

Study of the Interaction of Portland Cement and *Pinus* Wood for Composites using Bragg Sensors in Optical Fibers

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The potential usage of *Pinus* wood residues in cement-wood composites and the behavior of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, used as an additive were assessed in this work. In order to improve the interaction between the cement-wood composites, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and 12 different pre-treatment types were tested. Pre-treatments involved extractions in cold and hot water, NaOH solutions, and several $\text{Ca}(\text{OH})_2$ concentrations for different times. An evaluation of the mechanical features (compressive strength and tensile resistances) of composites was also performed using 50 mm cylindrical samples. The interaction of the composites was analyzed using Bragg sensors in optical fibers. *Pinus* residues were tested having particle size of 4.8 mm and a $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ content between 0% and 8%. The highest compressive strength was observed for the production of composites with 4.5% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and the hot and cold water pre-treatment. Conversely, for tensile strength, the highest performance occurred when NaOH was used as a pre-treatment. The technology for determining the temperature of composites using Bragg sensors in optical fibers was judged to be efficient.

Keywords: *Pinus* wood residues; Portland cement; Wood-cement composite; Bragg sensors; Optical fibers

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INTRODUCTION

Wood from the *Pinus* genus provides high quality materials for cellulose production. In addition, adequate technological advances have made them ideal for usage in sawmills. The mechanical processing of wood results in a large quantity of residues, which in agreement with Nahuz (2004), have not received the required attention.

The viability of composites produced by fibers or natural particles has been researched for several decades, with a long history of acceptance and application in civil construction, particularly in Europe and Asia. According to Semple and Evans (2004) and Moslemi (1989; 1993), produced materials with cement-wood composites showed a series of advantages including: large availability of stock, low specific weight, low permeability, capability of being sawed, and suitability for screw fastening and outer finishing, such as paints, *etc.* These features enable their use in the production of closing panels, linings, fabrics, sealing and masonry units, among others.

In addition to those advantages, materials based on cement-wood composites do not produce any toxic waste during their manufacturing process (Van Elten 2000; Semple and Evans 2004). Besides, they do not require pre-treatment with preservers (Ramirez-Coretti *et al.* 1998) and have a lower energy-output during the production process (Moslemi 1989). Therefore, cement-wood composites are being used as a viable alternative to asbestos-cement in Europe, Japan, and North America (Moslemi 1989).

The term compatibility, in the field of cement-wood composite research, refers to the cement hardening length, which may increase or decrease depending on the amount of wood added (Jorge *et al.* 2004). The strength of Portland cement mainly depends on the amount of two components, $2\text{CaO}\cdot\text{SiO}_2$ and $3\text{CaO}\cdot\text{SiO}_2$, and addition of any other materials, such as wood particles or organic/inorganic additives. These would affect the magnitude of the hydration reaction, as well as the reaction time and final strength (Hachmi and Campbell 1989).

The usage of a simple and reliable treatment represents one way to improve the compatibility of cement when incompatible species are present. Possibilities for treatments include: the maturing of wood or particles; use of a high-early-strength cement (Simatupang *et al.* 1998); extraction of the components that cause inhibition using hot or cold water (Gnanaharan and Dhamodaran 1985; Simatupang 1986; Hachmi and Campbell 1989; Beraldo and Rolim 1996; Jorge *et al.* 2004); extraction by alkaline solution, such as sodium or calcium hydroxide (Grandi 1991; Beraldo 1997; Latorraca 2000); impregnation of wood particles with waterproof materials (Agopyan 1991); impregnation of the wood particles with a blocking agent, such as sodium, magnesium, or aluminum sulfate, or silicate (Milani 2005); or the use of chemical additives to accelerate solidification (Beraldo *et al.* 2000; Latorraca, 2000; Wei and Tomita 2001; Semple and Evans 2004; Milani 2005).

Determining Temperature using Bragg Sensors in Optical Fibers

A Bragg sensor is a microstructure that can be inserted into the nucleus of an optical fiber ($\varnothing_{\text{nucleus}} \approx 10 \mu\text{m}$; $\varnothing_{\text{fiber}} \approx 125 \mu\text{m}$) using coherent ultraviolet radiation that is released by a laser. This microstructure relies on a small periodical and localized alteration on the refractive index, which is originated from photosensitivity. This is particularly appreciated in silica fibers that contain high quantities of germanium, or in standard optical fibers when exposed to a high-pressure hydrogen treatment (Ferreira *et al.* 2004).

According to Ferreira *et al.* (2004), when a broad spectrum light is directed on a fiber, which disturbs the diffraction network, there is a scattered line that results from the network's consecutive planes. For each network, there is a particular wavelength, in adequate conditions of resonance, where waves are produced on each plane, generating a strong reflection. This wavelength has been coined as the Bragg wavelength (λ_B), and is given by Eq. 1,

$$\lambda_B = 2n \Lambda_B \quad (1)$$

where n is the optical fiber's refractive index.

Like most optical fiber sensors, Bragg sensors are intrinsically sensitive to temperature, axial pressure, transversal deformations, and magnetic fields. As a result, Bragg sensors can be used to measure a large variety of physical properties (Ferreira *et al.* 2004). The Bragg sensor's dependence on temperature (T) can be obtained using Eq. 2,

$$\frac{\Delta\lambda_B}{\lambda_B} = \frac{\Delta(n_{ef}\Lambda)}{n_{ef}\Lambda} = \left(\frac{1}{\Lambda} \frac{\partial\Lambda}{\partial T} + \frac{1}{n_{ef}} \frac{\partial n_{ef}}{\partial T} \right) \Delta T = (\alpha + \zeta) \Delta T = \beta_T \Delta T \quad (2)$$

where β_T is the Bragg sensor's temperature sensitivity coefficient, α is the thermal expansion coefficient of the fiber, and ζ is the thermal-optical coefficient expressing the relation between the temperature and the effective refractive index.

Therefore, Bragg sensors can respond to temperatures changes, reflecting an optical signal with a well-defined spectral signature on the Bragg wavelength. The measured parameter is equivalent to an alteration of this spectral signature, which is observed by the variation of Bragg wavelength (Ferreira *et al.* 2004).

In this work, the interaction between Portland cement and *Pinus* residues will be analyzed by assessing the effects of twelve pre-treatments types and by using an innovative technique for temperature determination, through the use of Bragg sensors in optical fibers.

EXPERIMENTAL

Materials

The *Pinus* wood residues used for this research were sourced from the Madeireira Juruqui Co., Paraná, Brazil. After its collection, the wood waste was air-dried and sifted with ABNT (Brazilian Association of Technical Standards) normalized sieve number 4 to obtain a particle size of 4.8 mm.

The accelerator additive for solidification was calcium chloride dehydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$; IPC Nordeste, Brazil), which was added at 4.5% weight of the cement composite. The binder was Portland cement (Itambé, Brazil), type CPV ARI RS-high-early-strength with sulfur resistance, as specified by the ABNT-NBR 5.733 (1991) standard.

Wood-Cement Composite Production

The cement-wood composites, 200 g of Portland cement and 15 g of dry *Pinus* residues were used in this experiment. The ratio of cement to wood was 1:13.33 and the ratio of water to cement was equivalent to 0.40.

Sawdust was used under totally dry conditions for the thermometric analyses. As for the elaboration of sample specimens used for determining the physical and mechanical features, a unit was taken into account, after being corrected, for which residues were, in function of the expression (Eq. 3),

$$C_a = R_{a/c} \cdot C + (PSF - U) \cdot m \quad (3)$$

where, C_a is the storage water consumption in g/cm^3 , $R_{a/c}$ is the water to concrete ratio (%), PSF is the wood fibers saturation point, fixed at 30%, U is the wood waste unit content (%), and m is the wood trace sample mass (*Pinus* residues) in g/cm^3 .

As for the thermometric analyses of mixtures, a Bragg sensor was used, consisting of optical fibers composed of Silicon dioxide (SiO_2), Nufern® type GFI, and laser-engraved (Fig. 1a), with a Bragg wavelengths of 1.534 mm, 1.538 mm, 1.546 mm, and 1.558 mm, multiplexed to provide 4 simultaneous temperature readings. Fibers were connected to a broad-band optical source, and a signal was reflected through the engraved

sensors. Then, the signal was diffracted using optical optocouplers (Opto Link), for an Optical Spectrum Analyzer (OSA; Micron Optics SM 125), which was capable of indicated the Bragg wavelength for each sensor. The temperature readings were done in samples of 100 g, which were wrapped in aluminum foil and stored in thermal ampoules (Fig. 1b). Then, the optical fibers were inserted into the samples, beginning the hydration temperature readings for the composites (Fig. 1b).

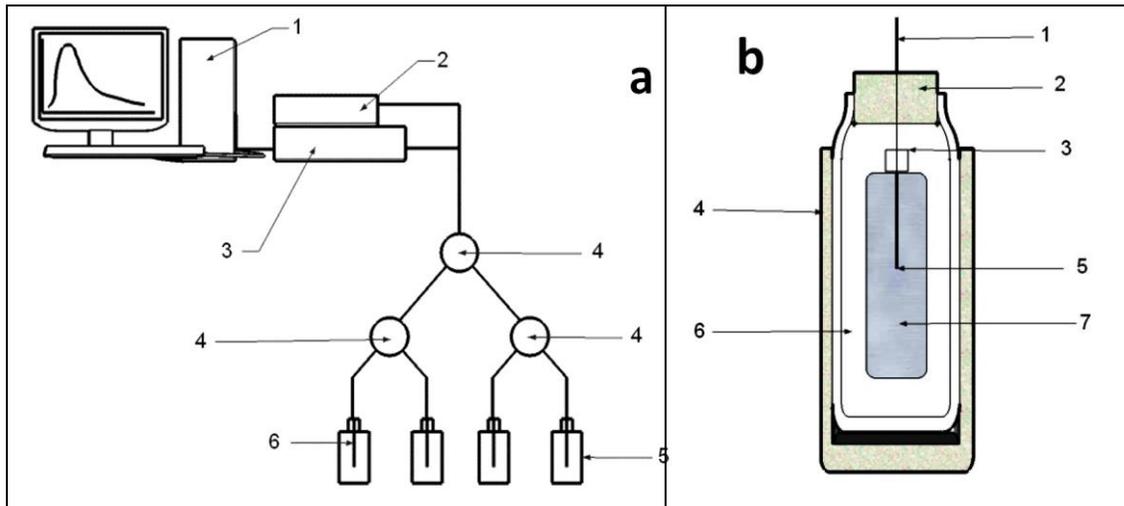


Fig 1. System schema for determination of heat of hydration of composites using Bragg sensors in optical fibers

1: Computer; 2: Optical Source broadband;
3: Optical spectrum analyzer; 4: Optocouplers;
5: Thermal ampoules; 6: Bragg sensors

1: Optical fiber; 2: Cover with thermal insulation; 3: Needle;
4: Thermal insulation; 5: Bragg sensors; 6: Thermal ampoule;
7: Composite

Influence of the $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$

To evaluate the effect of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ as an accelerator additive for curing of the Portland cement and to verify the additive content which would give the composite the best characteristics, results were evaluated for several levels solubilized in kneading the mixture with water (2%, 4%, 6%, and 8%) following by molding. Mixtures without $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ also were evaluated.

The minimum sample to be tested, in order to statistically guarantee the distribution and reliability of the results, was determined using Eq. 4, in according to Dal Molin *et al.* (2005),

$$n = z_{\alpha/2}^2 \cdot \frac{CV^2}{Er^2} \quad (4)$$

where, n is the number of replicates, Er is the estimated relative error tolerance, fixed at 10%, CV is the sample's variation coefficient, and $z_{\alpha/2}$ is a fixed value at the α level of 5.0%, therefore equivalent to 1.96.

An Emic mechanical mixer (AG-5, Instron Scientific, Brazil) was used to mix the materials. This mixer was equipped with a 5 L stainless steel cube, capable of mixing at speeds of 140 ± 5 rpm (low speed) and 285 ± 5 rpm (high speed). Materials were mixed following the amendment for the ABNT-NRB 7.215 (1997) standard.

The water content of the mixture was monitored and modified in relation to the wood moisture content, in order to maintain the fiber saturation point (FSP) at 30%, as shown in Eq. 3.

Mechanical Test

Tests for determining the physical and mechanical properties of the composites were conducted using cylindrical test specimens, with diameter of 50 mm and height of 100 mm, shaped along composites in 4 condensed layers with standardized sockets, as stated by the ABNT NBR 7.215 (1997) standard.

The initial ripening for the specimens was over a 24 h period in a temp-humid chamber at 23 ± 2 °C, and a minimal relative humidity of 95%, as specified by the ABNT NBR 9.479 (2006) standard. The specimens were encased in molds covered with an acrylic plaque, following the ABNT NBR 7.215 (1997) standard. After the ripening period, specimens were released from the molds, identified, and stored in the temp-humid chamber while immersed in water, until further testing.

Mechanical testing to determine the resistance to compression on the 28th day of ripening (RC 28d) and the tensile strength on the 28th day (RT 28d) were carried out following the ABNT NBR 7.215 (1997) and ABNT NBR 7.222 (1994) standards, respectively. To ensure that there was no influence or irregularities on the specimens' peak, and to guarantee rupture by simple compression, steel neoprene disks, with a hardness of 60 to 70 shores, were used. A universal testing machine (Emic, model DL 30000, Instron Scientific, Brazil) was used for the tests and computerized data collection.

Pre-treatment Effect on the Composites and Chemical Test

The effects of the 12 pre-treatments on the composites were explored. The pre-treatments included: extraction in cold water for 24 h (AF-24H), 48 h (AF-48H), and 72 h (AF-72H); extraction in hot water for 1 h (AQ-1H), 2 h (AQ-2H), and 3 h (AQ-3H); extraction in NaOH solutions at 1% mass fraction (NaOH-1%), 3% mass fraction (NaOH-3%), and 5% mass fraction (NaOH-5%); and extraction in calcium solutions $\text{Ca}(\text{OH})_2$ at 5% mass fraction ($\text{Ca}(\text{OH})_2$ -5%), 7% mass fraction ($\text{Ca}(\text{OH})_2$ -7%), and 10% mass fraction ($\text{Ca}(\text{OH})_2$ -10%). For all pre-treatments, the proportions were 10 L of water for the extraction for each kilogram of *Pinus* wood residues. After the extraction period, *Pinus* residues were washed and air-dried.

To evaluate the performance of the pre-treatments on the residues, chemical analyses were carried out using the extractive determination method. The analyses compared the contents of the removed extractives from the *Pinus* residues the twelve pre-treatments, following the TAPPI T 204 cm (1997) standard. These tests were carried out at the Pulp and Paper Laboratory at the Forest Engineering and Technologies Department of the Federal University of Paraná (UFPR; Brazil).

These were used as references to perform comparisons between standard mortar specimens produced with sulphate-resistant Portland cement with high early strength (CPV ARI RS), and those composites produced the same type of cement but including *Pinus* waste and either with or without $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ addition (PNCC and PN, respectively).

After the pre-treatment process of the *Pinus* composites was completed, the specimen's productions, as well as the mechanical characterization of composites were carried out at the Labmat (Construction Materials Laboratory) of the Federal Technological University of Paraná (UTFPR; Brazil).

Statistical Analysis

The statistical evaluation of the results was obtained through the analysis of variance (ANOVA), and the null hypothesis was rejected at $P < 0.05$. The treatments were compared using the Turkey-Kramer test.

RESULTS AND DISCUSSION

Influence of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ on the Portland Cement's Hydration

Hydration curves with respect to time in standard Portland cement mortar and in the produced compound with residues from untreated (natural) *Pinus* spp., both taken as references, are shown on Fig. 2. The figure shows the maximum temperatures (T_{max}) and the time it takes to attain such temperature, determined by the hydration reaction of the compound made of Portland (CPV ARI RS) and *Pinus* spp. residues, in relation to the different contents of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$.

When analyzing the different values for T_{max} , it can be observed that the highest value for T_{max} was determined by the standard Portland cement mortar (96.04 °C), whereas the lowest, was determined by the compound containing untreated *Pinus* spp. residues (70.24 °C). There were no significant statistical differences with 95% accuracy, for those T_{max} determined by the mixtures with contents of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ at 2.0%, 4.0%, and 6.0% as well as those containing 4.0%, 6.0% and 8.0% of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. The maximum temperature obtained by the compound without adding $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (70.72 °C) was obtained with *Pinus* residues, a vegetable species, which is highly compatible with cement, in agreement with the criteria of Sandermann and Kholer (1964), which set the parameter for $T_{\text{max}} > 60$ °C. In addition, under the criteria of Hofstrand *et al.* (1984), the inhibition index, $\text{IC} = 13.4419$, also indicates that *Pinus* residues are a non-inhibiting wood species ($\text{IC} < 30$).

In regard to the time needed to reach T_{max} , it can be observed that with the highest quantities additions of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, there were shorter the times for reaching T_{max} , given that there was not a significant difference between the mortar of standard Portland cement CPV ARI RS and the compound with 8.0% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, which also exhibited the highest T_{max} (78.51 °C). This preliminary analysis suggests an ideal 8.0% content of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$; nevertheless, such results must be reviewed to determine the mechanical features of such compounds.

Figure 2 clearly shows the inhibiting effect of *Pinus* residues. There was a determined T_{max} difference for both compounds (25.32 °C) and also a time difference to reach the temperature peak (4 h and 32 min). Hydration curves developed by the compounds along with the adding contents of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, besides the reference curves, are shown in Image 1B. Also, there was a clear effect of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, which significantly decreased the needed time to reach the temperature peak.

Cement hydration is the result of a series of exothermic chemical reactions originated from the cement compound, which releases heat. Hydration monitoring can be measured as the total accumulated heat (by varying temperature) over time. Research studies that have employed this technique include those from Lerch (1946), who already showed that the heat release rate by hydration largely depends on the chemical composition and physical features of cement, additional materials in the compound, and chemical additives and other substances.

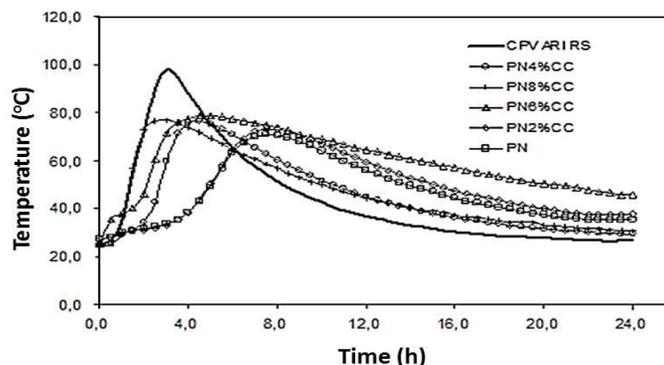


Fig. 2. Content influence of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ on the hydration composites

Table 1 shows the results for the effect of the calcium chloride content on the mechanical properties of the composites. The compressive strength showed significant differences with a confidence level of 95% for composites produced without adding $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and 2.0%; whereas the tensile strength showed significant differences for the composites with 2.0% of the calcium chloride. In regard to solidification-accelerating additives, Zhengtan and Moslemi (1985) cited by Semple and Evans (2000), described the effect of 30 substances on wood compounds' temperature and hydration time, from which, calcium chloride was one of the substances that obtained the best results. Other researchers also positively assessed the use of calcium chloride to reduce the inhibiting effects of wood on Portland Cement hydration; among these can be cited Kayahara *et al.* (1979); Lee and Short (1989); Soriano *et al.* (1998) cited by Semple and Evans (2000); Latorraca (2000); Ma *et al.* (2000); and Semple and Evans (2000).

Table 1. Influence of Calcium Chloride Content on the Mechanical Properties of the Composites

Composite + $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	Compressive Strength (MPa)	Tensile strength (MPa)
PN+0.0	24.59 (1.29)	1.95 (2.33)
PN+2.0	34.82 (3.45)	2.76 (2.32)
PN+4.0	37.94 (2.09)	2.62 (3.63)
PN+6.0	32.93 (3.43)	2.70 (3.06)
PN+8.0	31.16 (2.59)	2.40 (3.09)

Compressive strength and tensile strength at 28th day of ripening; In () CV: Coefficient of variation; PN: Composite *Pinus* spp. (not pretreated) with particle size 4.8 mm.

Sandermann and Kholer (1964) reported that highly compatible species, when mixed with cement, register a temperature above 60 °C, whereas incompatible species do not exceed 50 °C (Hofstrand *et al.* 1984; Iwakiri 2005). Lee and Hong (1986) introduced a compatibility indicator for interactions between cement and wood based on test results for determining the resistance to axial compression of cylindrical samples following the ASTM shape pattern. For that work, samples were made with Type I Portland cement and wood residues with a ratio of 13:1. The results indicated that the compressive strength was directly proportional to the maximum hydration temperature. The same methods were used by Beraldo (1994), Zucco (1999), Latorraca (2000), Pimentel (2000), and Beraldo and Carvalho (2004), among others.

Abdel-Kader and Darweesh (2010) evaluated the compressive strength of composites made with Portland cement and fibers from bagasse (1 to 4%) at 28 days of curing. The results of the compressive strength with 1% were 28 MPa and 10 MPa 4%, values well below those obtained in this investigation. Sotannde *et al.* (2012) evaluated the physical and mechanical properties of cement-bonded particleboards produced from *Azelia africana* wood residues. The average compressive strength ranged from 12.55 MPa in flake boards to 15.16 MPa in flake-sawdust boards.

In order to optimize the content of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, a non-linear regression analysis was conducted that best represent the variation in the compressive strength and tensile strength based on the results shown in Table 1. The equation was: $Y = 0.5577x^2 + 5.0689x + 25.487$, with $R^2 = 0.8576$. The resulting optimal value for calcium chloride was 4.5%. Composites were prepared with this percentage of calcium chloride and the obtained values for the compressive strength and tensile strength were 38.64 MPa and 2.67 MPa, respectively.

Analysis of the Pretreated *Pinus* Residues

According to the results shown in Table 2, the total content of extractives was 2.42%. The extractive values determined by NaOH solutions with ratios of 3% and 5% were significantly higher than the value of the total extractives. The most likely reason was the degradation of some hemicelluloses. For the other composites, the extractives values were significantly lower (P-values < 0.05).

Table 2. Extractives Analysis of the Pretreated *Pinus* Residues

Pre-Treatment	Extractives (%)	CV (%)
PN	2.42 C	2.21
AF-24H	0.89 F	4.59
AF-48H	0.98 E	1.93
AF-72H	1.04 E	3.01
AQ-1H	0.24 I	4.78
AQ-2H	0.36 H	6.59
AQ-3H	0.75 G	3.09
NaOH-1%	2.21 D	1.40
NaOH-3%	2.53 B	0.48
NaOH-5%	2.63 A	1.21
$\text{Ca}(\text{OH})_2$ -5%	-1.48 J	-4.82
$\text{Ca}(\text{OH})_2$ -7%	-2.18 K	-3.67
$\text{Ca}(\text{OH})_2$ -10%	-2.74 L	-1.20

¹Different letters denote the statistical difference between the averages in the columns at P-value < 0.05; CV: coefficient of variation; PN: Untreated *Pinus spp.* residues (without pre-treatment); AF-24H, AF-48H, and AF-72H: cold water extraction for 24 h, 48 h, and 72 h, respectively; AQ-1H, AQ-2H, and AQ-3H: hot water extraction for 1 h, 2 h, and 3 h, respectively; NaOH-1%, NaOH-3%, and NaOH-5%: extraction in sodium hydroxide solutions at a concentration of 1%, 3%, and 5%, respectively; $\text{Ca}(\text{OH})_2$ -5%, $\text{Ca}(\text{OH})_2$ -7%, and $\text{Ca}(\text{OH})_2$ -10%: extraction in calcium hydroxide solutions at concentrations of 1%, 3%, and 5%, respectively.

The only composites that did not display statistical differences were those prepared following the AF-48H and AF-72H pre-treatments. The negative values that resulted from pre-treatments containing $\text{Ca}(\text{OH})_2$ occurred because the external materials reached the cell walls of *Pinus* residue particles.

The pre-treatments carried out with hot water exhibited lower extractive values than those pretreated using cold water. This can be explained in relation to the time duration during which *Pinus* residues remained in contact with the cold water (24 h, 48 h, and 72 h), which was considerably longer than the hot water pre-treatment. Variation in extractive values may have occurred because the *Pinus* specimens were tested at the same time they were being used for the composites production, *i.e.*, in the presence of tree bark particles.

Hachmi and Campbell (1989) established that carbohydrates react with calcium, aluminum, and iron cations in cement, and through the hydrolysis of mannose and galactose, glucose acids slow down the hydration reaction of Portland cement, reducing its crystallinity and strength. Simatupang *et al.* (1998) found that wood extractives are responsible for inhibiting wood solidification. Their primary activity comes from phenolic compounds and free carbohydrates, whereas Hachmi *et al.* (1990) discovered that water soluble substances play a more significant role in inhibiting cement solidification. Hot water treatment usually removes water-soluble extractives, sugars, starches, and other amorphous polymers, which play an important role on the inhibition of the cement hydration (Ferraz *et al.* 2011).

Influence of Pretreatments on the Hydration of Portland Cement

To determine the possible influence of the pre-treatment of *Pinus* residues on Portland cement, thermometric analyses were employed. Composites, made of cement and *Pinus* residues, received all of the twelve pre-treatments, with or without 4.5% of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$.

Table 3 shows the effects of the pre-treatments when used for producing composites (with or without the addition of 4.5% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$). In both cases, it was observed, that the highest temperatures were obtained with the Portland cement (without *Pinus* residues). The pre-treated *Pinus* composites without $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ achieved the maximum temperatures at 63.79 °C (Ca(OH)_2 -7%) and 71.76 °C (AF-24H). However, the T_{max} for untreated *Pinus* residues composites was 70.72 °C.

As the time to reach the temperature peak increased, a significant decrease was observed when comparing the composites produced with untreated *Pinus* residues (7.63 h) and the *Pinus* composites pre-treated with NaOH (approximately 5 h). The other pre-treatments exhibited registered values that were above from the untreated *Pinus* residues composites, ranging from 8.03 h (AQ-1H) to 10.9 h (Ca(OH)_2 -10%).

Composites made from pine residues containing $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ at a 4.5% ratio and pre-treated, exhibited a very limited variation in T_{max} when it was compared to compounds produced with untreated *Pinus* residues composites (76.34 °C). These temperature values ranged from 72.24 °C (NaOH-3%) to 79.26 °C (Ca(OH)_2 -5%).

The time to reach the temperature peak in the *Pinus* residues in untreated composites were 4.85 h, with variations from 2.86 h (Ca(OH)_2 -5%) to 5.16 h (NaOH-5%), depending on the pre-treatment level. The most significant variations occurred for composites produced with Ca(OH)_2 . This resulted in diminutions of the time to reach the temperature peak, which was determined by the untreated residue at 1.75 h on average.

Among the chemical additives, chlorides such as CaCl_2 and FeCl_2 markedly accelerated the hydration process when they were added to cement paste. Nazerian *et al.* (2011) reported that the additives such as chlorides could be used effectively as accelerators to restrain the inhibitory influence of wood species.

Table 3. Comparison of Temperature and Hydration Time of Pre-treated Composites, with or without $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$

Composite Pre-treatment	No Added $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$				With Addition of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$			
	Tmax (C°)	CV (%)	Time to Tmax (h)	CV (%)	Tmax (C°)	CV (%)	Time to Tmax (h)	CV (%)
CPV ARI RS	96.04 A	1.44	3.10 H	3.23	96.04 A	1.44	3.10 F	3.23
PN	70.72 BCD	2.29	7.63 F	3.30	76.34 DEF	2.08	4.85 B	5.19
AF-24H	71.67 B	1.14	10.10 C	1.71	74.39 EFGHI	1.34	4.30 C	2.33
AF-48H	64.39 F	2.82	9.50 D	0.61	75.19 HGFED	1.05	3.46 E	1.67
AF-72H	68.37 EDC	4.92	9.63 D	3.34	72.68 HI	0.35	3.83 D	1.51
AQ-1H	67.76 ED	2.17	8.03 E	1.44	74.77 HGFED	0.81	4.26 C	2.71
AQ-2H	65.57 FE	2.31	10.56 B	2.19	73.56 GHI	0.89	3.10 F	5.59
AQ-3H	70.51 BCD	1.67	8.03 E	1.44	78.82 BC	5.02	4.76 B	4.37
NaOH-1%	70.95 BC	1.40	4.90 G	2.04	74.16 FGHI	0.20	4.03 CD	5.73
NaOH-3%	70.99 BC	0.43	5.06 G	1.14	72.24 I	0.48	4.10 CD	6.45
NaOH-5%	71.23 BC	4.34	5.06 G	1.14	76.68 CDE	1.01	5.16 A	1.12
$\text{Ca}(\text{OH})_2$ -5%	70.66 BCD	2.36	9.96 C	4.05	79.26 B	1.35	2.86 F	4.03
$\text{Ca}(\text{OH})_2$ -7%	63.79 F	0.89	10.53 B	1.10	77.27 BCD	2.38	3.00 F	5.77
$\text{Ca}(\text{OH})_2$ -10%	69.60 BCD	3.83	10.90 A	1.83	75.96 DEFG	2.58	3.43 E	1.68

¹Different letters denote the statistical difference between the averages in columns at P-value < 0.05; CV: coefficient of variation; CPV, ARI, and RS: Standard Portland cement mortar; PN: untreated *Pinus* residues (without pretreatment); AF-24H, AF-48H, and AF-72H: cold water extraction for 24 h, 48 h, and 72 h, respectively; AQ-1H, AQ-2H, and AQ-3H: hot water extraction for 1 h, 2 h, and 3 h, respectively; NaOH-1%, NaOH-3%, and NaOH-5%: extraction in sodium hydroxide solutions at a concentration of 1%, 3%, and 5%, respectively; $\text{Ca}(\text{OH})_2$ -5%, $\text{Ca}(\text{OH})_2$ -7%, and $\text{Ca}(\text{OH})_2$ -10%: extraction in calcium hydroxide solutions at concentrations of 1%, 3%, and 5%, respectively.

Influence of *Pinus* Residues and Pretreatments on the Composites' Mechanical Properties

Figures 3 and 4 show the RC 28 d and RT 28 d values for the reference composites (CPV, ARI, and RS), and the composites made with *Pinus* residues and different pre-treatments.

As expected, the highest strength values were exhibited by the standard Portland cement mortar, displaying significantly different statistics compared to the other composites produced with pine residues with the various types of pre-treatments tested. The results for composites from the RC 28d containing *Pinus* residues and AF-48 H, AQ-1H, AQ-2H, or AQ-3H pre-treatments showed lower strengths than those with the standard Portland cement mortar. The untreated *Pinus* yielded the lowest strength values, and adding 4.5% of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ did not change the strength of those composites. Composites produced with pine residues and the NaOH-1%, $\text{Ca}(\text{OH})_2$ -7% or $\text{Ca}(\text{OH})_2$ -10% pre-treatment yielded similar results.

Figure 3 shows the values for resistance to compression on the 28th day of ripening (RC 28d). As expected, the highest strength values were exhibited by the standard Portland cement mortar, displaying significantly different statistics than the other composites produced with pine residue with the various types of pre-treatments tested. The results for composites from the RC 28d containing pine residues and AF-48 H, AQ-1H, AQ-2H, or AQ-3H pre-treatments showed lower strengths than those with the standard Portland cement mortar. The untreated *Pinus* residues yielded the lowest strength values, and adding 4.5% of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ did not change the strength of those composites. Composites produced with pine residues and the NaOH-1%, $\text{Ca}(\text{OH})_2$ -7% or

Ca(OH)₂-10% pre-treatment yielded similar results. According to Gong *et al.* (2004) the compressive strength values required for material to be used as pavements range from 20 to 25 MPa. As the results of the compressive strength with pine residues are higher than required for this purpose.

Results for the RT 28d (Fig. 4) testing of composites produced with *Pinus* residues and the AF-24H or NaOH 5% pre-treatments showed immediately lower strengths than the standard Portland cement mortar composites. The lowest values resulted from composites produced with pine residues and pre-treated with Ca(OH)₂, as well as the compounds produced with untreated *Pinus* spp. residues (without pre-treatment).

The positive effect of pre-treatment, such as soaking and extracting of wood or fibers, respectively, in water or any other treatment is known to enhance compatibility and therefore mechanical properties. Also, the positive side effect of using the additives is the fact that the possibility to wash out aggressive extractives from the wooden particles and therefore mechanical properties are increased (Eusebio *et al.* 2000, Frybort *et al.* 2008). Nazerian *et al.* (2011) argued that impermeable hydrates are formed around unhydrated cement grains when extractives are present and therefore the need to remove them.

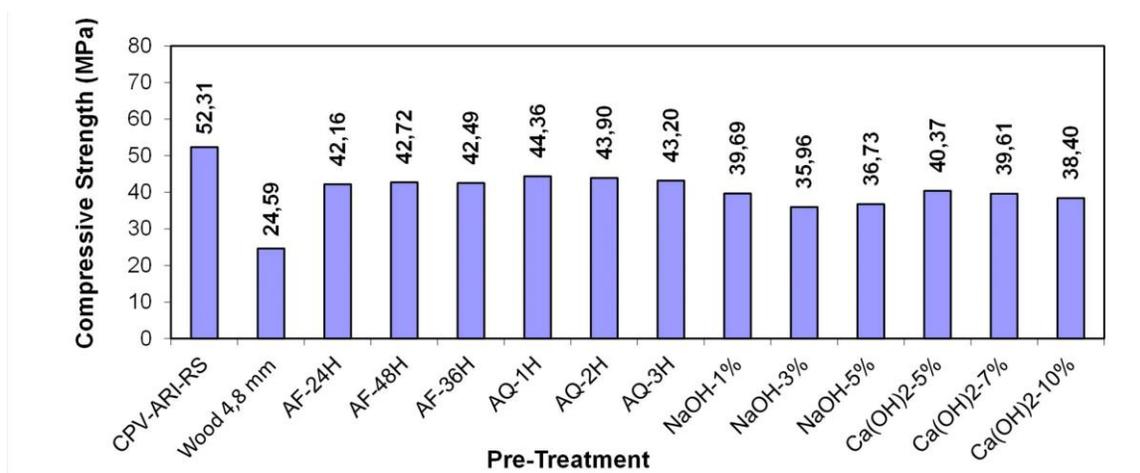


Fig. 3. The influence of *Pinus* residues and pretreatments on the composites' compressive strength

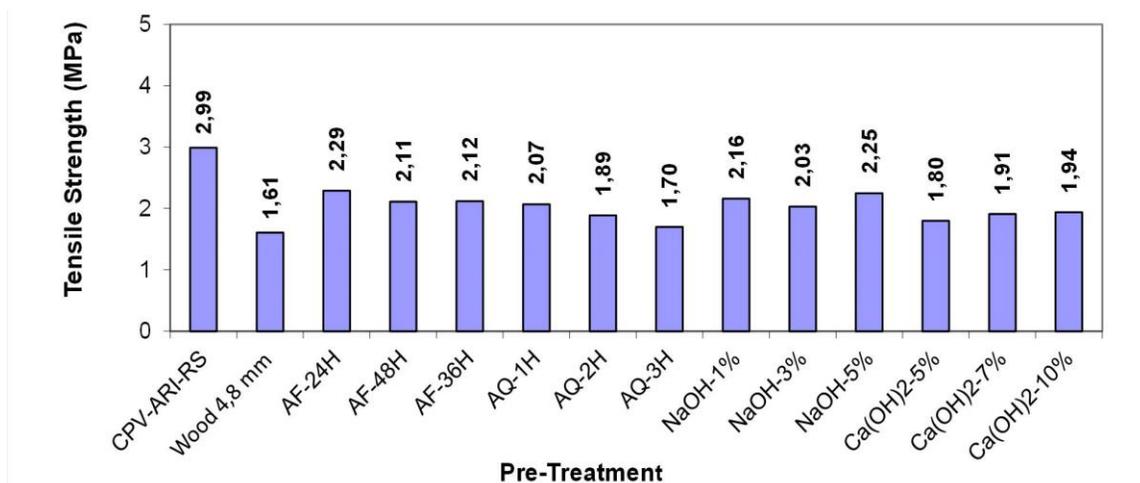


Fig. 4. The influence of *Pinus* residues and pretreatments on the composites' tensile strength

CONCLUSIONS

The thermometric analysis demonstrated that the *Pinus* residues were suitable, even in the presence of tree bark particles, for their use in cement-wood composites. The thermometric analysis showed that the $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ compound could be proposed as a potential accelerating solidifier for increasing the strength of *Pinus* composites. However, the needed amount of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ to achieve the most significant improvement on the composites' mechanical properties was not determined in this study.

The chemical analysis showed that the most effective pre-treatment, in terms of wood extractives removal, involved the NaOH conditions. The assimilation of $\text{Ca}(\text{OH})_2$ by the *Pinus* residues was also observed.

The use of Bragg sensors in optical fibers confirmed the efficiency of the NaOH pre-treatments for significantly decreasing the amount of time needed to reach the maximum temperature (T_{max}) for the hydration of the composites. On the other hand, the use of *Pinus* residues and the different pre-treatments did not considerably alter the maximum temperatures for the composites' hydration reactions.

The best performance for compressive strength was obtained by the *Pinus* composites containing 4.5% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and pre-treated with the hot and cold water. The best result for tensile strength performance was obtained by the *Pinus* composites pre-treated with the NaOH solutions, 4.5% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and the hot and cold water.

Considering the objectives proposed in the research, the feasibility of using *Pinus* residue in Portland cement mixtures was demonstrated for the production of blocks with purpose to construction.

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