].

Fire buildings causes human and materials losses. Fire safety is an important aspect in constructions. In 2016, based on 39 country statistics thousands of people died in building fires [3]. The aim of this research work is to improve fire resistance of CBPB which will be advantageous for both scientific and industrial field. In scientific side, new research prospective to scientists will be opened on Cement wood composites, while in case of industrial field a more fire resistance construction material will be made.

Since CBPB is a composite material made of cement and wood increasing the fire resistance of the weakest component it the best solution, which is wood in this case. Ignition and combustion of wood is occurred because the thermal decomposition (pyrolysis) of cellulose and the reactions of pyrolysis products with each other and with gases in the air, usually oxygen. Untreated wood chars with speed of 1 mm per min [4]. Based on wood combustion process decomposition of wood molecules (cellulose, hemicellulose and lignin) is the reason of wood pyrolysis. the best solution to overcome the problem of wood pyrolysis is to modify the wood molecules with fire retardants (FR’s).

Fire retardants have two kinds of actions: physical and chemical. For the physical action, there are many ways to delay ignition. Cooling is one method, where fire retardants can decrease the materials temperature. Coating is another way of delaying ignition where fire retardants can form a protective layer that prevents the underlying material from combusting. Dilution is the third way in which the retardants release water and carbon dioxide during burning [5]. CBPB is composite material within the B-s1, d0

classification of fire resistance (MSZ EN 13501-1:2007+ A1:2010) [6], [7]. Using fire retardants as pre-treatments for wooden particles used in the CBPB could upgrade it to the A2 or A1 classification. However, the used FR's must be eco-friendly, non taxic, cheap and does not affect the CBPB initial properties.

Objectives

In light of the mentioned problem, Several objectives are defined to achieve the main goal :

- ✓ Define the influencing factors on the fire retardations performance
- ✓ Examine the validity of the hypothesis "good wettability gives good fire retardancy". By using contact angle measurement and fire tests (Linder test, the single flame source test and calorimeter bomb test)
- ✓ Effect of Fire retardants on Cement curing, using hydration test during 24 hours
- ✓ Production of CBPB made of treated wood particles of Scots pine and poplar
- ✓ Investigation of the effect of fire retardants on the CBPB properties and compare them to the standard requirement MSZ EN 634-2:2007
- ✓ Compare the Fire resistance of the produced CBPB to the EN standard classification *EN ISO 13501-1:2007 +A1:2010.*
- ✓ Comparison of the thermal and mechanical characteristics of the produced CBPB's and the effect of fire retardants treatment on the cement wood mixture curing using advanced analytical techniques (TGA, SEM, XRD, DMA)

Research methodology

Part I: Primarily tests

In this part, primarily tests were conducted to collect some information on the chosen fire retardants and their effect on fire resistance of wood and cement curing.

Materials

Borax ($Na_2B_4O_7$) 25 g/l of concentration, DSHP (Na_2HPO_4) 25 and 77 g/l, DAHP ($(NH_2)_4HPO_4$) 25 and 300 g/l and finally PEG 400 were used as fire retardants on two wood species Scot spine (*Pinus sylvestris*) and poplar hybrid I214 (*Populus cv. euramericana I214*). For hydration test, Portland cement CEM I 42.5 N, and Sodium Silicate (Na2SiO3) with density of 1.09 g/m^3 were used.

Description of used experimental methods

Surface roughness

CBPB is made of cement and wood particles which are rough, it was decided to take the surface roughness into consideration as influencing factor on FR's performance. Scot's pine and poplar were cut into specimens with (250x90x10) mm and separated into 3 groups to be prepared with sawn, planed, sanded surfaces. Surface roughness test was made and the P profile has been evaluated based on R_a, R_z, R_{max}.

Wettability test

Sawn, planed and sanded specimens of Scots pine and poplar were prepared with dimension (250x90x10) mm. Prior to testing, specimens have been conditioned at room temperature of 20 °C and RH of 65 % until reaching constant weight of 6.1 %. Since FR's were used as test liquids and no literature data was found (liquid tension) of FR's, the wettability was evaluated based on the FR's droplet spread on wood surface via contact angle measurement.

Fire tests

Three fire tests were chosen to investigate the fire resistance of the selected FR's on Scots pine and poplar. The single flame source test to investigate the fire spread, Lindner and calorimeter test to check the smouldering.

For Linder test, Sawn, planed and sanded poplar and Scot's pine were cut into specimens of (100x100x10) mm. Specimens were kept at a room temperature of 20 °C with a relative humidity of 65 % for 24 hours. Subsequently, the surface of each of the species was treated by spreading 5 g

of each fire retardant with a brush. Specimens were allowed to dry for 24 hours in an ambient room condition. Later, test was made based on MSZ 9607/1-83. For the single flame source test, preparations and treatment was similar as Linder test only specimens' dimension is different (250x90x10) mm. The single flame source test was accomplished according to standard MSZ EN ISO 11925-2:2011. Calorimeter bomb test MSZ EN ISO 1716:2011, was made with hammer-milled particles of poplar and Scots pine that soaked in FR's and kept in RH = 65 % and T = 20 °C.

Hydration test

Since no information was found on FR's effect on cement curing a hydration test was made in order to register the temperature change of the first 24 hours of cement curing. Cement mixture were created with the use of Portland cement CEM I 42.5 N, Sodium Silicate (SS) and the FR's (Borax, DSHP 25 g/l, DSHP 77 g/l, DAHP 25 g/l, DAHP 300 g/l, PEG 400). In total, 7 groups of mixture were generated, one for each FR and one as control.

Part II: CBPB's tests

Wood particle extractives and size distribution

Since wood particles of poplar and scots pine was not hammer-milled with the same equipment. Sieving test was made to measure the quantitative wood particles size distribution of poplar and Scots' pine. 100 g of wood particle were passed through 7 sieves with diameter of 0.314, 0.5, 1, 2, 3, 4, 5 mm. Wood cement compatibility is based on the inhibitors content inside the wood. Sugar and tannin content measurement was done in order to confirm that the wood particles are suitable for CBPB production.

CBPB production, mat formation and processing

Three layered CBPB's were manufactured from pre-treated Scot's pine and poplar particles, the surface layers made of fine particles (0-2 mm) while core layer made with larger particles (2-5 mm). Sodium silicate was used as additive to increase the cement wood compatibility first with 2 %, then 5 % of the cement weight. A mixture of Polydiallyldimethylammonium chloride + Montmorillonite (PDDA and MM) were used as well with different amount 0.2 % and 20 % of the cement weight.

Mechanical properties

After 15 days of CBPB's curing, all produced CBPB's were cut and tested according to CBPB's requirements **MSZ EN 634-2:2007**, the following standard test and requirements were made:

- Testing of flexural strength and flexural elasticity factor: MSZ EN 310
- Tensile strength test perpendicular to the leaf plane: MSZ EN 319
- Determination of thickness swelling after soaking: MSZ EN 317

Fire properties

Based on the euro class system the following standardized tests were adopted:

- Fire technical testing of building products – non combustibility: EN ISO 1182
- Fire technical testing of building products – ignitability test: EN ISO 11925-2

Characterization methods used for testing specimens

The comparaison of cement wood bonding between the diffrent CBPB's were made using (SEM) images and the crystaline phases within CBPB were observed based on (SEM and XRD). Thermal gravimetric Analysis (TGA) were performed to examine mass loss in temperature range from room temperature to 950 °C in order to to specify the transformations of the cement phase to compare it to the mechanical properties. Dynamic mechanical analysis (DMA) was conducted to study the effect of temperature on mechanical properties of the produced CBPB's.

Experimental analysis for tests

Part I: Primarily tests

(R) Software was used to conduct experimental analysis for surface roughness and wettability tests. t-test was used with a 95 % confidence interval to determine significant diffrences within means based on the propability of p-value ($P < 0.05$). Dot plot observation was made to identify

outliers. Descriptive statistics analysis with (Statistica software) supported the observations. In some cases, normal distribution was violated and a few extreme outliers were detected and deleted. Factorial analysis of variances (ANOVA) was conducted for Linder, calorimeter bomb and the single flame source tests in order to show effect sizes of input variables.

Part II: CBPB's tests

Using statistica Software, the analysis of variance (ANOVA) was performed with a 95 % confidence interval to determine significant diffrences within means based on the propability of p-value ($P < 0.05$). Mehcanical properties analysed in 3 ways, via Nested ANOVA were additives types form a group and the four additives amount levels form two subgroups, Main effect ANOVA (MANOVA) by using only two, namely low and high levels of the variable "Amount" regardless of the type of additives and finally full factorial ANOVA. Non-combustibility test results analysis was performed with one-way ANOVA, Main and full factorial ANOVA.

Results

Surface roughness of poplar was found higher than of Scots' pine. Wettability test results on sanded, sawn, and planed poplar I214 solid wood surfaces showed that poplar's wettability is worse than of Scots pine, contact angle values of poplar have been significantly higher. Increase of FR's concentration decreases the wettability of poplar while has no influence on scots pine wettability. Significant effect of machined surfaces was observed on poplar with high concentration of additives, indicating that roughness has a strong influence when the amount of the FR is high. For fire tests results demonstrate poplar achieved the best fire resistance. As fire retardants, DAHP and DSHP with 300 g/l and 77 g/l of concentration obtained the best results in both wood species. Borax displayed excellent flame spread prevention qualities. wettability was found inverse proportionate to fire retardancy. This contradicts the original presumption "good wetting gives good fire retardancy".

FR's have strong effect on cement hydration, based on hydration test, Borax has no influence on cement curing while PEG 400 prevent cement from curing. DAHP and DAHP with 25 g/l concentration showed slight delay in hydration time. In other hand, DAHP with 300 g/l and DSHP with 77 g/l caused a peaks rise in the first 3 hours for DAHP and 1.5 hour for DSHP with

temperature peak of 34 °C for DAHP while similar to control specimens for DSHP with temperature 28 °C.

Based on all results it was decided to use only high amount of fire retardants. However, DAHP 300 g/l had stronger effect on CBPB curing than expected for this reason it was reduced to 150 g/l. Sieving test showed that poplar has larger particles than of scots pine. Both wood species found suitable for CBPB with 0.5 % of sugar content. Tannin content of scots pine found higher than of poplar. For scots pine it was 0.45 % while for poplar 0.25 %.

Based on standard tests EN 310, EN 317 and EN 319 for physical and mechanical properties of CBPB's, fire retardants reduced the mechanical properties of CBPB's. The type of additives and kind of pre-treatment in the case of both the Scots pine based and poplar-based panels has direct influence of CBPB's, with the exception of the thickness swelling of the panels made from Scot's pine particles.

Using additives with 2 % of cement weight for SS and 0.2 % of cement weight for PDDA+MM was sufficient for curing control samples were not enough for pre-treated CBPB's. However, SS is a good additive with use of 5% of cement weight for Borax and DSHP 77g/l with both wood species, while having a negative effect on DAHP 150 g/l and scots pine control samples. In other hand, PDDA+MM has good influence on the mechanical properties of the CBPB with 20 % of cement weight on DSHP 77g/l and DAHP 150 g/l while negative effect on Borax pre-treated CBPB's. The DAHP 150 g/l with both additives at high amount and Borax with PDDA+MM as additive with 20 % of cement weight on poplar have positive effect of decreasing the TS to almost 0.5 %.

Fire retardants has no significant influence on the increase of fire resistance of scots pine based CBPB except for DAHP 150 g/l with PDDA+MM while has a significant influence on poplar based CBPB. The used additive showed significant effect in both cases Scots pine and poplar based CBPB. The interaction of pre-treatment and additive not significant in case of scots pine while significant in case of poplar based CBPB. Interaction of pre-treatments with PDDA+MM has better effect on fire resistance of the CBPB than of SS. Fire retardants pre-treatments for wood particles used in CBPB production proved as effective pre-treatment to increase the fire resistance of wood. In addition, it could predict the performance of the FR's

pre-treatment based on its influence on wood species. DAHP 150 g/l has increased fire resistance of CBPB's and upgrade the fire classification of poplar based CBPB from B-s1, d0 to A_1 with SS as an additive with 5% amount or with PDDA+MM with 20% amount and CBPB was soaked into SS solution.

TGA test results came compatible with mechanical and fire test results. XRD patterns and SEM images show that no new phases appeared in the CBPB's. DMA proved that temperature have negative influence on the CBPB's. For both wood species, poplar-based panels have higher loss modulus than of Scots pine-based panels that means that specimens with highest MOR have highest elasticity properties.

Main conclusions of the research

The research summarised below indicate the achievements as well as implications.

1. Several FR's have been tested in order to find the most convenient ones for improving the fire resistance of poplar and Scots pine. poplar's wettability was found significantly worse than of Scots pine, irrelevant from machining type relative to Scots Pine. With increasing concentration of the FR, the wettability of poplar gets worse, whilst the wettability of Scots pine remains mostly unchanged and the contact angle values of sanded, sawn and planed poplar surfaces are significantly different, indicating that roughness has a strong influence when the concentration of the FR is high**. [FZB-JP-1], [FZB-JP-4], [FZB-CP-1], [FZB-CP-2]**

2. Wettability has been found to be invers proportionate to fire retardancy. This contradicts the original presumption "good wetting gives good fire retardancy". I can state that good wetting FR, doesn't result good fire resistance. **[FZB-JP-1], [FZB-JP-4], [FZB-CP-1], [FZB-CP-2]**

3. Hydration test, proved that FR's and their concentrations have strong influence on the cement hydration. Test results showed that, PEG 400 is not suitable for CBPB production it doesn't allow cement to cure even after months of cement curing. In other hand, borax showed same behaviour as control samples that indicate it has no effect on cement curing hydration process. However, for DAHP and DSHP with 25 g/l slight prolongation of hydration time was observed. The increase in

concentration for DAHP to 300 g/l and DSHP to 77 g/l led to a faster rise in the peaks in the first 3 hours for DAHP and 1.5 hour for DSHP **[FZB-JP-4], [FZB-CP-4]**

4. Based on standard test EN 310, EN 317 and EN 319 for physical and mechanical properties of CBPB's, Fire retardants have significant negative influence on the properties of the CBPB and are significantly influenced by the type of additives and kind of treatment in the case of both the Scots pine and poplar-based panels, with the exception of the thickness swelling of panels that made of Scots pine particles. However, with increase in the additive amount from 0.2 % to 20 % in case of PDDA+MM and from 2 % to 5 % for SS, the properties improve as well. Most of good properties achieved on poplar with DAHP 150 g/l. As example: TS on poplar DAHP 150 g/l decreased the TS to 0.68% with SS and 0.77% with PDDA+MM**. [FZB-CP-6], [FZB-CP-7], [FZB-JP-5]**

5. Based on (ANOVA), interaction between additive and treatment has strong effect. SS with 5 % of cement weight is effective with borax and DSHP and not effective with DAHP, while PDDA+MM with 20 % of cement weight is effective with DSHP and DAHP and have no effect with borax. **[FZB-CP-6], [FZB-CP-7], [FZB-JP-5]**

6. Fire retardants have no significant effect on the fire resistance of scots pine based CBPB except for DAHP 150 g/l with PDDA+MM while has a significant effect on poplar based CBPB. The used additive showed significant effect in both cases Scots pine and poplar based CBPB. The interaction of treatment and additive found to be significant for poplar-based panel while opposite for scots pine-based panels. **[FZB-CP-6], [FZB-CP-5]**

7. Fire retardants pre-treatments improved the fire resistance of CBPB. It could state that DAHP 150 g/l has advantage on not only increasing fire resistance of CBPB's but upgrading the fire classification of poplar based CBPB from B-s1, d0 to A_1 with 5 % of SS as an additive or with 20 % of PDDA+MM covered with SS. represent one of the measurements of sample P-DA-SS-5 %, which prove that ΔT is lower than 30 °C that make it within the standard requirement of A_1 classification. **[FZB-CP-6], [FZB-JP-5]**

8. XRD and SEM images proved that no new crystalline phases were created only the usual crystalline phases in cement wood mixture appeared such as Alite, Portlandite, Calcite, Ferrite and Ettringite. That contradict the assumption of new crystalline my form because of FR's and that is the reason that prevent cement curing. **[FZB-JP-6]**

9. DMA test indicate that temperature have negative influence on the CBPB's and high storage modulus is associated with high MOR and the inverse as well. Poplar-based panels have higher loss modulus than of Scots pine-based panels that lead to conclusion CBPB's made of poplar is more elastic than made of Scots' pine. [**FZB-JP-6].**

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List of publications

List of journal publications:

Brahmia Fatima Zohra, Tibor L, Péter György Horváth, Csiha, Csilla. (2020). Comparative analysis of wettability with fire retardants of Poplar (Populus cv. euramericana I214) and Scots pine (Pinus sylvestris). Surfaces and Interfaces, *18*: doi.org/10.1016/j.surfin.2019.100405 **[FZB-JP-1]**

Brahmia Fatima Zohra, Péter György Horváth, Tibor L. Alpár. (2020)."Effect of Pre-Treatments and Additives on the Improvement of Cement Wood Composite: A Review." BioResources 15.3, pp 7288-7308. DOI: 10.15376/biores.15.3.Brahmia **[FZB-JP-2]**

Brahmia Fatima Zohra, Péter György Horváth, Tibor L. Alpár (2020). Flame retardancy of Scots pine (Pinus sylvestris) by using polyethylene glycol 400 and phosphoric acid. *International Journal of Psy. Reh*, *24*(4), pp 507-515. DOI: 10.37200/IJPR/V24I4/PR201029 **[FZB-JP-3]**

Fatima Zohra Brahmia, Kovacs Zsolt, Péter György Horváth, Tibor L. Alpar. (2020) Comparative study on fire retardancy of various wood species by using PEG 400, phosphorus and boron compounds to use in cement-bonded wood-based products. Surfaces and Interfaces, 21: https://doi.org/10.1016/j.surfin.2020.100736 **[FZB-JP-4]**

Fatima Zohra Brahmia, Kovacs Zsolt, Péter György Horváth, Tibor L. Alpar. Influence of fire retardants pre-treatments on mechanical and fire properties of cement bonded particle board. (Submitted). **[FZB-JP-5]**

Fatima Zohra Brahmia, Péter György Horváth, Janos Madarasz, Tibor L. Alpar. Thermal and mechanical characteristics of fire retardants pre-treated cement bonded particle board. (Submitted). **[FZB-JP-6]**

List of conference papers:

Brahmia Fatima Zohra, Péter György Horváth, Tibor L. Alpár. Improve fire resistance of scots pine (pinus sylvestris) by using fire retardant. Pécsi

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Brahmia Fatima Zohra, Péter György Horváth, Tibor L. Alpár. Enhancing the fire resistance of poplar (Populus cv. euramericana I214) by using different fire retardants. The 8th Hardwood Conference- with special focus on new aspects of Hardwood utilization from science to technology. pp 118-119. 25-26 October 2018. Sopron Hungary. (Oral presentation) **[FZB-CP-2]**

Brahmia Fatima Zohra, Péter György Horváth, Tibor L. Alpár. Improve fire resistance of Date palm leaflet (Phoenix dactylifera I.). The 7th international scientific conference on advances in mechanical engineering. pp 223. 7-8 November 2019. Debrecen, Hungary. (Poster presentation) **[FZB-CP-3]**

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Brahmia Fatima Zohra, Péter György Horváth, Tibor L. Alpár. Effect of Fire retardants pre-treatments on the mechanical properties of Cement Bonded Particle Board made of Poplar hybrid I214. 9th Hardwood Conference. 9th Hardwood Proceedings: Part I. With Special Focus on "An Underutilized Resource: Hardwood Oriented Research" Sopron, Hungary (2020) 304 p. pp. 57-63. (Oral presentation) **[FZB-CP-7]**