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Characterizing the setting of cement when mixed with cork, blue gum, or maritime pine, grown in Portugal I: temperature profiles and compatibility indices

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Abstract Data are presented on the effects that cork, blue gum, or maritime pine, all grown in Portugal, have on cement setting. These materials were mixed with cement either without any treatment or after being extracted previously with a range of solvents (ranging from nonpolar to very polar). Other experiments were carried out in which extractives or calcium chloride were added to the cement paste. All lignocellulosic substrates have detrimental effects on cement setting, which is mostly seen by a delay in attaining the maximum temperature in the process. However, the addition of calcium chloride was able to overcome this disadvantage. Extraction of the substrates with some polar extraction agents before addition to the cement paste only slightly improved compatibility, and the addition of waterbased extractives to a cement paste affects the setting much less than the lignocellulosic material by itself. Several thermal compatibility indices, including a new index proposed in this article, were calculated from data taken from temperature profiles, and conclusions are presented on the performance of the setting systems, as compared with a neat cement paste. In addition, comments are expressed on the level of accuracy offered by the indices applied in this study, and how such accuracy can be checked or improved by matching them to the physical properties of the woodcement composites.

Key words Wood · Cork · Cement · Temperature profiles · Compatibility indices

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Introduction

Cement-bonded composites in the form of panels are most often, but not exclusively, made with wood particles or fibers.¹ Such panels are well established in the market place. This is because, for some applications, like prefabricated construction,² wood–cement composites, or in a more general sense, composites made of cement and lignocellulosic materials,³ have advantages over most common wood composites including organic resin-bonded panels. Compared with these, wood-cement composites have better dimensional stability, better resistance to biodeterioration⁴ and fire, have no formaldehyde emission originating from the binder, and can be used as a means of recycling wood residues,⁵ including preservative-treated wood at the end of its service.⁶ Compared with concrete, one advantage is that wood-cement composites are less dense and can be shaped, cut, drilled, railed, and sanded readily.

Manufacturing a panel with a given wood or other lignocellulosic material for the first time, either in the laboratory or on an industrial scale, is not likely to be a straightforward process. One of the problems that may be encountered is that wood species interact with cement, causing a hindrance in its hardening. Consequently the compatibility, which refers to the degree of cement setting when it is allowed to harden in the presence of a given wood in a fragmented form, must be assessed. With the diversity of lignocellulosic materials that may be used the range of compatibility goes from "compatible" to "not compatible", with "moderately compatible" in between.⁷ Western larch (*Larix occidentalis* Nutt.) is an example of a wood species that is not compatible.⁸

The compatibility of a lignocellulosic substance can be assessed by thermal and mechanical methods. Cement hardening is exothermic, and a plot of temperature versus time can be used to assess compatibility. Typical hydration temperature curves have three phases: (1) initial temperature rise (small but rapid), (2) dormant period (where temperature does not rise or may even show a small decrease), and (3) cement hardening (exhibited by clear temperature rise).⁹ Several parameters can be obtained from such plots, such as: T_{max} (maximum temperature attained), t_{max} (time to T_{max}), and S_{max} (maximum slope during cement setting phase). A compatible lignocellulosic would have t_{max} , T_{max} , and S_{max} that are similar to a neat cement paste. Therefore, these factors, taken alone, or as basis for calculation of indices, have been used to indicate the degree of compatibility between cement and some wood species.¹⁰⁻¹²

The measurement of the heat evolved during cement setting provides the so-called C_A factor to assess the extent of cement hardening. This is defined as the ratio of the amount of heat released from a mixture of wood and cement, and that released from a neat cement paste. It was applied by Hachmi et al.,¹³ who considered it the best thermal wood compatibility ranking method. More recently, however, Karade et al.¹⁴ have demonstrated some deficiencies in this method and proposed a new index based on the duration of the dormant period.

Although working in some specific cases, for a given group of wood species and a given set of laboratory conditions, concern has been raised over the consistency that different thermal inhibition indicators can present, and on how they can be correlated to the physical properties (which comprise the compatibility assessment by physical methods). For example, Hachmi et al.¹³ found that the classification of wood species regarding their compatibility with cement can depend on the classification method used, or the form by which wood is applied (e.g., flour or wool)¹⁵ or the ratio of wood to cement.¹⁴ In order to obtain experimental data that may correlate better or more consistently with the properties of the final product made on a larger scale, Lee and Hong¹⁶ suggested a simple compression test of cylindrical samples, and Wei et al.¹⁷ measured modulus of rupture (MOR) and internal bond (IB) in panels, for the same purpose. Although mechanical methods provide some useful data, they can also provide inaccurate indicators because the reinforcing effect of a particle in a matrix, even if the particle is moderately compatible, will tend to increase toughness.

The work presented in this article deals with the acquisition of temperature profiles from pastes of cement and cork, pine, or blue gum in a range of conditions. The data obtained were used to calculate T_{max} , t_{max} , and S_{max} , as well as several compatibility indices. A new compatibility index is proposed. Comments are drawn on the effects the presence of the substrates can impart on cement setting, and which treatments or additives can lead to better cement hardening performance. Also, a comment is made on the validity of the information given by compatibility indices, taken alone.

Materials and methods

Three lignocellulosic materials, all of Portuguese origin, were taken from the furnish of three industries. Blue gum chips were provided by a pulp mill, with a size range of 7–42 mm. These were milled further in a Wiley mill to pass through a 6-mm screen. The dust produced was removed

from the particles. In the interpretation of the results presented, it was assumed that blue gum particles were composed of sapwood, because blue gum trees are usually cut at an age of only 10–12 years when intended for pulping.

Pine was supplied by a particleboard plant. The particles had a size range of 0.14–5mm, and were taken from the furnish, used for the core layer of the panels. Because these particles were small, they were not processed further. The pine particles were also assumed to be composed of sapwood. This is because the sources of raw material for the particleboard plant are mainly small round wood, sawmill residues, and slabs from the outer parts of saw logs.

Cork was offered by a cork particleboard plant, which used cork residues, from stopper cutting or from low quality cork planks. The fraction applied had a size range of 1-2 mm, and was classified as high density (110–130 kg/m³).

To obtain a temperature profile, the components were mixed thoroughly in the dry state. Then a given volume of water, or a solution of extractives, was added, followed by further mixing. All experimental conditions applied are indicated in detail in the tables shown in the next section of this article. Pastes were transferred to plastic bags that were then placed inside a round box made of expanded polystyrene and thermally isolated with glass wool. Finally, a thermocouple was inserted in the paste and temperature data were recorded by a computer every 10min over 24h. All data plots and index calculations were made on the basis of temperature rise above room temperature.

The cement used in this study was Portland cement type I, 42.5 R, manufactured by Secil-Companhia Geral de Cal e Cimento, Portugal. The mixtures contained 200g of cement and 15g of wood or cork (dry basis). Because the wood particles absorb some water, the proportion of water added was calculated using the following formula:

This gives very high cement/wood ratios, as compared with mixtures used for panel manufacture in industry. However, this was necessary to obtain useful temperature profiles with our assembly, because low ratios imply low temperature rises, and the information in such cases given by plots is not accurate.

As a standard for comparison purposes, a temperature profile was obtained with neat cement. Then, to test the effect of the addition of a common setting accelerator, calcium chloride, $CaCl_2.2H_2O$, was added in dosages of 2% and 5% (cement basis).

Lignocellulosic substrates were used as received with the exception of the milling procedure as mentioned above, or after extraction with a solvent. The solvents used were petroleum ether, diethyl ether, ethanol, water, or an aqueous solution of NaOH (0.1%). Extractions with the organic solvents were carried out with a Sohxlet apparatus for a 4-h period, followed by drying at 45°C until constant weight was attained. The samples were then kept in a desiccator until use for mixing with cement. In the case of water and the 0.1% NaOH solution, extractions were performed at room

temperature with the lignocellulosic particles suspended in the liquid medium. About 120g of a given material was dispersed in 51 of water or 0.1% NaOH, stirred for 1h, and then filtered. This procedure was repeated three times to ensure good extraction. Finally, the lignocellulosic particles were dried and stored as for the organic solvent-extracted particles.

In order to assess the influence that water-soluble extractives alone may have on cement setting, cement pastes were also prepared with the addition of small portions of extractive solutions from cork, pine, or blue gum. Extractive solutions for this purpose were obtained by immersing 15g of particles in 90 ml of water for 24 h, with sporadic stirring. The suspensions were then filtered, and the filtrates concentrated to 50ml, when necessary, by heating in an oven at 40°C. All 50ml of extractive solution was added to 200g of cement to achieve the water/cement proportion outlined above. Only the addition of water extractives was investigated because in the case of organic solvent extractives, such organic materials would be difficult to mix thoroughly in the water-cement paste. Also, the solvent itself would interfere. In the case of 0.1% NaOH extractives there is the possibility that the sodiumion could interfere in the setting process.

Three replicate experiments were conducted for each combination of variables. However, in some cases, where replicate plots deviated significantly from each other, four or five experiments were performed, in order to obtain a more confident average.

 T_{max} , t_{max} , and S_{max} were calculated for each condition, and used to calculate the following compatibility indices:

$$I_{1}(T) = \frac{T_{\max}(c) - T_{\max}(s)}{T_{\max}(c)} \times 100,$$

$$I_{2}(t) = \frac{t_{\max}(s) - t_{\max}(c)}{t_{\max}(c)} \times 100,$$

$$I_{3}(S) = \frac{S_{\max}(c) - S_{\max}(s)}{S_{\max}(c)} \times 100,$$

and

$$I^{x}(T,t,S) = (-1)^{n-1} \times I_{1}(T) \times I_{2}(t) \times I_{3}(S) \times 10^{-4}, \quad n = 1,2,3;$$

where *n* denotes the number of negative elements (either I_1 , I_2 , or I_3 in this case) on the right side of the equation, (*c*) refers to neat cement paste, and (*s*) refers to sample, i.e., cement paste plus another component.

Indices I_1 to I_3 are simple and give only information on the extension of T_{max} , t_{max} , and S_{max} of a neat cement paste by the addition of any substance or additive. However, index $I^x(T,t,S)$ takes into account simultaneously the changes on T_{max} , t_{max} , and S_{max} in order to assess the degree to which cement setting was impaired or improved. This index, as written, is an adapted version of the index proposed by Hofstrand et al.¹¹

For any index, the rule is that the higher the index, i.e., the most positive, the higher the hindrance of cement hydration. On the other hand, if the value of a given index was to be negative, then it means that the sample presented a better setting performance in terms of temperature profile than the standard, neat cement. This is why the parameter $(-1)^{n-1}$ is included in the formula. In this way, if any one, two, or all three elements of the equation are negative, then the value of the index becomes negative and it indicates an improvement, which is true. However, without the multiplication by $(-1)^{n-1}$, with *n* being the number of negative elements on the right side of the formula, the occurrence of two negative elements would make the index positive, indicating a mathematically worse result, which is not the case in practical terms. With the modified index, an improvement in either T_{max} , t_{max} , or S_{max} would always result in a negative value for *I*.

However, index $I^{x}(T,t,S)$ has a drawback in that when one or two parameters on the right side of the equation are positive they would make the overall value of the index more negative, because the other elements of the equation are negative, and they are multiplied together. However, the opposite effect should occur: any positive parameter should make the index higher or less negative. Therefore, another index is proposed, as follows. By summing the three elements of the equation, as obtained from T_{max} , t_{max} , and S_{max} , there is no need to multiply by $(-1)^{n-1}$ and a positive element contributes to higher values, and a negative one leads to lower values. It is truly an average, and the magnitude of this index can be compared with that of the simpler indices $I_1(T)$, $I_2(t)$, and $I_3(S)$:

$$I^{+}(T,t,S) = \frac{1}{3} [I_{1}(T) + I_{2}(t) + I_{3}(S)]$$

Results and discussion

Figures 1–3 provide a qualitative analysis of the thermal behavior of water–cement–pine pastes, with some variations on curing conditions. Only figures concerning pine are presented here as the general trends obtained were more or less the same as for cork and blue gum. A quantitative analysis is given in Tables 1–4. For all compatibility indices presented in Tables 1–4, neat cement paste is the reference.



Fig. 1. Temperature profiles of cement paste, neat, with added calcium chloride as setting accelerator, with added pine particles, and pine and calcium chloride

Figure 1 shows the effect of the addition of a common curing accelerator for cement, calcium chloride (CaCl₂.2H₂O). It clearly improved S_{max} and t_{max} , but not T_{max} , and the effect was stronger for the higher addition (5%, cement basis). The retardation effect of the presence of pine particles in the paste is also clear. The addition of calcium chloride, especially at 5%, markedly reduced the detrimental effects of the presence of pine. t_{max} was brought to levels shorter than that obtained with neat cement, although with a concomitant lower T_{max} .



Fig. 2. Effects on temperature profiles of the addition of solventextracted pine particles



Fig. 3. Effects on temperature profiles of the addition of pine particles or pine water extractives to cement paste

It is important, however, to keep in mind that the parameter T_{max} , as such, may not accurately reflect any impairment of cement curing. This is because the mass of a neat cement paste is less than that of a paste containing a lignocellulosic material. The heat in a specimen is derived from the cement, the weight of which is constant. Consequently, the T_{max} of a sample containing lignocellulosic material will be lower than that of neat cement even if it is completely inert, because the lignocellulosic material will absorb some of the heat generated by the hydration reactions. T_{max} will be lowered further if the lignocellulosic material retards the hydration of cement. Separation of the two phenomena is difficult and is a topic of further research.

Figure 2 shows that the extraction of pine with several polar extraction agents (ethanol, water, and 0.1% NaOH solution) reduces t_{max} when compared with the paste containing unextracted pine. However, in terms of the three indicators, T_{max} , S_{max} , and t_{max} , the performance is still lower when compared with a neat cement paste. Nonpolar solvents like petroleum ether and diethyl ether did not give a significant advantage.

The addition of pine or pine extractives to a cement paste definitely affected cement setting (see Fig. 3 and Table 3). In this case, with an addition of a small quantity of extractives dissolved in the water to make the paste, the decrease in $T_{\rm max}$ indicates that the extractives interfere with the cement hydration reactions. The hydration profile for pine implies greater hindrance. Two explanations for this



Fig. 4. Comparison of the thermal behavior of cement pastes with added cork, pine, or blue gum particles

Table 1. Parameters obtained from temperature profiles, and compatibility indices calculated with them, after experiments with cement paste and pastes with added curing accelerator or extractives

	Neat cement	Cement paste with additive							
		2% CaCl ₂	5% CaCl ₂	Cork extractives	Pine extractives	Blue gum extractives			
$T_{\rm max}(^{\circ}{\rm C})$	70.4 (1.10)	52.0 (1.27)	56.8 (0.85)	62.0 (1.45)	60.6 (0.40)	63.1 (0.42)			
$t_{\rm max}$ (h)	5.0 (0.33)	3.3 (0.17)	0.9 (0.06)	7.6 (0.48)	8.7 (0.58)	7.8 (0.51)			
$S_{\rm max}$ (°C/h)	45.4 (3.36)	33.0 (1.37)	60.8 (1.24)	30.0 (2.84)	28.4 (1.63)	33.1 (1.84)			
$I_1(T)^{\rm a}$	_	26.1	19.3	11.9	13.9	10.4			
$I_2(t)$	-	-34.0	-82.0	52.0	74.0	56.0			
$I_3(S)$	-	27.3	-33.9	33.9	37.4	27.1			
$I^{x}(T, t, S)$	-	-2.4	-5.4	2.1	3.9	1.6			
$I^+(T, t, S)$	-	6.5	-32.2	32.6	41.8	31.2			

All experiments used three replicates. Data for T_{max} , t_{max} , and S_{max} are given as means with standard deviations in parentheses ^aSee text for definitions of indices

Table 2. Parameters obtained from temperature profiles, and compatibility indices calculated with them, after experiments with cement paste with cork, cement paste with cork and curing accelerator, or cement paste with cork extracted with the solvents indicated

	Cement paste with natural cork	Cement paste with cork and $CaCl_2$		Cement paste with solvent-extracted cork				
		2% CaCl ₂	5% CaCl ₂	Petroleum ether	Diethyl ether	Ethanol	Water ^a	0.1% NaOH
$ \frac{T_{\max}(^{\circ}C)}{t_{\max}(h)} $ $ S_{\max}(^{\circ}C/h) $	40.3 (0.96)	33.7 (0.85)	45.5 (2.55)	35.0 (0.95)	40.1 (1.05)	41.4 (0.85)	42.6 (1.16)	43.2 (0.70)
	8.2 (0.25)	5.9 (0.25)	2.1 (0.10)	8.3 (0.17)	7.5 (0.17)	7.4 (0.25)	7.2 (0.24)	7.3 (0.42)
	8.2 (0.13)	12.3 (0.32)	32.2 (0.72)	6.7 (0.39)	8.3 (0.57)	9.1 (0.29)	9.9 (0.67)	11.1 (0.62)
$ \begin{array}{c} I_{1} \left(T \right) \\ I_{2} \left(t \right) \\ I_{3} \left(S \right) \\ I^{*} \left(T, t, S \right) \\ I^{+} \left(T, t, S \right) \end{array} $	42.8	52.1	35.4	50.3	43.0	41.2	39.5	38.6
	64.0	18.0	-58.0	66.0	50.0	48.0	44.0	46.0
	81.9	72.9	29.1	85.2	81.7	80.0	78.2	75.6
	22.4	6.8	-6.0	28.3	17.6	15.8	13.6	13.4
	62.9	47.7	2.7	67.2	58.2	56.4	53.9	53.4

All experiments used three replicates. Data for T_{max} , t_{max} , and S_{max} are given as means with standard deviations in parentheses ^aFour replicates for water-extracted cork samples

Table 3. Parameters obtained from temperature profiles, and compatibility indices calculated with them, after experiments with cement paste with maritime pine, cement paste with pine with curing accelerator, or cement paste with pine extracted with the solvents indicated

	Cement paste with natural pine	Cement paste with pine and $CaCl_2$		Cement paste with solvent-extracted pine					
		2% CaCl ₂	5% CaCl ₂	Petroleum ether	Diethyl ether	Ethanol ^a	Water ^b	0.1% NaOH	
$T_{\max} (^{\circ}C)$	30.7 (0.60)	32.4 (0.67)	43.8 (0.92)	31.7 (1.41)	34.3 (0.72)	39.4 (1.20)	37.6 (2.26)	39.3 (0.67)	
$t_{\max} (h)$	11.5 (0.17)	7.3 (0.00)	2.4 (0.10)	10.5 (0.28)	9.9 (0.10)	8.3 (0.40)	8.0 (0.49)	7.9 (0.10)	
$S_{\max} (^{\circ}C/h)$	4.6 (0.09)	9.2 (0.29)	28.5 (1.63)	5.1 (0.19)	6.1 (0.11)	8.0 (0.87)	7.6 (0.95)	8.7 (0.25)	
$ \begin{array}{c} I_{1} \left(T \right) \\ I_{2} \left(t \right) \\ I_{3} \left(S \right) \\ I^{x} \left(T, t, S \right) \\ I^{+} \left(T, t, S \right) \end{array} $	56.4	53.9	37.8	55.0	51.3	44.0	46.6	44.2	
	130.0	46.6	-52.0	110.0	98.0	66.0	60.0	58.0	
	89.9	79.8	37.2	88.8	86.6	82.4	83.3	80.8	
	65.9	20.1	-7.3	53.7	43.5	23.9	23.3	20.7	
	92.1	60.1	7.7	84.6	78.6	64.1	63.3	61.0	

All experiments used three replicates. Data for T_{max} , t_{max} , and S_{max} are given as means with standard deviations in parentheses ^aFour replicates

^bFive replicates

Table 4. Parameters obtained from temperature profiles, and compatibility indices calculated with them, after experiments with cement paste with blue gum, cement paste with blue gum with curing accelerator, or cement paste with blue gum extracted with the solvents indicated

	Cement paste with natural blue gum	Cement paste with blue gum and CaCl ₂		Cement paste with solvent-extracted blue gum				
		2% CaCl ₂	5% CaCl ₂	Petroleum ether ^a	Diethyl ether	Ethanol ^a	Water	0.1% NaOH
$T_{max} (^{\circ}C)$	33.7 (0.64)	33.7 (1.36)	46.4 (1.48)	33.2 (1.27)	34.0 (1.05)	38.1 (1.77)	39.5 (0.47)	36.9 (0.30)
$t_{max} (h)$	9.5 (0.33)	6.8 (0.17)	2.2 (0.09)	9.7 (0.36)	9.4 (0.10)	7.8 (0.30)	7.6 (0.10)	7.8 (0.25)
$S_{max} (^{\circ}C/h)$	5.7 (0.18)	9.9 (0.48)	34.0 (3.60)	5.1 (0.36)	5.8 (0.39)	7.6 (0.95)	8.0 (0.19)	7.4 (0.36)
$ \begin{array}{c} I_{1} \left(T \right) \\ I_{2} \left(t \right) \\ I_{3} \left(S \right) \\ I^{*} \left(T, t, S \right) \\ I^{+} \left(T, t, S \right) \end{array} $	52.1	52.1	34.1	52.8	51.7	45.9	43.9	47.6
	90.0	36.0	-56.0	94.0	88.0	56.0	52.0	56.0
	87.4	78.2	25.1	88.8	87.2	83.3	82.4	83.7
	41.0	14.7	-4.8	44.1	39.7	21.4	18.8	22.3
	76.5	55.4	1.1	78.5	75.6	61.7	59.4	62.4

All experiments used three replicates. Data for T_{max} , t_{max} , and S_{max} are given as means with standard deviations in parentheses ^aFour replicates

are that the weight of the particles will reduce T_{max} and S_{max} and lengthen t_{max} , plus there maybe some extractives still present in the pine particles. There may be, however, a third explanation.

Earlier publications resulting from this research,^{17,18} pointed out that lignocellulosic materials, when added to a cement suspension, could interact on the basis of an adsorption phenomenon. Some cations, that enter into solution

when cement is mixed with water, i.e., potassium (K^+) and calcium (Ca^{2+}) could be adsorbed to some extent by lignocellulosic particles. Thus, calcium, which is an essential cation to form the crystal formations that give rise to cement hardening¹⁹ is removed from solution, reducing the availability for cement-hardening reactions and causing their impairment to some degree. Therefore, the problem of cement-hardening hindrance should not only be ascribed to wood extractives, because insoluble materials may also play a role.

Comparing the three substrates used in this work (Fig. 4), cork appears to be the most compatible followed by blue gum and then by pine. This is surprising because cork was found to have the highest overall extractive content of the three materials.¹⁷ Consequently, this result may corroborate the hypothesis that adsorption onto solid material may also contribute to cement-hardening hindrance. Another factor that may contribute to the specificity of cork is its impermeability, contributing to make it more compatible. However, the trends shown in Fig. 4 are only indicative of cork, pine, and blue gum, because of the limitation in sampling. To be able to make generalizations, a broader study, with samples from different regions, tree ages, and tree parts, would be necessary.

Table 1 presents the thermal indicators and the calculated compatibility indices for a neat cement paste and those with added calcium chloride or extractives. The main benefit from the accelerator addition is seen in the effect on $I_2(t)$, where a negative value means an improvement in relation to the neat cement paste, which turns the overall index $I^x(T,t,S)$ negative also. Because advantages were also obtained in terms of S_{max} , index $I^+(T,t,S)$ is also negative, which strongly indicates a better hardening of cement. All additions of extractives, either from cork, pine, or blue gum, were detrimental, with the strongest effect shown by pine extractives.

Regarding the addition of cork or cork extractives to a cement paste (Table 2), the inclusion of calcium chloride gives benefits, mainly with a level of 5% incorporation, as shown by lower index values in comparison with cement paste with cork alone. The application of cork that was previously extracted with water or 0.1% NaOH solution had better T_{max} , t_{max} , and S_{max} values. Ethanol and diethyl ether were also advantageous in terms of t_{max} , but extraction with petroleum ether provided no advantage. An important aspect in Table 2 is that whereas index $I^{*}(T,t,S)$ gives a negative value, and, hence, a better situation than the standard, when calcium chloride as added at 5%, index $I^{*}(T,t,S)$ is positive, although small, meaning that there was no overall advantage.

Table 3 shows that the addition of calcium chloride to pine-containing pastes had similar benefits to those observed above. However, in the same way as noted in Table 2, the contradiction between $I^{x}(T,t,S)$ and $I^{+}(T,t,S)$ are also improved. The extraction of pine proved beneficial in terms of t_{max} , as shown by $I_{2}(t)$, and, as a consequence, $I^{x}(T,t,S)$ and $I^{+}(T,t,S)$ and $I^{+}(T,t,S)$ are also improved. With blue gum (Table 4), the trends were close to those of cork. From Tables 2–4, and

taking into account the compatibility indices for the substrates applied in the natural state, it can be seen that cork presented the least hindrance to cement curing, followed by blue gum, and pine.

Although thermal compatibility indices provide a simple and useful way of assessing the curing behavior of a given cement paste and for comparing several conditions, they still lack some precision, and conclusions should be made with caution. For example, by considering Fig. 2 and the results presented in Table 3, then we perceive that plots obtained with pine extracted with ethanol, water, and 0.1% NaOH are almost superimposed. However, the indices $I_2(t)$ for the same conditions differ by up to 8 units. Therefore, there is some doubt as to what a significant difference will be for a given index that shows significantly different curing behavior. From the data presented in this article, it is not clear which index is better, $I^{*}(T,t,S)$ or $I^{+}(T,t,S)$.

To validate the compatibility indices, their absolute values and their variations must be compared with the mechanical properties of the composites made from cement and a given wood additive. This work is currently underway. Panels are being manufactured in the range of conditions indicated in Tables 1–4. Then, mechanical properties, including MOR, modulus of elasticity, and IB, will be measured. The differences in such properties will be assessed against the corresponding differences in the compatibility indices and in the T-t plots. It should be possible to estimate a threshold level for variation in a given index, which corresponds to a significant variation in the physical properties, and to assess which index of the five presented in this article best indicates compatibility.

Conclusions

Temperature profiles provide a simple way to qualitatively assess the curing behavior of cement pastes to which lignocellulosic substrates are added. The trends exhibited by cork, blue gum, and pine were similar across the range of setting conditions of cement pastes.

The inclusion of cork, pine, or blue gum in a cement paste hinders cement setting, as shown by the increase of $t_{\rm max}$, and the reduction of $T_{\rm max}$ and $S_{\rm max}$. The addition of a setting accelerator, calcium chloride in this case, at a level of 5% (cement basis), however, is able to overcome the negative effect of the presence of the lignocellulosic substrates, by shortening $t_{\rm max}$ to levels even lower than that obtained with the standard, a neat cement paste. Nevertheless, $T_{\rm max}$ is still lower than the standard.

Extraction of the substrates with some polar extraction agents, like ethanol, water, or 0.1% NaOH solution, can give a slight benefit in terms of thermal behavior, by short-ening $t_{\rm max}$. On the other hand, no systematic advantage was found with the nonpolar solvents petroleum ether and diethyl ether.

The addition of water extractives from cork, blue gum, or pine to a cement paste has a small effect by making T_{max} and S_{max} smaller and t_{max} longer. However, the effect is

smaller than that imparted by the substrate itself, for three reasons. A decrease of $T_{\rm max}$ may be brought about either by a lower extent of cement hardening, but also by the presence of a given mass of wood or cork or other lignocellulosic material that does not contribute to heat generation, but, instead, absorbs it. In addition, agents other than extractives may be involved in the impairment of cement-curing reactions. Also, the adsorption of cations like calcium on lignocellulosic surfaces may play a role. This process would remove the ions from solution, making them less available for the formation of the crystal forms that lead to cement hardening. Probably because of this, of the three substrates investigated in this work, cork showed the least degree of cement-setting hindrance, although it presented the higher overall extractive content.

Although thermal compatibility indices provide a simple and quantitative way of assessing cement setting, they need to be validated against the physical properties of wood– cement composite manufactured in the same conditions as those applied to obtain temperature profiles. Such verification would facilitate the determination of a threshold variation that could be taken as significant, and determine which index definitions really correlate to the levels of physical properties.

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