Advanced wood cement compatibility with nano mineral

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Abstract - Conventional utilization of wood concerning cement are formworks. Wood was always preferred as formworks at building grounds because of its natural advantages: like availability, easy to work with it, it can be easily removed and reused after setting of concrete. Most wood species are more or less not compatible with cement hydration.
Hydration and so final strength of WCC is sensitive on wood extractives. Water dissolves water soluble chemicals of wood - some of these are inhibitors: hemicelluloses, sugars, tannins. The process of inhibition: sugars absorb on Alit (tricalcium silicate), creates a gel around it and water can not access it so the hydration can not occur.
In our research new additives were applied to increase the joining powers between wood (Populus spp.) and portland cement, so the strength of the final product. The applied additive was montmorillonite nano particles and PDDA to modify the surface charge of wood fibers. The results of comparison tests were very satisfying, the increase of bending strength was above 20%.

Keywords: cement bonded wood composite / nano mineral / surface charge

1. INTRODUCTION

Wood cement products are produced and used since 1895. The most known product types are wood wool (excelsior) boards, cement bonded particle boards, fiber cement products or building blocks. All have both advantages like stable against bio degradation, good fire resistance, no formaldehyde emission and disadvantages like longer pressing time (slow curing), high density (weight), not every wood species are compatible with cement (ALPAR 2000). In Hungary wood wool insulation boards are produced exclusively from I-214 poplar (Populus euramericana cv. ‘I-214’) and cement-bonded particleboard made from Scotch pine (Pinus sylvestris).

The main problem is when producing cement bonded wood composites (WCC) the incompatibility between cement and wood. Cement is set up of so called clinker minerals like Alit (tricalcium silicate), Belit (dicalcium silicate), tricalcium aluminate and tricalcium aluminate ferrite, which are creating calcium silicate hydrates when adding water during an exothermal reaction (BALAZS 1987). Hydration and so final strength of WCC is sensitive on wood extractives. Water dissolves water soluble chemicals of wood - some of these are inhibitors like sugars (eg. hexoses: mannose, glucose) and tannin and hemicellulose (eg. glukomannan, xylan, arabinogalactan, galactan), and these are hindering or stopping this hydration of cement. Sugars absorb on surface of Alit, creates a gel skin around it and water can not access the clinker particle

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(LIEBER AND RICHARTZ 1972). Smaller amount of hemicelluloses (0.1%) also decreases significantly the curing strength of cement and has great influence on hydration properties. Miller et al. also assessed that pentoses (xylose, arabinose) has less effect on hydration of cement. They could determine that 1% increase of hemicellulose results 50% drop on strength and 1% increase of sugar 50% drop on strength (MILLER AND MOSLEMI 1991). Hence pH value of cement is 9, basic, hemicellulose dissolves to water soluble monosaccharides by peeling reaction (SCHUBERT ET AL 1990). Broad leaves species has higher total amount of mono-, di- and polysaccharides than conifers, so these are less suitable for WCC production. Cements hardening and curing could be accelerated by injection of CO_2 or in most common technologies by adding different additives as curing agents (ALPAR ET AL 2004). Common additives are magnesium chloride ($MgCl_2$), calcium chloride ($CaCl_2$), water glass (Na_2SiO_2), aluminum silicate ($Al_2(SO_4)_3$) or silica fume (ALPAR 2009). ALPAR AND RACZ (2009) compared Scots pine and I-214 poplar when producing cement-bonded particle board by using different additives: $CaCl_2$ and Na_2SiO_2. The calcium chloride was combined with calcium formate and resulted higher strength values in case of both species. DEL MENEÉIS ET. AL. (2007) produced cement-bonded OSB from pine (Pinus tadea) and Portland cement by mixing them 1:1. Cement was partly substituted by silica fume in a ratio of 0%, 10% and 20%. Best results were shown in case of board with substituted cement by 10% of SiO_2. Besides increase of strength values he most important result was the elimination of inhibition effect of wood on cement hydration.

Different wood species are containing different kind and in different amount hemicelluloses and sugars, so they have different effect on hydration. Already in 1964 SANDERMAN ET AL. analyzed more than 90 wood species regarding their effect on cement hydration. Since in Hungary the the ratio of poplar is above 13% (Annual report of Central Agricultural Office 2010) it is an important resource for veneer, plywood, particleboard, wood wool board production, packaging and energy industry. There are above 30 clones of poplar in Hungary, many of them developed by Hungarian Forestry Research Institute (TOTH 2006). As mentioned I-214 polar is the only suitable raw material for wood wool board production but in many cases forestries doesn't even know exactly what clones were harvested, and if a not adequate supply occurs the board company creates uncured insulation boards. To find a satisfying solution on timber delivery by chance cement compatibility os poplar clones and possible curing agents should be tested in research. KLASZ (2008) specialized on testing hydration temperatures, total sugar content and tannin content of 20 poplar clones. During this research five more potentially suitable poplar clones were determined for WCC production.

Still producers has problems with some unsound lots of supplied logs. Hence poplar is a typically species with wet heart wood (heart wood's moisture content can be 50-100% higher than that of sapwood) it may occur fungi attack (like brown rotting where cellulose and hemicellulose id decomposed by fungi) in heart wood (MOLNAR 2006). Based on the above introduced results and on the industrial needs experiments with new additives were evaluated to develop a stable composition for wood wool board production even with partly unsound poplar logs.

2. MATERIALS AND METHODS

The Hungarian wood wool company (Knauf Insulation Ltd.) produces heat insulation boards exceptionally from I-214 poplar (Populus x euramericana 'I-214'). Their suppliers provide in some cases unsound logs where fungi attach can be noticed after 1-2 months of storing. In these cases the heartwood of poplar turns into reddish color. The fungus of brown rotting decomposes cellulose and hemicellulose into simple sugars, which works as inhibitors for cement hydration.

In this research sound an unsound I-214 poplar was selected for testing with new additives. Also conventional additives were tested as control materials.

Magnesium chloride ($MgCl_2$) has double role during cement-bonded board production. On one hand it accelerates hydration, so decreases the chance to absorb sugars on Alit, on other hand it increases the initial strength of cement. $MgCl_2$ is used in a mixture with Ca-formate in a ratio of 1:3 in watery solution of 4%. Ca-formate is added to decrease corrosive behavior of $MgCl_2$ (in the following: MC).

Montmorillonite is a clay mineral:

$$n\,(Ca, Mg)O.Al_2O_3.4SiO_2\,.H_2O + +x\,H_2O \tag{1}$$

Its crystal structure is built up from an octahedron hydrargillit [aluminum-hydroxid $Al(OH)_3$] layer between two tetrahedron Si-O grid. Montmorillonite has strong alkalic substitution ability, it has significant negative charge surplus. Its specific surface is 750 m^2/g, and it can absorb water 20-30 times as much as its volume (ASSELMAN AND GARNIER 2000). PDDA or poly(diallyldimethylammonium chloride) is a charge substituter. It is a cationic polymer with high charge density, which gives the ability of good flocking (MARCELOA ET AL 2005). Both PDDA and montmorillonite were newly applied in such use with wood-cement composites. The cement was commercial Portland cement, type CEM I 42.5 based on EN 197-1.

During this research total sugar content and tannin content of both sound and unsound poplar were determined by analytical methods. Tannin content is determined by hot water extraction: 10 grams of wood particles were boiled in 200 cm^3 distilled water for 30 minutes. After filtering the extraction 0.7 grams of lead-acetate were added and from sedimented precipitate the amount of tannin was determined. The maximal allowed amount of tannin is 0.4% on oven dry wood. Total sugar content is determined after precipitation of tannin. After addition of sulphuric acid the further precipitate was filtered and than another extraction was made in boiling water for 30 minutes (wood sugars are reduced to monosaccharides). PH value of this solution was set to 8-9, and 1 cm^3 Fehling-solution was added. Further 2 minutes boiling was needed than. If after boiling the color of solution turns into blue the wood has less total sugar content then 0.5%, which is considered acceptable for WCC production.

Also pH value of wood was measured by a Mettler Toledo EL-20 pH meter after 10 minutes of hot water extraction.

On small samples hydration temperature was measured for different recipes of raw materials. Hydration temperature was measured by an AHLBORN 8590-9 type digital data receiver, which contains 9 input channels. There was used NiCr-Ni thermocouples, which has a measuring range of -25°C ... +400°C. Sampling cycle was set to 10 minutes and total measuring time was 24 hours. The evaluated properties were T_{max} - maximal temperature, t_{Tmax} - time to reach T_{max}.

Recipes for sound an unsound I-214 poplar are shown in Table 1.

Table 1. Recipes for hydration test on sound and unsound I-214 poplar

Mark sound	Mark unsound	Wood [g]	Cement [g]	TDMC1 [g]	MC2 [%]	MM3 [%]	PDDA [%]	Water [%]
S0	U0	10.4	22.1	32.5	37.0	-	-	-
S1	U1	10.4	22.1	32.5	37.0	0.05	-	-
S2	U2	10.4	22.1	32.5	-	0.05	-	37.0
S3	U3	10.4	22.1	32.5	-	-	0.05	37.0
S4	U4	10.4	22.1	32.5	37.0	0.05	0.05	-
S5	U5	10.4	22.1	32.5	37.0	-	0.05	37.0
S6	U6	10.4	22.1	32.5	-	0.05	0.05	37.0

Notes: 1: Total dry matter content, 2: 1:3 mixture of magnesium-chloride and calcium-formate in 4% of water solution, 3: montmorillonite

Experimental wood wool boards were also made in laboratory. Wood wool was prepared by Knauf Insulation Ltd. in technological condition and provided to our institute. Boards with dimensions of 400 mm x 400 mm x 25 mm were made in a Siempelkamp laboratory press on room temperature, where specific pressure was 2.56 MPa and pressing time was 24 hours. After pressing the boards were stored for further 14 days before testing. The desired board density was 400 kg/m^3.

Recipes for experimental boards were the same as in case of hydration tests shown in Table 1, but recalculated for the desired volume and density.

Bending properties of boards were tested based on standard EN 310. Factory requirement for bending strength (MOR) is ≥ 1.0 MPa.

3. RESULTS AND EVALUATION

Tannin and total sugar content results of sound and unsound I-214 poplar are shown in Table 2. In case of sound poplar both average and maximal tannin content is below requirement (0.4%). Regarding sugar content average value is slightly above requirement (0.5%), and maximal value was 0.7%. Still less then 25% of the samples exceeded the 0.5% limit, which is acceptable, because in an global mixture of logs there is no effect of these exceeds on hydration.

Table 2. Tannin and sugar content of sound and unsound I-214 poplar

	Sound I-214			Unsound I-214		
	Tannin [%]	Sugar [%]	pH	Tannin [%]	Sugar [%]	pH
Average	0.17	0.51	8.1	1.7	1.39	6.69
St.Dev.	0.0259	0.0759	0.0989	1.6104	0.9366	0.6845
Max	0.25	0.7	8.32	4.6	3.0	7.45
Min	0.15	0.4	7.9	0.15	0.5	5.6

In case of unsound poplar with red heart wood the average tannin content is four times higher than required. The maximal value was even as high as 4.6%. 65% of the samples have exceeded the requirement. Also average sugar content of these samples were almost three times higher than the required value, and minimal value was at the limit. 90% of the samples exceeded the requirement. PH value of unsound wood was found slightly acidic contrary to the sound wood which was a bit basic.

Hydration test of small samples were unfortunately unsatisfying in case of unsound wood. Neither the $MgCl_2$ nor the combination of PDDA and montmorillonite did not conclude to success. Results and observations are shown on Table 3. In the following only results of sound samples will be evaluated.

Table 3. Results of hydration tests

Mark sound	Rating[1]	T_{max}[2]	T'_{max}[3]	Cured	Mark unsound	Rating[1]	T_{max}[2]	T'_{max}[3]	Cured
S0	9	31.8	31.8	Y	U0	1	24.1	22.1	N
S1	8	31.6	31.6	Y	U1	1	24.2	22.4	N
S2	8	31.2	31.5	Y	U2	2	26.1	23.6	N
S3	7	31.6	31.7	Y	U3	0	21.8	21.4	N
S4	10	31.6	31.6	Y	U4	0	21.9	21.5	N
S5	6	31.6	31.6	Y	U5	0	21.6	21.2	N
S6	10	31.8	31.8	Y	U6	0	21.7	21.3	N

Notes:
1: rating of consistency of sample from 0-10 (10 is best)
2: maximal hydration temperature in the first 4 hours
3: maximal hydration temperature between the first 4 and 20 hours

On Figure 3. hydration temperature curves are shown, which are very close to each other. An intensive initial peak in the first 30 minutes is followed by a resting stage in the next 1,5 hours. After this starts an exothermal period which reaches its maximum after further 8 hours. This maximum is practically the same as the initial was. Also the results in Table 3. shows the same values for T_{max} and T'_{max}. The 'Rating' column contains observations evaluation, the rating from 0-10 shows the consistency, the hardness of the samples (10 is the best, 0 is uncured). There are no significant differences between the hydration temperature measurement results of different sound samples, so visual and manual observations were done to determine the effect of additives on hydration, which is valued by rating.

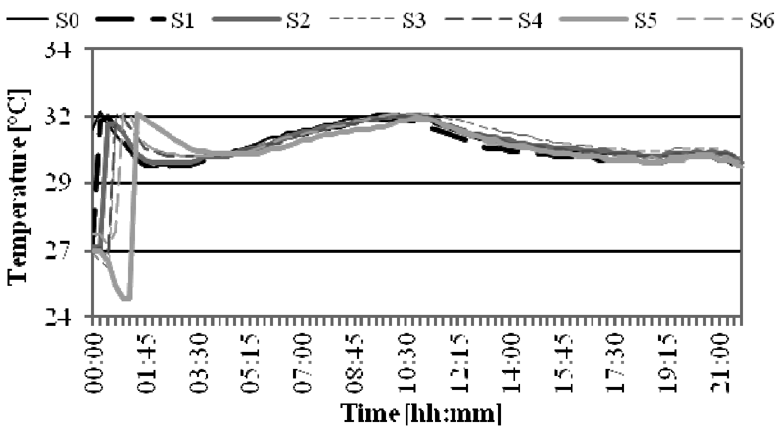

Figure 3. Hydration temperature curves of sound I-214 samples

Every sound samples were cured well, still a top list could be set up. Using montmorillonite alone or with MC performed slightly weaker than the control sample with MC. Weakest were samples made with PDDA itself or in combination with MC. Best results were reached by use of montmorillonite and PDDA. Further advances were not observable when also MC was added, so it is unnecessary besides montmorillonite and PDDA.

As conclusion for hydration tests on small samples the combined utilization of montmorillonite and PDDA was found the best.

When producing experimental boards, those made from unsound wood did not cured well, still in case of use montmorillonite with PDDA together 1.2 MPa MOR could be reached. Other samples where montmorillonite and PDDA was not or was separately used no measurable strength was found.

Bending strength results of samples made from sound I-214 poplar are shown in Table 4.

Table 4. Statistical results of MOR of sound I-214 poplar

Sample	S0	S1	S2	S3	S4	S5	S6
Mean of MOR [MPa]	3.62	2.89	2.94	2.27	4.82	1.86	4.79
St.dev.	0.5042	0.6321	0.7036	0.6901	0.5624	0.4518	0.7702
Sample numbers [pcs.]	24	24	24	24	24	24	24

The results of experimental boards showed similar trend as the observations of hydration tests. All samples has fulfilled the factory requirement of $\geq$ 1.0 MPa. Boards with montmorillonite and PDDA featured the best performance. PDDA as a charge substitute helped to join montmorillonite nano particles to wood surface so during hydration of cement a better connection could be established between the two main raw materials.

4. CONCLUSIONS

Concluding the basic findings of the research are:

- There are differences in tannin content, sugar content and pH between sound and unsound I-214 poplar wood.
- None of the additives tested improved hydration test results in case of unsound poplar wood.
- Montmorillionite – PDDA additive combination gave the best results in bending tests of samples made from sound poplar wood, improving MOR more than 20% compared to control samples.
- Although none of the additives affected the hydration results, samples made from unsound poplar wood using the montmorillionite – PDDA additive combination met the minimum factory requirement for MOR of $\geq$ 1.0 MPa.

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