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Effects of Selected Pre-treatment Methods on the Hydration Behaviour of Rattan-Cement Mixtures

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Abstract: The influence of calcium chloride ($CaCl_2$), magnesium chloride ($MgCl_2$), hot-and cold-water pre-treatments, and prolonged storage on the hydration behaviour of particles extracted from *Calamus deerratus* and *Laccosperma secundiflorum* rattan canes mixed with cement was investigated. While the untreated rattans inhibited cement setting, pre-treatments generally improved compatibility. The addition of chemical additives and aqueous pre-treatments enhanced the compatibility of the rattan-cement composites while peeling of silicified epidermis generally reduced the compatibility parameters. Pre-storage positively influenced the hydration behaviour of the *L. secundiflorum* composites while it negatively affected the *Calamus* composites. Statistical analyses revealed that all the pre-treatment methods employed significantly improved the hydration behaviour of the rattan-cement mixes except water and $CaCl_2$ treatments. The compatibility indices based on the maximum hydration temperature (T_{max}), compatibility factor (C_A), setting time (t_{max}) and time ratio indices (t_R) did not consistently predict the hydration behaviour of the rattan composites. A modified time ratio index based on the threshold temperature (40°C) is proposed for prediction of the hydration behaviour of rattan-cement mixes.

Keywords: Calamus deerratus, Laccosperma secundiflorum, compatibility indices, hydration behaviour.

INTRODUCTION

Different lignocellulosics such as particles extracted from hardwoods and softwoods, agricultural residues, manufacturing wastes etc. have been tested and certified useful for cement bonded composites (CBCs) production over the years (Gnanaharan and Dhamodharan, 1985; Ajayi, 2006). Assessment of the compatibility level of these lignocellulosics with cement has been carried out using the hydration test method based on different indices (Sanderman and Kohler, 1964; Weatherwax and Tarkow, 1964; Hofstrand *et al*., 1984, Hachmi *et al*., 1990; Karade *et al*., 2003; Pereira *et al*., 2006; Olorunnisola, 2008). Olorunnisola (2008) proposed a new scheme based on comparing the setting time of composites with that of the neat cement as the means

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for judging the suitability of a candidate lignocellulosic for cement composite manufacture, while Jorge *et al.* (2004) noted the suitability of setting time and maximum hydration temperature as predictors of the inhibitory properties of such cement mixes. Since heat is needed for the formation of cement bond (Neville and Brooks, 1987; Neville, 1995) there may be a link between the time ratio index proposed by Olorunnisola (2008) and the maximum hydration temperature. This work therefore investigated the effectiveness of different compatibility schemes in predicting the hydration behaviour of two rattan species (*Calamus deerratus* and *Laccosperma secundiflorum)* when mixed with cement.

MATERIALS AND METHODS

Matured stems of *C. deerratus* and *L. secundiflorum* were harvested from Gambari forest reserve, Ibadan, Oyo state, Nigeria. The harvested canes were separated into two parts. One part was manually peeled to remove the silicified epidermis, while the other part was left intact. Both the peeled and unpeeled canes were cross-cut into 6 cm length, air-dried for 3 weeks and stored for 0 and 6 months in a ventilated room at temperature of 29 ± 3ºC. After storage, the chopped canes were hammer milled and sieved. Particles that passed through the 0.85 mm sieve and were retained in the 0.60 mm sieve were collected and separated into two portions *i.e.*. those to be used 'as is' and those to be subjected to pre-treatments. Pre-treatments involved soaking different portions of the particles in de-ionised cold (25˚C) and hot water (80˚C) for 30 minutes each, draining, re-washing with de-ionised water for 5 minutes to remove soluble extractives, and air drying for 14 days to an average moisture content of 10 per cent.

Hydration Test

200g of cement and 15g of cane particles were dry-mixed and then wetted with 93 ml of de-ionised water for both *C. deeratus* and *L. secundiflorum,* respectively until homogeneous slurries were formed (Adefisan and Olorunnisola, 2007). The neat cement was mixed with 90 ml of de-ionised water. Calcium chloride ($CaCl_2$) and magnesium chloride ($MgCl_2$) were used as chemical accelerators. Each accelerator was dissolved in the de-ionised water at two concentration levels, *i.e.*. 0 and 3 per cent (by weight of cement). The mixtures were placed in thermally sealed thermos flasks at room temperature (28 ± 3ºC) and the rise in temperature was recorded at an interval of 10 minutes for 24 to 27 hours via a data logger using a T-type thermocouple. Three replicates of each mixture were prepared. The parameters measured included the maximum temperature (T_{max}) and time to attain maximum temperature (t_{max}). The compatibility was assessed using the four indices shown in Table 1.

RESULTS AND DISCUSSION

The results of the hydration experiments are shown in Tables 2 and 3

Table 1. Cement compatibility assessment schemes

S/No.	Parameters	Classification Index	Reference
1	Setting time (time to reach maximum temp., t_{max})	Suitable (<15h) Unsuitable (> 20h)	Hofstrand *et al.* (1984)
2	Maximum hydration temp.	Suitable (T_{max} > 60°C) Intermediately Suitable (T_{max} = 50 - 60°C) Unsuitable (T_{max} < 50°C)	Sandermann and Kohler, (1964)
3	Compatibility Factor	Compatible: C_A > 68% Moderately compatible: 68% > C_A > 28% Not Compatible: C_A < 28%	Hachmi *et al.* (1990)
4	Time ratio (t_R): ratio of setting time of wood/cement mix to neat cement i.e. $t_R = t_{WC}/t_{NC}$	$1 \leq t_R \geq 1.5$ (Suitable) $1.5 < t_R \geq 2.0$ (Acceptable) $t_R > 2.0$ (Inhibitory)	Olorunnisola (2008)

Maximum hydration temperature of rattan-cement composites

The maximum hydration temperature attained ranged between 37.0 to 46.6°C and 43.1 to 45.1°C without pre-treatment and from 37.4 to 65.7°C and 43.1 to 62.5°C when subjected to varying pre-treatment measures for the *Calamus* and *Laccosperma* composites respectively (Tables 2 and 3). Based on the Sandermann and Kohler (1964) criterion (Table 1), the untreated rattans are not compatible with cement having T_{max} less than 50°C. Pre-treatment of the rattan particles generally improved their compatibility with cement. The greatest improvement was observed for particles pre-treated with 3 per cent $CaCl_2$ while those subjected to prolonged storage recorded the least.

Table 2. Compatibility assessment of *C. deerratus* composites

Pre-treatments	Particle Type	t_{max}	Remarks	T_{max}	Remarks	C_A	Remarks	t_R	Remarks
Control (None)	Unpeeled	26.5	U	46.6	U	72.5	C	3.7	I
	Peeled	3.7	S	37.0	U	65.2	MC	0.5	S
3% $CaCl_2$	Unpeeled	7.4	S	65.7	S	101.5	C	1.0	S
	Peeled	3.7	S	37.4	U	65.9	MC	0.5	S
3% $MgCl_2$	Unpeeled	11.1	S	62.8	S	99.7	C	1.4	S
	Peeled	3.8	S	37.8	U	65.4	MC	0.5	S
Cold Water	Unpeeled	7.8	S	57.9	IS	97.7	C	1.1	S
	Peeled	8.5	S	57.1	IS	97.6	C	1.2	S
Hot Water	Unpeeled	7.2	S	58.6	IS	99.0	C	1.0	S
	Peeled	8.6	S	57.7	IS	99.1	C	1.2	S
Pre-Storage	Unpeeled	3.7	S	38.7	U	70.2	C	0.5	S
for 6 Months	Peeled	3.7	S	39.3	U	70.3	C	0.5	S

Keys: A-Acceptable, C- Compatible, MC- Moderately Compatible, I- Inhibotory, U- Unsuitable
IS-Intermediately suitable, S-Suitable

Table 3. Compatibility assessment of *L. secundiflorum* composites

Pre-treatments	Particle Type	t_{max}	Remarks	T_{max}	Remarks	C_A	Remarks	t_R	Remarks
Control (None)	Unpeeled	25.7	U	43.1	U	71.2	C	3.6	I
	Peeled	24.7	U	45.1	U	71.1	C	3.4	I
3% $CaCl_2$	Unpeeled	11.3	S	60.9	S	102.4	C	1.6	A
	Peeled	8.7	S	62.5	S	103.5	C	1.2	S
3% $MgCl_2$	Unpeeled	23.1	U	49.3	U	78.9	C	3.0	I
	Peeled	22.7	U	51.0	IS	80.1	C	2.9	I
Cold Water	Unpeeled	8.6	S	56.8	IS	98.0	C	1.2	S
	Peeled	7.4	S	58.0	IS	98.5	C	1.0	S
Hot Water	Unpeeled	8.3	S	56.6	IS	97.8	C	1.2	S
	Peeled	7.7	S	55.5	IS	95.7	C	1.1	S
Pre-Storage	Unpeeled	20.4	IS	43.2	U	77.0	C	2.8	I
for 6 Months	Peeled	20.1	IS	46.0	U	81.0	C	2.6	I

Keys: A-Acceptable, C-Compatible, MC-Moderately Compatible, I-Inhibotory, U-Unsuitable, IS-Intermediately Suitable, S-Suitable

Generally, composites made from the *Laccosperma* particles had higher T_{max} than those of *Calamus* suggesting that *C. deerratus* species inhibited cement setting more than *L. secundiflorum*. Dahunsi (2000) and Adefisan (2010) had noted the preponderance of strengthening tissues (sclerenchyma cells) in *Laccosperma* canes as against storage tissues (parenchyma cells containing cement inhibitors *i.e.*. starches and tannins) in the *Calamus* canes. Presence of more cement inhibitors in the *Calamus* particles may have lowered the T_{max} in comparison with those of the *Laccosperma* composites.

Whereas peeling of the silicified epidermis lowered the T_{max} of the *Calamus* composites, it increased that of the *Laccosperma* composites (Table 2 & 3). This suggests that in the preparation of rattan particles for CBC production only canes from the *Laccosperma* species should be peeled. Also, while *Calamus* cane particles were more amenable to hot water extraction, those of the *Laccosperma* were amenable to cold water. Alberto *et al*. (2000) had noted that the more inhibitory lignocellulosic materials required hot water extraction to enhance their compatibility with cement. It stands to reason, therefore, that *Calamus* species was more amenable than *Laccosperma* species to hot water treatment. However, although rattan composites made from cold and hot water treated particles formed hardened pastes, they were regarded as intermediately suitable based on Sandermann and Kohler (1964) classification. This implies that the Sandermann and Kohler (1964) index did not accurately predict the hydration behaviour of the rattan composites.

Prolonged storage apparently did not improve the compatibility of the rattan particles since composites made from these particles had T_{max} less than 50°C (Table 2). Also, composites pre-treated with $CaCl_2$ recorded higher T_{max} than those treated with $MgCl_2$ which is attributable to the higher reactivity of calcium over magnesium (Bodner and Pardue, 1999). Duncan's multiple range tests showed that while the pre-treatments and peeling had significant effects ($p \leq 0.05$) on the T_{max}, the effect of different species did not influence the T_{max} of the rattan composites. No significant difference existed in T_{max} of the rattan particles subjected to aqueous extraction 'and those pre-treated with $CaCl_2$ (Table 4).

Table 4. Duncan's Multiple Comparison for t_{max}, T_{max}, C_A and t_R

	Compatibility Schemes			
Levels	t_{max}	T_{max}	C_A	t_R
Pre-treatments				
None	20.1^{A}	43.0^{C}	70.0^{C}	2.8^{A}
Cold water	8.1^{C}	57.4^{A}	97.9^{A}	1.1^{C}
Hot Water	8.0^{C}	57.1^{A}	97.9^{A}	1.1^{C}
3% $CaCl_2$	7.8^{C}	56.6^{A}	93.3^{A}	1.1^{C}
3% $MgCl_2$	15.2^{B}	50.2^{B}	81.0^{B}	2.0^{B}
6 Months	12.0^{BC}	42.1^{C}	$74.6B^{C}$	$1.6B^{C}$
Processing				
Unpeeled	13.4^{A}	53.4^{A}	88.8^{A}	1.8^{A}
Peeled	10.3^{B}	48.7^{B}	82.8^{B}	1.4^{B}
Species				
C. deerratus	8.0^{B}	49.8^{A}	83.7^{B}	1.1^{B}
L. secundiflorum	15.7^{A}	52.3^{A}	87.9^{A}	2.1^{A}

Means with the same letters as superscripts in a column are not statistically different

Setting time of rattan-cement composites

As shown in Tables 2 and 3, the setting times (t_{max}) for the rattan-cement mixtures ranged between 3.7 to 26.5 h and 24.7 to 25.7 h without rattan particle pre-treatment and from 3.7 to 11.1 and 7.4 to 23.1 h for pre-treated composites. Based on the index proposed by Hofstrand *et al.* (1984), the untreated *Laccosperma* and unpeeled *Calamus* particles were not compatible with cement while those of the peeled *Calamus* were suitable for CBC manufacture. Whereas visual examination revealed that the peeled *Calamus* composites did not form hardened pastes after 24 to 27 h of experimentation, Hofstrand *et al.* (1984) index indicated that they were suitable for CBC production. This suggests that Hofstrand *et al.* (1984) index did not accurately predict the hydration behaviour of the rattan composites.

The greatest improvement in t_{max} was exhibited by composites subjected to prolonged storage for the *Calamus* composites and those treated with cold and hot water for the *Laccosperma* composites. Here also, it was found that the addition of $CaCl_2$ substantially reduced the t_{max} of the rattan composites more than $MgCl_2$ due to the higher reactivity of calcium over magnesium (Bodner and Pardue, 1999).

Duncan's Multiple Range Test (DMRT) revealed that while peeling, species and pre-treatment significantly affected the t_{max} of the rattan composites, no significant difference existed in the t_{max} of composites made from particles of the rattan species subjected to aqueous extraction and those treated with $CaCl_2$ (Table 4).

Compatibility factor

The compatibility factor (C_A) of the rattan composites are shown in Tables 2 and 3. The rattan particles were generally compatible with cement based on Hachmi *et al.* (1990) classification. However, since composites made from the untreated *Laccosperma* and unpeeled *Calamus* particles formed hardened pastes with cement while those of the peeled *Calamus* did not form cohesive bonds, it means that particles extracted from the peeled *Calamus* were not compatible with cement. This suggests that the compatibility factor proposed by Hachmi *et al*. (1990) did not again accurately predict the hydration behaviour of the rattan-cement composites. Whereas peeling reduced C_A of the *Calamus* composites, improvement in C_A was observed in composites made from the peeled *Laccosperma*. Composites pre-treated with $CaCl_2$ again had higher C_A than those treated with $MgCl_2$ suggesting $CaCl_2$ as a better chemical accelerator than $MgCl_2$. Cold water pre-treatment and prolonged storage improved the C_A of the *Laccosperma* composites. Peeling, species and pre-treatment significantly affected the C_A of the rattan composites (Table 4).

Time ratio index

The t_R indices of the rattan composites are shown in Tables 2 and 3. It ranged from 0.5 to 3.7 and 3.4 to 3.6 without pre-treatment and between 0.5 and 1.4 and 1.0 and 3.0 when subjected to different pre-treatment measures. Based on Olorunnisola's (2008) classification, the untreated rattans were generally unsuitable for CBC production. The greatest improvement in t_R was observed in composites made from *Calamus* stored for 6 months and *Laccosperma* treated with cold and hot water. Whereas composites made from the pre-treated *Calamus* canes were classifiable as being suitable for CBC manufacture, those made from the *Laccosperma* particles ranged from 'inhibitory to suitable'.

However, composites made from the *Calamus* canes stored for 6 months and those of the untreated peeled *Calamus* did not form hardened pastes after 24 to 27 h, it means that the t_R index also did not accurately predict the hydration behaviour of the rattan composites. Statistical analyses revealed that peeling, species and pre-treatment significantly affected the t_R of the rattan composites and no significant difference existed in the t_R of composites made from particles subjected to aqueous extraction and those treated with $CaCl_2$ (Table 4).

Proposed Compatibility Index / modification of the Time Ratio Index

The results obtained from the investigation of the effectiveness of selected compatibility indices (setting time, maximum hydration temperature, compatibility factor and time ratio index) suggested that none of indices are perfect in predicting the suitability of the material for rattan-cement composites.

A close examination of Tables 2 and 3 seem to indicate a threshold temperature of 40°C for crystalline bond formation in the rattan-cement composites. This observation seems to concur with the report of Olorunnisola (2008) in which composites made from the untreated *Laccosperma*, coconut and mixture of untreated rattan and coconut had T_{max} less than 40°C and were regarded as inhibitory to cement setting. Therefore, if 40°C is regarded as the threshold T_{max}, modifications can then be made to the time ratio index proposed by Olorunnisola (2008) that:

i. composites with T_{max} less than 40°C are inhibitory irrespective of the t_R values
ii. composites with T_{max} greater than 40°C and $1 \lesssim tR \geq 1.5$ are suitable, further pre-treatment unnecessary
iii. composites with T_{max} greater than 40°C and $1.5 < t_R \geq 2.0$ are acceptable, further pre-treatment recommended, and
iv. composites with T_{max} greater than 40°C and $t_R > 2.0$ are inhibitory, further pre-treatment is highly recommended.

The application of the proposed temperature dependent time ratio index is presented in Table 5. The proposed scheme seems to predict the hydration behaviour of the rattan-cement composites more consistently than the other methods. Based on the modified time ratio index, it is obvious that the untreated rattans, especially the peeled *Calamus*, are inhibitory to cement setting and would need to be pre-treated prior to CBC production while those subjected to varying levels of pre-treatments are compatible. This new scheme is therefore recommended for evaluating the compatibility of rattan with cement for CBC production.

Table 5. Proposed Compatibility Index / modification of the Time Ratio Index

		C. deerratus			*L. secundiflorum*		
Pre-treatments	Particle Type	T_{max}	t_R	Remarks	T_{max}	t_R	Remarks
Control (None)	Unpeeled	46.6	3.7	I	43.1	3.6	I
	Peeled	37.0	0.5	I	45.1	3.4	I
3% $CaCl_2$	Unpeeled	65.7	1.0	S	60.9	1.6	A
	Peeled	37.4	0.5	I	62.5	1.2	S
3% $MgCl_2$	Unpeeled	62.8	1.4	S	49.3	3.0	I
	Peeled	37.8	0.5	I	51.0	2.9	I
Cold Water	Unpeeled	57.9	1.1	S	56.8	1.2	S
	Peeled	57.1	1.2	S	58.0	1.0	S
Hot Water	Unpeeled	58.6	1.0	S	56.6	1.2	S
	Peeled	57.7	1.2	S	55.5	1.1	S
6 Months	Unpeeled	38.7	0.5	I	43.2	2.8	I
	Peeled	39.3	0.5	I	46.0	2.6	I

Keys: A- Acceptable, I- Inhibitory, S-Suitable

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