Composites Part B 84 (2016) 25–32

Contents lists available at ScienceDirect

Composites Part B

journal homepage: www.elsevier.com/locate/compositesb

Influence of wood treatments on mechanical properties of wood–cement composites and of Populus Euroamericana wood fibers

A. Quiroga [a], V. Marzocchi [b], I. Rintoul [c, *]

[a] Universidad Tecnológica Nacional, Facultad Regional Santa Fe, Lavaise 610, S3004EWB Santa Fe, Argentina
[b] Instituto de Tecnología Celulósica, Universidad Nacional del Litoral, Santiago del Estero 2654, S3000AOJ Santa Fe, Argentina
[c] Instituto de Desarrollo Tecnológico para la Industria Química, Universidad Nacional del Litoral, Consejo Nacional de Investigaciones Científicas y Técnicas, Ruta Nac.168 Km 472 Paraje "El Pozo", S3000GLN Santa Fe, Argentina

ARTICLE INFO

Article history:
Received 15 September 2014
Received in revised form
19 May 2015
Accepted 22 August 2015
Available online 2 September 2015

Keywords:
A. Ceramic–matrix composites (CMCs)
A. Foams
A. Wood
B. Mechanical properties

ABSTRACT

Wood–cement composites are interesting materials for structural and isolation purposes. Dimensional stability, economic factors and resistance to environmental degradation are features that can be exploited for housing components. The main inconvenient affecting its manufacture is the incompatibility between wood and cement, caused by setting inhibitory substances present in woods. Wood treatments are multivariable processes required for the appropriate cement setting reaction on wood surfaces. Treatment conditions affect the mechanical properties of the resulting composites. This work evaluates the simultaneous influence of the variables ruling three widely used wood treatments – water extraction, degradation by alkaline hydrolysis and retention of inhibitory substances – on the mechanical properties of wood fibers and of resulting wood–cement composites. Populus Euroamericana wood fibers and Portland cement were selected as case materials. The alkaline hydrolysis was found as the most effective treatment for the suppression of inhibitory substances and the highest decrease on mechanical properties of resulting composites. Empirical relationships describing the dependence of the compressive modulus of elasticity and compression strength of wood–cement composites with the wood treatment variables are presented.

1. Introduction

Housing deficiency has continuously grown during the last years in South America. Thus, the need to develop alternative materials for rapid construction methods has become an important factor for social development. This is especially important in Argentina, Brazil and Chile, where regional based materials are now investigated for rapid housing construction under emergency situations such as floods and earthquakes.

Wood–cement composites (WC) are interesting materials due to their high durability, dimensional stability, toughness, fire resistance, good acoustic and thermal insulation properties, resistance to biological degradation, rapid production and low production costs [1,2]. Since more than 100 years, boards made of WC have been widely used for various housing components in Europe and the United States [3], due to the quite short time for housing assembly. In South America, conventional building materials such as ceramic brick have been always preferred for housing construction industry. Therefore, the knowledge of local raw materials and resulting WC is rather limited, impairing its production at industrial scale. Cultural issues coming from south European immigration, great clay deposits near the urban centers and abundant and cheap energy resources for brick kilns can be listed as the main reasons for the historic preference of ceramic brick [4]. However, the increment of energy and logistic costs and the need of rapid construction technologies to cover the increasing growing rate of urban centers can be identified as the driving forces for the exploration of alternative sustainable building materials made of renewable resources [5]. At the global scale, the climatic and tectonic catastrophes such as the Katrina hurricane in 2005, the tsunamis in Southeast Asia in 2004 and 2006 and the earthquakes in Haiti and Chile in 2010, have pushed the improvement and

Abbreviations: CA, coating agent; CS, compressive strength; C MOE, compressive elasticity modulus; H_2O/W, water–wood fiber ratio; *T*, temperature; *t*, time; T MOE, tensile elasticity modulus; WC, wood–cement composites; W, wood fibers; Y, property, response.

* Corresponding author. INTEC UNL-CONICET, Ruta Nac.168 Km 472 Paraje "El Pozo", S3000GLN Santa Fe, Argentina. Tel./fax: +54 342 4511370x1100.
E-mail address: irintoul@santafe-conicet.gov.ar (I. Rintoul).

http://dx.doi.org/10.1016/j.compositesb.2015.08.069
1359-8368/

development of building materials for rapid reconstruction of densely populated areas under disaster conditions [6,7].

The need of rapid construction and the sustainability of the industry of building materials require high production wood rates. This can be achieved by selecting fast growing tree species and the implantation of intensive forestation fields in tropical humid areas. In these conditions, trees may grow more than 1 m per year [8]. However, as cellulose is actually a polysaccharide, the faster the tree growth, the higher the concentration of sugars and hemicelluloses in the growing wood [9]. Sugars and hemicelluloses are setting inhibitory substances and therefore, responsible of the well-known incompatibility of wood and cement. This problem has been subject of many studies, especially for European and North American woods [10–14]; however there is a lack of knowledge concerning South American woods. The presence of inhibitory substances promotes the formation of impermeable membranes around non-hydrated cement grains, impairing the water access into them [15–17]. This undesirable phenomenon causes a reduction of the material cohesion. Moreover, it implies an extra challenge to optimize wood treatments for minimizing the inhibitory effects of extractives naturally present in woods during cement setting in the production of WC [18]. It has been proved that the nature of the extractives determines the extent of the inhibitory effect [19]. In general, the grade of setting inhibition depends on the amount and type of sugars. For example, fructose does not affect cement setting up to concentrations of 0.50% [20], while glucose inhibits completely this process with concentrations of 0.25% [20]. Conversely, some sugars such as raffinose can even improve the properties of the cement at concentrations up to 0.125% [21]. Calcium lignosulfonate with high contents of mannose, glucose, galactose, xylose and arabinose was found to short the setting time of Portland cement [22]. Aliphatic sugar alcohols and sucrose at very low concentrations act as delayed accelerators [23]. Moreover, the addition of a large quantity of sucrose was reported to increases the mechanical properties of concrete, decreases the setting time and improves concrete behavior in water [24]. On the other hand, the addition of lignosulfonates, tartaric acid, sucrose, calcium gluconate, glucose, glycolic acid, molasses, sodium borate, sodium citrate, sodium heptonate, sodium hexametaphosphate, sodium pyrophosphate and sugar-free calcium lignosulfonate were reported to retard or even poison the setting of cement [25–27].

Different wood treatments can be applied to minimize inhibition problems, most of them based on extraction, alkaline hydrolysis and retention of sugars and hemicelluloses [28–32]. Although these treatments effectively improve the performance of cement setting on wood surfaces, each one acts in a very different way. Aqueous extraction removes inhibitory water soluble compounds [33], while alkaline hydrolysis degrades hemicelluloses and sugars into non-inhibitory substances [33]. In the retention treatment, a thin coating is formed on the wood surface and inhibitory substances are not released to the setting medium. Wood treatments may diminish the final mechanical properties of the resulting composites.

Various parameters play simultaneously during wood treatments. Particularly, process variables have cross-dependence effects on the efficiency to diminish the inhibitory nature of wood extractives. For example, immersion in cool water during 60 min greatly improved the wood–cement compatibility of rattan, however, no effect was observed in hot water [34]. Moreover, effect of the concentration of calcium chloride was enhanced by the temperature of water revealing the cross-dependence of these process conditions [35]. Conversely, only extraction in hot water was reported as efficient for the compatibility of palm fibers and cement [36]. The effect of different non-polar and high polar solvents was also studied in the extraction treatment. Normally, the extraction in hot water and polar solvents results with the highest efficiency to minimize the inhibitory effects of wood extractives [37–39]. The cross-dependence between the process parameters is also present in more sophisticated wood treatments. Reaction time, pressure and lignin, waxes and sugars contents are cross-dependent parameters when bagasse, eucalyptus and pinus wood wastes are extracted by steam in autoclave [40,41]. Fiber size, reaction time, sodium hydroxide, calcium hydroxide and fiber/Portland cement ratio also report cross-dependency during a degradation treatment [42,43]. The sugar content in the exploded fibers by degradation of the cellulose into oligosaccharides is intimately related to the conditions of the explosion treatment [44]. The cross-effects of pressure, time, temperature and concentration of gaseous CO_2 and supercritical CO_2 in the wood–cement compatibility were confirmed [45–48]. The process conditions for improving the wood–cement compatibility and stabilization of wood in the WC by heat treatments of wood were subject of study [49]. Finally, sugar cane fibers were treated with sulfuric acid to transform the cellulose fibers in cellulose sulfoacetate and to degrade and modify the inhibiting substances to non-inhibiting substances [50]. In general, the treatments result in a degradation of the wood mechanical properties. Evidently a multitude of wood treatments are still under investigation. These works suggest that the optimal set of process conditions is the result of the cross-dependence effects of the process parameters on the structure and chemical composition of the woods.

A complementary strategy to the wood treatments is the addition of inorganic chemicals to the cement paste, known as accelerators, in order to compensate the retardation induced by the inhibitory substances [30,51]. Accelerators such as calcium hydroxide and calcium chloride usually improve the properties of WC [52–55]. Exemplary, the addition of sodium silicate, aluminum sulfate, calcium silicate hydrate, fly ash, rice husk ash, active silica, latex, zinc, aluminum and iron chlorides and/or their ionic species and activated charcoal to the cement paste were reported to reduce the inhibitory effects of wood extractives and sugars [56–61].

In the present contribution, simultaneous and cross-dependence influences of the process parameters concerning different conventional wood treatments were evaluated on mechanical properties of wood fibers (W) of Populus Euroamericana harvested in subtropical forests of South America and of final WC. Water extraction, degradation by alkaline hydrolysis and retention of inhibitory substances were evaluated. Tensile tests of W and compression tests of WC were performed for the evaluation of the mechanical behavior. Resulting data were analyzed using experimental designs based on response surface methods [31,32,62,63]. Tensile elasticity modulus (T MOE) of W, compressive elasticity modulus (C MOE) and compressive strength (CS) of WC, were evaluated for a precise selection of the most convenient treatment to be applied to the full scale process in future trials.

2. Materials and methods

2.1. Materials

Sapwood fibers of Populus X Euroamericana CV, coming from the subtropical Northeastern of Argentina and Portland cement CPN40 IRAM 50.000 (Minetti, Argentina) were selected as case materials. Populus X Euroamericana CV is particularly fast growing tree specie that is implanted in sustainable tropical and subtropical forests of South America. The main destination of this wood is building elements and furniture [8]. Building elements and furniture use the heartwood of the trees only. Sapwood, is the growing part of the tree and concentrates most of sugars and oligosaccharides for the synthesis of cellulose, lignin and the other wood constituents [64]. The fast growing nature of Populus

Euroamericana in Subtropical forests promotes a high concentration of these cement setting inhibitory substances in its sapwood. Sapwood is usually discharged or burned in wood drier facilities. Sapwood, comprehences almost half of the tree's mass and is an abundant and cheap forest residue that deserves investigation as raw material for building elements.

Calcium hydroxide (Loma Negra, Argentina), a 20 wt% polyacrylic aqueous solution (Sinteplast, Argentina) and demineralized water were used for the wood treatments.

2.2. Treatments

W were treated according to three different methods: water extraction, alkaline hydrolysis and retention of inhibitory substances by coating. In the first method, W were immersed into a water bath at $T = 25$, 62.5 and 100 °C during periods of $t = 5$, 25 and 45 min. In the second method, alkaline hydrolysis was performed at room temperature immersing W into a calcium hydroxide solution during $t = 4$, 24 and 72 h and $[Ca(OH)_2] = 5.6$, 11.1 and 22.2 g/l. In the last method, acrylic styrene was used as a coating agent (CA) to form a thin film on the W surface and thus, impairing the pass of undesirable substances to the setting medium. The polymer is presented as a concentrated aqueous solution. This solution was diluted in 4 parts of water. The W was immersed during 5 min in the diluted solution. Fresh and recycled solutions of CA were tested. After each treatment, W were withdrawn from the bath and dried prior to be used in the board synthesis. Water–wood (H_2O/W) ratios were 20, 30 and 40 g/g for extraction and hydrolysis, and for coating method was fixed in 26.67 g/g.

For each treatment, all conditions were mixed up factorially. Ten different samples were prepared according to a factorial combination of H_2O/W, T and t variables for the extraction process; [CA], t and the number of uses (n) for the coating process, and $[Ca(OH)_2]$, t and H_2O/W for the hydrolysis process. Based on Taguchi experimental design methods [26,27], a system of 9 equations and 9 unknown coefficients was obtained with the experimental conditions of first nine specimens, while the tenth was reserved for control. This method is specially recommended for the study of industrial processes with a large number of variables [31,32]. Simultaneously, the repeatability of board synthesis was verified. All the test conditions are summarized in Table 1.

The Taguchi method proposes that a property or response (Y) can be expressed as a polynomial function of three variables (A, B, and C) according to equation [26,27].

$$Y = \sum_{h,k,l} a_{h,k,l} A^h B^k C^l \quad (1)$$

Here, each term of the sum is composed of an empirical coefficient ($a_{h,k,l}$) determined by a least squares fit multiplied by a group of variables powered to a non-negative integer exponent. The higher the complexity of the response to a given variable, the higher is the number of terms containing such variable and the higher is the grade of the exponents in these terms. The indexes h, k, and l are non-negative integers going from 0 to ∞. This polynomial function has infinite terms and can describe any functionality $Y(A, B, C)$. However, 9 experiments performed in different conditions give us the possibility to define a polynomial fit of 9 terms only. The selection of the 9 terms with the best fitting combination was carried out using experimentally obtained raw data and iterating using Octave software to get the best least squares fit. Octave is a free mathematical software that solve equation systems easily.

The variables A, B and C correspond to T, t and H_2O/W variables of the extraction process; [CA], t and n of the coating process and $[Ca(OH)_2]$, t and H_2O/W of the hydrolysis process. The coefficients, group of variables and exponents were obtained by least square fitting to the experimental response values of C MOE and CS for extraction, coating and hydrolysis processes conditions.

The resulting equation set was plotted as a 3-D surface in the space of variables. Subsequently, the plots could be used to conclude tendencies, behavior and responses to the simultaneous variation of the process conditions.

2.3. Board synthesis

Thirty laboratory boards were obtained using W treated according to Table 1. Preliminary trials were first done to adjust the cement paste composition. The cement paste was prepared with Portland cement and demineralized water. The higher the water content, the lower the viscosity of the resulting cement paste. The viscosity of the paste is critical to ensure a homogeneous distribution of the paste over the surface of the W. In preliminary test it was observed that if the viscosity is too low, the cement paste spills through the W and cumulate at the bottom of the mold. Conversely, if the viscosity is too high, the cement paste cannot be homogeneously distributed over the surface of the W and results in irregular lumps. In both cases, the resulting material has very poor properties. The optimal ratio between water and Portland cement was achieved by trial and error and resulted 840 cm^3 of water per 900 g of Portland cement. The dynamic viscosity of such paste was 12 Pa s. However, the water content largely exceeded the amount chemically needed for setting. The cement paste was then incorporated and homogeneously distributed in 450 g of treated W and placed into a mold of 30 × 30 × 7 cm^3 under pressure of 1.0 kg/cm^2 during 72 h. After that, the mold was opened and the obtained WC of 30 × 30 × 7 cm^3 was removed from the mold and left to complete the cement setting and drying the water excess during 2 weeks at room temperature. It is important to mention that vibration is not advisable to accommodate the mixture into the mold cavity. Vibration promotes the slipping of the cement paste to the

Table 1
Experimental conditions for extraction, coating and hydrolysis treatments.

N°	Extraction			Coating			Hydrolysis		
	H_2O/W (g/g)	T (°C)	t (min)	[CA] (l/l)	t (min)	Uses (n°)	$[Ca(OH)_2]$ (g/l)	t (h)	H_2O/W (g/g)
1	20	25	5	0.333	5	1	22.2	4	20
2	20	25	45	0.333	5	2	22.2	4	40
3	20	100	5	0.333	180	1	22.2	72	20
4	20	100	45	0.333	180	2	22.2	72	40
5	40	25	5	0.083	5	1	5.6	4	20
6	40	25	45	0.083	5	2	5.6	4	40
7	40	100	5	0.083	180	1	5.6	72	20
8	40	100	45	0.083	180	2	5.6	72	40
9	30	62.5	25	0.167	60	1	11.1	24	30
10	30	62.5	25	0.167	60	2	11.1	24	30

bottom of the mold. If the cement paste is homogeneously distributed through the surface of the W, the compaction by pressuring the mold is sufficient to ensure the filling of the mold cavity. Subsequently, the samples were cut in cubes of 7 cm side, and then tested for evaluation of mechanical properties. WC synthesis using non-treated W was carried out also. The above described procedure was performed using non-treated W while keeping all the other conditions.

2.4. Individual wood fiber samples

Individual W samples were prepared according to conditions summarized in Table 1. Thirty groups of W were reserved for T MOE determinations. The average dimensions of the samples were length 160 mm, width 3 mm and thickness 0.2 mm approximately. The width and thickness of the fibers were measured using a Precision Micrometer (Testing Machines Inc., USA).

2.5. Mechanical testing

Compression trials of WC were performed in a testing machine Instron 1137 (Illinois, USA) in the direction perpendicular to molding. The C MOE and CS were determined for each wood treatment.

Individual W were tested in an Instron 3344 (Illinois, USA) machine for determination of T MOE. Thirty specimens per condition, ten conditions per treatment and three different treatments totalizing 900 T MOE measurements. Treated W were compared against non-treated samples. The cross-section areas of the W were individually calculated from thickness and width measurements. For each W sample, its cross area was obtained and used for the T MOE determination. The average cross area resulted 0.6 mm^2.

Mechanical testing was made under controlled room conditions at 23 °C and at 50% of relative humidity.

3. Results and discussion

The use of non-treated W in the synthesis of WC resulted in the complete inhibition of cement setting. The material presented is absolutely non-cohesion. It looked just like dirty WF which could be easily disaggregated by hand. This result can be explained by the high sugar and hemicellulose content of the fast growing wood used in this work. Conversely, all chemical and physical treatments demonstrated a good performance for avoiding setting inhibition. However, they have induced important changes on the mechanical properties of W and WC. Table 2 shows the experimental average T MOE of treated W; and the experimental C MOE and CS for WC produced with treated W.

In general, non-treated W presented an average T MOE of about 1200 MPa and a standard deviation (SD) of 1100. T MOE of treated samples resulted significantly increased depending on test conditions.

The high dispersion of T MOE values of W strands can be explained in terms of its own nature and its manufacturing process. Sapwood is a very heterogeneous part of the tree, its properties may greatly vary from one tree to another and from trees harvested in different parts of the forest with differential soil, humidity and insolation conditions [64]. The manufacturing process involves the separation of sapwood by debarking and sawing of heartwood. Bark, sapwood and heartwood are not perfectly concentric in the tree trunk. Therefore, sapwood may be separated dragging part of the bark and heartwood. Then, the sapwood pieces must be mechanized in strands by a blading process. Sapwood is a fibrous material. The fibers are mostly oriented according to the axial direction of the trunk and the sapwood pieces are cut following approximately the axial direction of the trunk. However, branches and knots deviates the fibers from the axial direction of the trunk and the geometrical axis of the sapwood pieces do not match perfectly with the fibers direction. Consequently, the obtained W strands presents highly dispersed properties. This dispersion, is later transferred to the treated W.

Average T MOE was about 1600 MPa with SD = 800, 1800 MPa with SD = 1000, and 2100 MPa with SD = 1100 for extraction, hydrolysis and coating treatments, respectively.

The maximum and minimum T MOE measured in 300 total specimens per treatment, were 7890–186 MPa for extraction, 7287–268 MPa for hydrolysis and 7174–203 MPa for coating. In addition, the difference between maximum and minimum T MOE measured within one sample of 30 specimens corresponding to a given test condition, could be as high as 7419 MPa for extraction, 6660 MPa for hydrolysis and 6971 MPa for coating treatment. As observed, highly dispersed values were obtained in T MOE determinations. Therefore, a very high number of specimens had to be tested in order to get reliable information about the influence of the process variables on the mechanical properties of W.

The normal dispersion on T MOE measurements was 13% for extraction, 19% for hydrolysis and 18% for coating treatment. Thus, T MOE could be considered as affected by a given process parameter when its influence resulted higher than the cited values. Based on this assumption, the increase of the H_2O/W ratio during extraction, the decrease of the immersion time during hydrolysis and the increase of CA concentration during coating treatment were considered as responsible for the T MOE increase. The rest of the variables could not be taking into account since their effects were within the normal dispersion range. The variation of T MOE may be explained by the effect of low molar mass substances on the structure and hence the mechanical properties of W. Low molar mass substances acts as plasticizer of the rigid ligno-cellulosic structure of wood [64]. Normally, when such substances are removed, the material increases its elasticity modulus. In general, the removal of low

Table 2
Experimental T MOE of W, and C MOE and CS of WC for extraction, coating and hydrolysis treatments.

N°	Extraction			Coating			Hydrolysis		
	T MOE (MPa)	C MOE (MPa)	CS (MPa)	T MOE (MPa)	C MOE (MPa)	CS (MPa)	T MOE (MPa)	C MOE (MPa)	CS (MPa)
1	1120	1.03	0.11	2488	0.89	0.09	2329	0.98	0.07
2	1579	0.82	0.07	2320	1.09	0.10	1945	0.98	0.07
3	1311	1.09	0.10	1883	0.70	0.06	1458	1.40	0.11
4	1563	0.61	0.08	2203	0.65	0.08	1684	0.75	0.07
5	1808	1.31	0.10	2357	1.09	0.13	1683	1.15	0.08
6	1617	0.89	0.10	1608	1.31	0.15	1981	1.09	0.09
7	2135	1.23	0.10	1637	0.89	0.08	1484	0.89	0.06
8	1908	0.93	0.11	1674	0.61	0.09	1828	1.03	0.10
9	1692	0.98	0.11	2322	0.70	0.07	1892	1.09	0.12
10	1206	1.09	0.11	2591	0.52	0.09	1339	1.23	0.11

molar mass substances can be favored by increasing H_2O/W ratio [65]. The effect of the immersion time could be explained in terms of the mass transfer and diffusive processes. Immediately after the raw W is immersed into the extraction bath, the water starts to infiltrate the wood. As a consequence, low molar mass soluble substances are dragged inside the wood bulk. If the W is removed from the immersion bath before the wood reaches its maximum absorption capacity, the wood surface may reduce its concentration of low molar mass substances increasing its rigidity. After the maximum absorption, soluble substances are not longer dragged and start to diffuse from the wood bulk to the wood surface recovering the initial elasticity. If the immersion time is too long, the soluble substances are released to the extraction medium and the wood increases its rigidity again. Finally, the action of the CA is hypothesized to increase the rigidity of the W by enhancing the bonding of the wood fibers. Fig. 1 may help to visualize the effects of W water extraction, alkaline hydrolysis and polymeric coating treatments on the T MOE of W strands.

Additional information about the influence of the studied variables on treated W, could be get from compressive tests of WC. In this case, hundreds of individual W were cement-bonded and formed a new whole and more uniform material.

In general, CS of WC obtained with W treated by extraction and coating was, in both cases, mostly higher than those obtained with W treated by hydrolysis. It is important to note that the CS range for extraction was constant around 0.10 MPa with slightly variations according to the experimental conditions. For hydrolysis method, although the maximum CS was achieved (0.15 MPa), the average CS was lower than the other two treatments (0.08 MPa). The average CS in the retention method (0.09 MPa) resulted slightly lower than extraction (0.10 MPa).

These observations hypothesize a decrease of W mechanical properties caused by the aggressive alkaline medium which promotes disaggregation and breaking of wood constitutive fibers and/or a diminution of the bonding capacity of Portland cement to the wood surface. Extraction and coating treatments have not affected significantly the integrity of W and/or the bonding capacity of cement to the wood surface. Thus, the mechanical properties are preserved.

The experimental $a_{h,k,l}$ coefficients to compose the response surfaces functionality of C MOE, and CS to the variables of the extraction, coating, and hydrolysis processes were build-up and presented in Table 3. The response surfaces equations of the extraction, coating, and hydrolysis processes are the most important result of this contribution.

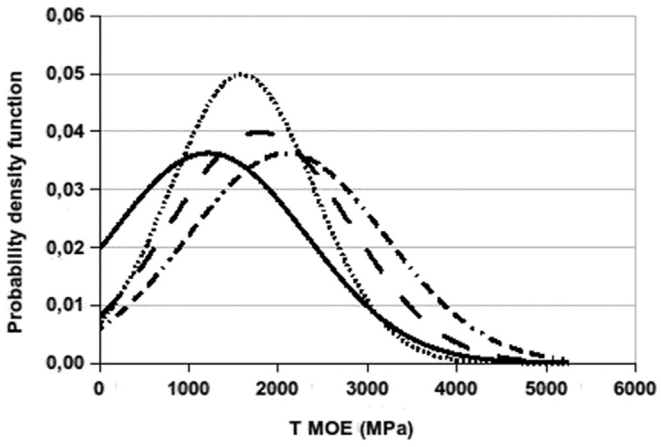

Fig. 1. Probability density distribution of averaged T MOE of sapwood strands of Populus Euroamericana non-treated (continuous line), extracted in water (dotted line), alkaline hydrolyzed (dashed line) and coated (2 dots 3 dashes line).

Clearly, all terms present individual variables. This fact confirms that the variables of the extraction, coating and hydrolysis processes act independently on C MOE and CS responses. In addition, the response of C MOE of the extraction process required grade 3 terms on the T and H_2O/W variables and grade 2 terms on the t variable. The response of C MOE of the coating process required grade 3 terms on the [CA] and t variables and grade 2 on the n variable. The response of the C MOE of the hydrolysis process required grade 4 terms on the [$Ca(OH)_2$] and grade 2 on the t and H_2O/W variables. The response of CS of the extraction process required grade 3 terms on the T and H_2O/W variables and grade 2 terms on the t variable. The response of CS of the coating process required grade 3 terms on the [CA] and n variables and grade 2 on the t variable. The response of CS of the hydrolysis process required grade 4 terms on the [$Ca(OH)_2$] and grade 2 on the t and H_2O/W variables.

Fig. 2 presents the projection of the response-surface models of C MOE and CS with T and t on H_2O/W. Fig. 3 presents the projection of the response-surface model of C MOE and CS with t and H_2O/W on [$Ca(OH)_2$]. And Fig. 4 presents the projection of the response-surface model of C MOE and CS with t and n on [CA]. Experimental results and conditions are also shown in the plots.

For the extraction treatment, C MOE increased with the increment of the H_2O/W ratio and the decrease of the immersion time. For a given time, C MOE remained approximately constant when temperature was varied from 25 to 62.5 °C. Interestingly, C MOE resulted significantly lower for conditions carried out at 100 °C than those performed at 25–62.5 °C. For hydrolysis treatment, C MOE increased with the increment of the H_2O/W ratio, with the increase of the $Ca(OH)_2$ concentration and with the decrease of the immersion time. For coating treatment, C MOE decreased with the increment of the CA concentration. However, C MOE showed slightly differences for fresh and recycled coating solution. Finally, C MOE was not affected by immersion times in the range of 1–3 h and increased significantly when immersed 5 min in the coating solution.

The variation of C MOE can be explained by variations of the concentration of inhibitory substances on the wood surface and hence on the mechanical properties of W and the bonding capacity of cement to the wood surface. Normally, when inhibitory substances are removed from the wood surface, the W increases its elasticity modulus and the setting of Portland cement on the wood surface progress without interference, developing good mechanical properties. In general, the removal of low molar mass inhibitory substances can be favored by a higher H_2O/W ratio. As before, the effect of the immersion time may be explained in terms of the mass transfer and diffusive processes which allows diminishing the concentration of inhibitory substances on the wood surface. Hence, faster cement setting and stronger bonding between cement and wood surface. The same mechanism would be applicable for hydrolysis and coating methods. The constant C MOE due to the temperature increase from 25 to 62.5 °C may be considered within the experimental error. However, the decrease of C MOE observed at 100 °C can be explained by the extended damage of wood fibers and the increment of the concentration of inhibitory substances on the wood surface. The alkaline treatment showed the highest C MOE increment. It can be supposed that the aggressive alkaline medium could degrade and extract a higher amount of soluble substances than the extraction treatment. Therefore, an increment of the mechanical properties is expected.

Finally, the coating treatment increased the retention of low molar mass substances inside the W. Therefore, the original flexibility was preserved and WC resulted with the lowest C MOE.

Table 3
Experimental surface-responses of C MOE and CS of WC for extraction, coating and hydrolysis process variables.

Extraction process

$$C\ MOE = 1.6 \times 10^{-8} + 1.9 \times 10^{-6}T - 1.9 \times 10^{-4}t - 1.0 \times 10^{-6}H_2O/W + 3.2 \times 10^{-5}T^2 + 1.4 \times 10^{-8}t^2 - 3.4 \times 10^{-5}H_2O/W^2 - 6.6 \times 10^{-8}T^3 + 4.3 \times 10^{-6}H_2O/W^3$$

$$CS = -4.9 \times 10^{-10} - 4.7 \times 10^{-8}T + 6.9 \times 10^{-6}t + 3.9 \times 10^{-8}H_2O/W + 2.6 \times 10^{-6}T^2 - 4.3 \times 10^{-9}t^2 + 1.3 \times 10^{-6}H_2O/W^2 - 5.1 \times 10^{-9}T^3 + 2.1 \times 10^{-7}H_2O/W^3$$

Coating process

$$C\ MOE = 6.4 \times 10^{-1} - 4.7 \times 10^{-1}\,[CA] - 1.7 \times 10^{-4}t + 5.2 \times 10^{-1}n - 2.1 \times 10^{-1}\,[CA]^2 + 1.2 \times 10^{-8}t^2 + 2.8 \times 10^{-1}n^2 - 7.5 \times 10^{-2}\,[CA]^3 - 1.9 \times 10^{-1}t^3$$

$$CS = 7.0 \times 10^{-2} - 9.6 \times 10^{-2}\,[CA] - 1.8 \times 10^{-5}t + 5.7 \times 10^{-2}n - 4.2 \times 10^{-2}\,[CA]^2 + 1.3 \times 10^{-9}t^2 + 3.2 \times 10^{-2}n^2 - 1.5 \times 10^{-2}\,[CA]^3 - 1.9 \times 10^{-2}n^3$$

Hydrolysis process

$$C\ MOE = 3.3 \times 10^{-7} + 1.4 \times 10^{-6}\,[Ca(OH)_2] + 7.2 \times 10^{-6}t + 1.4 \times 10^{-5}H_2O/W + 3.3 \times 10^{-6}\,[Ca(OH)_2]^2 - 2.9 \times 10^{-11}t^2 + 5.9 \times 10^{-4}\,H_2O/W^2 - 1.2 \times 10^{-5}\,[Ca(OH)_2]^3 + 4.1 \times 10^{-6}\,[Ca(OH)_2]^4$$

$$CS = 2.5 \times 10^{-8} + 1.0 \times 10^{-7}\,[Ca(OH)_2] + 6.6 \times 10^{-7}t + 1.1 \times 10^{-6}H_2O/W + 2.5 \times 10^{-7}\,[Ca(OH)_2]^2 - 2.6 \times 10^{-12}t^2 + 4.5 \times 10^{-5}\,H_2O/W^2 - 8.8 \times 10^{-7}\,[Ca(OH)_2]^3 + 3.2 \times 10^{-7}\,[Ca(OH)_2]^4$$

4. Conclusions

Water extraction, alkaline hydrolysis and coating of the wood surface are convenient technological strategies to avoid setting inhibition phenomena. However, the selection of W treatments depends mostly on the final applications of WC. The alkaline hydrolysis is recommended to obtain boards for rigid structural components such as internal walls and roofing. Contrarily, the coating method is more appropriated when elasticity properties are desired such in case of plates for acoustic insulation.

Empirical relationship for C MOE and CS of WC with T, t and H_2O/W variables for the extraction process, [CA], t and n for the coating process and [$Ca(OH)_2$], t and H_2O/W for the hydrolysis process were developed.

The influence of W treatments on mechanical properties of WC could be explained in terms of the mass transfer of low molar mass water soluble inhibitory substances between the immersion medium and the wood fibers, and hence by physical–chemical aggression to the fiber structure and the modification of the bonding properties of cement to the wood surface.

The CS of WC obtained with W treated by extraction and coating was, in both cases, higher than the obtained with W treated by hydrolysis due to a less aggressive immersion medium.

The C MOE increased with the increment of the H_2O/W ratio and the $Ca(OH)_2$ concentration. The C MOE also increased with the decrease of the immersion time and CA concentration. Temperature and number of uses of coating solution did not affect significantly the C MOE.

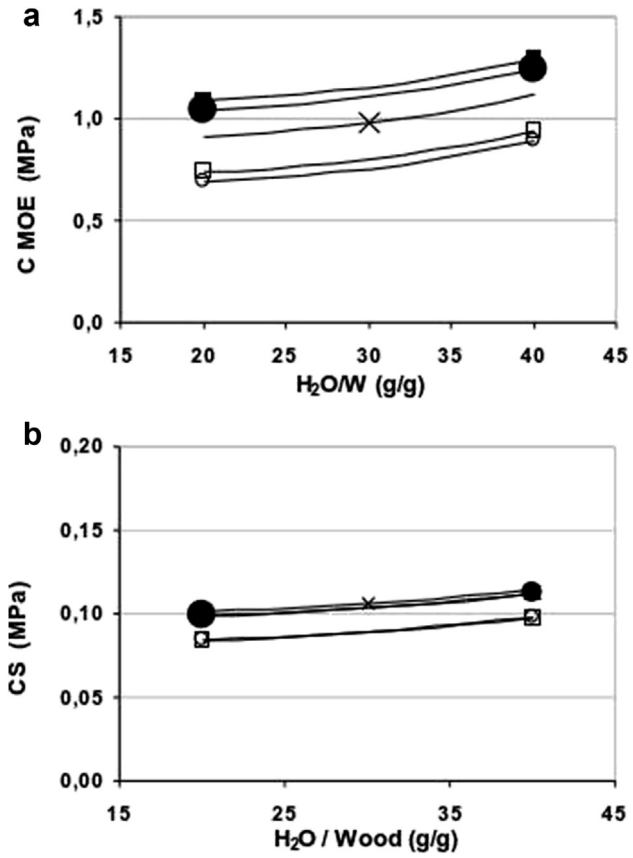

Fig. 2. Modeled surface response of (a) compressive MOE and (b) compressive strength of WCC vs. WF extraction process variables. Modeled functionality: full lines. Experimental conditions: T = 25 °C (square), T = 100 °C (circle), t = 5 min (full symbol), t = 45 min (empty symbol) and T = 62.5 °C − t = 25 min (cross).

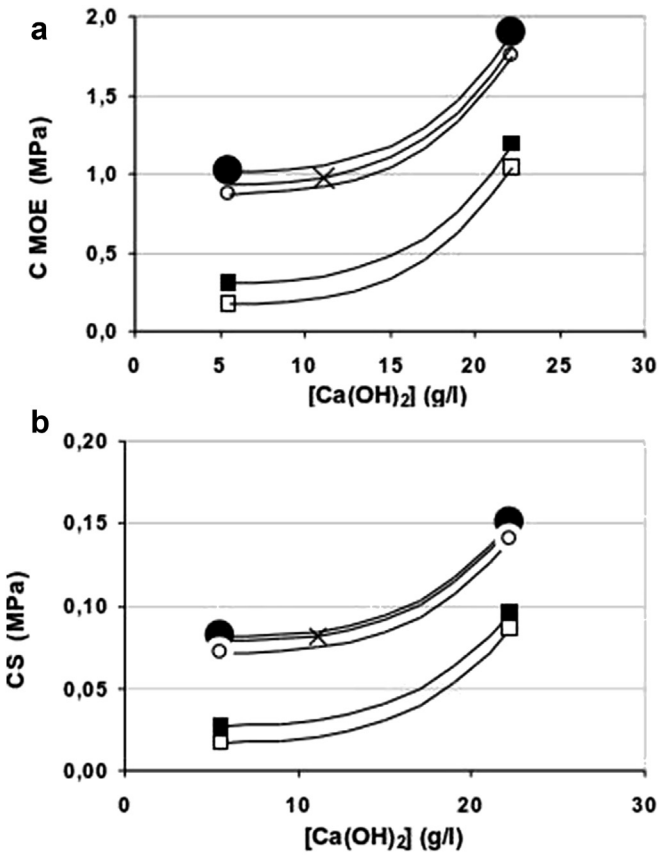

Fig. 3. Modeled surface response of (a) compressive MOE and (b) compressive strength of WCC vs. WF hydrolysis process variables. Modeled functionality: full lines. Experimental conditions: H_2O/WF = 20 g/g (square), H_2O/WF = 40 g/g (circle), t = 4 h (full symbol), t = 72 h (empty symbol) and H_2O/WF = 30 g/g − t = 24 h (cross).

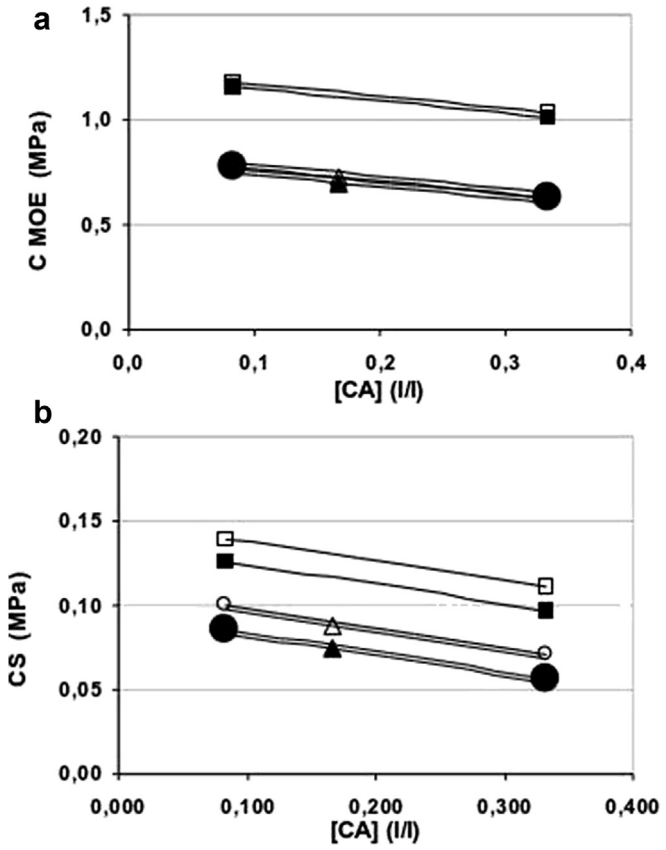

Fig. 4. Modeled surface response of (a) compressive MOE and (b) compressive strength of WCC vs. WF coating process variables. Modeled functionality: full lines. Experimental conditions: $t = 5$ min (square), $t = 60$ min (triangle), $t = 180$ min (circle), fresh coating solution (full symbol), recycled coating solution (empty symbol).

In all the cases, treated W resulted in higher elasticity modulus than non-treated W.

The highest T MOE increment was observed for coated W, followed by hydrolyzed and extracted W. The inhomogeneous nature of W prevented an accurate determination of the influence of the treatment variables on mechanical properties of individual wood fibers. A better understanding of the behavior of W tensile properties will be achieved by increasing the number of tested specimens per sample. It is also suggested to take into account the orientation factor due to tensile and shear components according to the wood grain direction in T MOE determinations.

Acknowledgments

The authors thank Adrian Yoris for the WC synthesis and Diego Marzocchi for the T MOE determinations and Cerámica Litoral for the financial support.

References

[1] Del Menezzi CHS, De Castro VG, De Souza MR. Production and properties of a medium density wood–cement boards produced with oriented strands and silica fume. Maderas: Cienc Tecnol 2007;9(2):105–15.
[2] Lee AWC. Physical and mechanical properties of cement bonded southern pine excelsior. For Prod J 1984;34(4):30–4.
[3] Van Elten GJ. Production of wood wool cement board and wood strand cement board (Eltoboard) on one plant and applications of the products. In: Proceedings 10th int. inorganic-bonded fiber composites conference, São Paulo, Brazil; 2006. p. 1–11.
[4] Bianucci MA. El Ladrillo: origen y desarrollo. Resistencia: Instituto Argentino de Cerámica Roja; 2009.
[5] Ainstein L. Urbanizacion, medio ambiente y sustentabilidad en Argentina. Cuad Urbano 2012;12(12):173–89.
[6] Transitional settlement and reconstruction after natural disasters [UN report]. Department for International Development; 2008. Coordination of Humanitarian Affairs.
[7] Abhas KJ. Safer homes, stronger communities. In: Handbook for reconstructing after natural disasters. Washington DC: The World Bank – The International Bank for Reconstruction and Development; 2010. p. 161–72 [chapter 10].
[8] Tortorelli LA. Maderas y Bosques Argentinos. Buenos Aires: Orientación Gráfica Editora; 2009.
[9] Van Soest PJ, Mertens DR. Composition and nutritive characteristics of low quality cellulosic wastes. Fed Proc 1974;33(8):1942–4.
[10] Defo M, Cloutier A, Riedl B. Wood–cement compatibility of some Eastern Canadian woods by isothermal calorimetry. For Prod J 2004;54(10):49–56.
[11] Pereira C, Caldeira F, Ferreira JMF, Irle MA. Characterization of cement-bonded particleboards manufactured with maritime pine, blue gum and cork grown in Portugal. Eur J Wood Wood Prod 2012;70(1–3):107–11.
[12] Wei YM, Guang Zhou Y, Tomita B. Hydration behavior of wood cement-based composite. I: evaluation of wood species effects on compatibility and strength with ordinary portland cement. J Wood Sci 2000;46(4):296–302.
[13] Zhengtian L, Moslemi AA. Effect of western larch extractives on cement setting. For Prod J 1986;36(1):53–4.
[14] Hofstrand AD, Moslemi AA, Garcia JF. Curing characteristics of wood particles from nine northern Rocky Mountain species mixed with portland cement. For Prod J 1984;34(2):57–61.
[15] Bruere GM. Set-retarding effects of sugars in portland cement pastes. Nature 1966;212(5061):502–3.
[16] Thomas NL, Birchall JD. The retarding action of sugars on cement hydration. Cem Concr Res 1983;13(6):830–42.
[17] Birchall JD, Thomas NL. Mechanism of retardation of setting of OPC by sugars. Br Ceram Proc 1984;35:305–15.
[18] Karade SR. Cement-bonded composites from lignocellulosic wastes. Constr Build Mater 2010;24(8):1323–30.
[19] Jorge FC, Pereira C, Ferreira JMF. Wood–cement composites: a review. Holz Roh Werkst 2004;62(5):370–7.
[20] Sandermann W, Brendel M. The 'cement poisoning' effect of wood content materials and their dependence on the chemical constitution. Holz Roh Werkst 1956;14(8):307–13.
[21] Frybort S, Mauritz R, Teischinger A, Müller U. Cement bonded composites – a mechanical review. BioResources 2008;3(2):602–26.
[22] Wang X, Pang Y, Yang D, Lou H, Qiu X. Effect of composition of calcium lignosulfonate on setting of portland cement with anhydrite. Adv Mater Res 2012;557–559:877–82.
[23] Zhang LH, Catalan LJJ, Balec RJ, Larsen AC, Esmaeili HH, Kinrade SD. Effects of saccharide set retarders on the hydration of ordinary portland cement and pure tricalcium silicate. J Am Ceram Soc 2010;93(1):279–87.
[24] Khazma M, El Hajj N, Goullieux A, Dheilly RM, Queneudec M. Influence of sucrose addition on the performance of a lignocellulosic composite with a cementious matrix. Compos Part A 2008;39(12):1901–8.
[25] Bishop M, Barron AR. Cement hydration inhibition with sucrose, tartaric acid, and lignosulfonate: analytical and spectroscopic study. Ind Eng Chem Res 2006;45(21):7042–9.
[26] Luke K, Luke G. Effect of sucrose on retardation of portland cement. Adv Cem Res 2000;12(1):9–18.
[27] Ramachandran VS, Lowery MS. Conduction calorimetric investigation of the effect of retarders on the hydration of portland cement. Thermochim Acta 1992;195(C):373–87.
[28] Lee AWC, Short PH. Pretreating hardwood for cement-bonded excelsior board. For Prod J 1989;39(10):68–70.
[29] Moslemi AA, Garcia JF, Hofstrand AD. Effect of various treatments and additives on wood–portland cement–water systems. Wood Fiber Sci 1983;15(2):164–76.
[30] Zhengtian L, Moslemi AA. Influence of chemical additives on the hydration characteristics of western larch wood–cement–water mixtures. For Prod J 1985;35(7):37–43.
[31] Cochran WG, Cox GM. Diseños experimentales. Ciudad de México: Editorial Trillas; 1978.
[32] Davies CL. Design and analysis of industrial experiments. Edinburgh: Oliver & Boyet; 1954.
[33] Alberto M, Mougel E, Zoulalian A. Compatibility of some tropical hardwoods species with Portland cement using isothermal calorimetry. For Prod J 2000;50(9):83–8.
[34] Olorunnisola AO. Effects of pre-treatment of rattan (*Laccosperma secundiflorum*) on the hydration of Portland cement and the development of a new compatibility index. Cem Concr Compos 2008;30(1):37–43.
[35] Olorunnisola AO, Adefisan OO. Trial production and testing of cement-bonded particleboard from rattan furniture waste. Wood Fiber Sci 2002;34(1):116–24.
[36] Nasser RA, Al-Mefarrej HA. Evaluation of using midribs of date palm fronds as a raw material for wood–cement composite panels industry in Saudi Arabia. Acta Hortic 2010;882:1071–82.
[37] Pereira C, Caldeira Jorge F, Irle M, Ferreira JM. Characterizing the setting of cement when mixed with cork, blue gum, or maritime pine, grown in Portugal I: temperature profiles and compatibility indices. J Wood Sci 2006;52(4):311–7.

[38] Matsushita Y, Miyawaki S, Yasuda S. Manufacture of wood–cement boards VIII: cement-hardening inhibitory compounds of Keyaki. J Wood Sci 2003;49(3):281–4.
[39] Yasuda S, Ima K, Matsushita Y. Manufacture of wood–cement boards VII: cement-hardening inhibitory compounds of Hannoki. J Wood Sci 2002;48(3):242–4.
[40] Lopez R, Aviles R, Servin JM. Lignin and waxes in composites formed by sugar cane bagasse and portland cement. Inform Tecnol 1999;10(2):259–64.
[41] de Sá VA, Bufalino L, Albino VCS, Corrêa AA, Mendes LM, Almeida NA. Mixture of three reforestation species on the cement–wood panels production. Rev Arvore 2012;36(3):549–57.
[42] Lopez R, Vargas Z, Guzman NA, Alvarez A. Superficial modification of sugar cane waste pulp fiber for the elaboration of agglomerates of portland cement. Inform Tecnol 1999;10(4):231–7.
[43] Macèdo AN, de Lima AM, Fonseca FO, Lavôr BVA. Statistical analysis of the mechanical behavior under compression of cement–wood composite. Rev Mater 2011;16(2):658–67.
[44] Wei YM, Tomita B, Hiramatsu Y, Miyatake A, Fujii T. Study of hydration behaviors of wood–cement mixtures: compatibility of cement mixed with wood fiber strand obtained by the water-vapor explosion process. J Wood Sci 2002;48(5):365–73.
[45] Qi H, Cooper PA, Hooton D. The investigation of basic processes of rapidly hardening wood–cement–water mixture with CO_2. Eur J Wood Wood Prod 2010;68(1):35–41.
[46] Hermawan D, Hata T, Kawai S, Nagadomi W, Kuroki Y. Effect of carbon dioxide-air concentration in the rapid curing process on the properties of cement-bonded particleboard. J Wood Sci 2002;48(3):179–84.
[47] Simatupang MH, Habighorst C, Lange H, Neubauer A. Investigations on the influence of the addition of carbon dioxide on the production and properties of rapidly set wood–cement composites. Cem Concr Compos 1995;17(3):187–97.
[48] Hermawan D, Hata T, Umemura K, Kawai S, Nagadomi W, Kuroki Y. Rapid production of high-strength cement-bonded particleboard using gaseous or supercritical carbon dioxide. J Wood Sci 2001;47(4):294–300.
[49] Govin A, Peschard A, Guyonnet R. Modification of cement hydration at early ages by natural and heated wood. Cem Concr Compos 2006;28(1):12–20.
[50] Nascimento B, Filho GR, Frigoni ES, Soares HM, Da Silva Meireles C, Cerqueira DA, et al. Application of cellulose sulfoacetate obtained from sugarcane bagasse as an additive in mortars. J Appl Polym Sci 2012;124(1):510–7.
[51] Nazerian M, Gozali E, Ghalehno MD. The influence of wood extractives and additives on the hydration kinetics of cement paste and cement-bonded particleboard. J Appl Sci 2011;11(12):2186–92.
[52] Ashori A, Tabarsa T, Amosi F. Evaluation of using waste timber railway sleepers in wood–cement composite materials. Constr Build Mater 2012;27(1):126–9.
[53] Okino EYA, De Souza MR, Santana MAE, Alves MVDS, De Sousa ME, Teixeira DE. Cement-bonded wood particleboard with a mixture of eucalypt and rubberwood. Cem Concr Compos 2004;26(6):729–34.
[54] Ashori A, Tabarsa T, Sepahvand S. Cement-bonded composite boards made from poplar strands. Constr Build Mater 2012;26(1):131–4.
[55] Fan M, Ndikontar MK, Zhou X, Ngamveng JN. Cement-bonded composites made from tropical woods: compatibility of wood and cement. Constr Build Mater 2012;36:135–40.
[56] Faria G, Chastre C, Lúcio V, Nunes A. Compression behaviour of short columns made from cement-bonded particle board. Constr Build Mater 2013;40:60–9.
[57] Thomas JJ, Jennings HM, Chen JJ. Influence of nucleation seeding on the hydration mechanisms of tricalcium silicate and cement. J Phys Chem C 2009;113(11):4327–34.
[58] Sudin R, Swamy N. Bamboo and wood fibre cement composites for sustainable infrastructure regeneration. J Mater Sci 2006;41(21):6917–24.
[59] De Lima AJM, Iwakiri S. Use of wood residues deriving from the production of sawnwood of *Pinus* spp, silica fume and rice husk ash in wood cement composites. Sci For 2010;38(87):459–69.
[60] Semple KE, Cunningham RB, Evans PD. Manufacture of wood–cement composites from *Acacia mangium*: mechanistic study of compounds improving the compatibility of *Acacia mangium* heartwood with portland cement. Wood Fiber Sci 2004;36(2):250–9.
[61] Sauvat N, Sell R, Mougel E, Zoulalian A. Study of ordinary portland cement hydration with wood by isothermal calorimetry. Holzforschung 1999;53(1):104–8.
[62] Sorfa P. Properties of wood–cement composites. Appl Polym Symp 1984;40:209–16.
[63] Dos Santos RC, De Cássia Oliveira Carneiro A, Castro AFNM, Castro RVO, Pimenta AS, De Oliveira Araújo S, et al. Inhibitory effect of candeia wood blended with mineral binders. Sci For 2012;40(93):113–9.
[64] Baeza J, Freer J. In: Hon David NS, Shiraishi Nobuo, editors. Wood and cellolosic chemistry. 2nd ed. New York: Marcel Dekker Inc.
[65] Bin N, Zhiqiang W, Haiqin W, Xiaoning L. Wood–cement compatibility review. Wood Res 2014;59(5):813–26.