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EFFECTS OF CHEMICAL ADDITIVES ON THE HYDRATION BEHAVIOUR OF CEMENT COMPOSITES FROM *CALAMUS* AND *LACCOSPERMA* CANES

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Abstract
The effects of Calcium Chloride ($CaCl_2$) and Magnesium Chloride ($MgCl_2$) on the maximum hydration temperature (T_{max}), setting time (t_{max}) and Time ratio (t_R) of *Calamus deerratus* and *Laccosperma secundiflorum* particles mixed with Portland cement was investigated. Particles of rattan canes were mixed with cement, water and chemical additives. Hydration tests were performed in thermally sealed thermos flasks while hydration parameters: T_{max} and t_{max} were measured after 24 hrs. The t_{max}, T_{max} and t_R ranged between 25.7 to 26.5hrs, 43.1 to 46.6°C and 3.6 to 3.7 respectively without pre-treatment and were between 7.4 to 23.1 hrs, 49.3 to 65.7°C and 1.0 to 3.0 respectively when pre-treated with chemical additives. Findings showed that untreated rattans generally inhibited cement setting probably due to inherent sugar content. Particles of *Laccosperma* canes inhibited cement setting more than those of the *Calamus* canes. The addition of both $CaCl_2$ and $MgCl_2$ significantly improved the T_{max} but reduced the t_{max} and t_R of the rattan-cement mixes. Addition of $CaCl_2$ enhanced the hydration behaviour of the rattan composites more than $MgCl_2$.

Keywords: *Calamus deerratus*, *Laccosperma secundiflorum*, cement composite, hydration behaviour, chemical additives.

Introduction

Rattans are spiny climbing plants belonging to the palm family known as *Calamoidea*. There are about 600 rattan species distributed in the tropical and sub-tropical regions of the world. Four genera namely *Laccosperma*, *Calamus*, *Eremospatha* and *Oncocalamus* are endemic to Nigeria with *Calamus deerratus* representing the largest available species while *Laccosperma secundiflorum* species are used for skeletal structures of baskets and furniture (Liese, 2002; Lucas and Dahunsi, 2004). Although the primary use of rattan canes are largely for basketry and furniture works, yet they are now gaining prominence as furnish for cement bonded composites (CBC) production due to their availability and accessibility (Olorunnisola, 2005; Olorunnisola *et al.*, 2005; Olorunnisola, 2008; Olorunnisola and Adefisan, 2008). Olorunnisola and Adefisan (2002) noted the usefulness of mixed rattan furniture waste for the production of low stressed internal building components while cement bonded composites made from *L. secundiflorum* particles were found to possess adequate dimensional stability for outdoor applications (Olorunnisola, 2005).

Furthermore, since different rattan canes exhibit different physical and mechanical properties (Dahunsi, 2000) which may affect CBC production, it is necessary to investigate the compatibility of different rattan canes for CBC manufacturing. A major limitation in rattan cement composites production is the inherent sugar which may likely affect rattan-cement interactions (Dahunsi, 2000; Adefisan and Olorunnisola, 2007). Pre-treatment measures such as the application of chemical accelerators may be incorporated into the composite mixes to enhance the formation of strong crystalline bonds by increasing the hydration temperature and reducing the setting times (Ramachandran, 1994; Soriano *et al.*, 1998). Semple and Evans (2002) noted the accelerating effects of chlorides in cement composite mixes. It was found that the addition of calcium chloride enhanced the hydration temperature and reduced the setting time. However, different chemical additives have diverse accelerating effects when incorporated in cement composites production (Semple and Evans, 2002). Therefore, the effect of different chemical accelerators on the hydration behaviour of rattan-cement mixes should be explored.

This work examines the compatibility of different rattan species namely *Calamus deerratus* and *Laccosperma secundiflorum* with cement and the effects of calcium chloride ($CaCl_2$) and magnesium chloride ($MgCl_2$) on the hydration characteristics of rattan cement mixes using the hydration test approach.

Material and Methods

Material preparation

Matured stems of *Calamus deerratus* and *Laccosperma secundiflorum* canes were harvested from Gambari Forest Reserve Ibadan, Oyo state, Nigeria. These were identified through comparison with stocks kept in the herbarium of the Department of Botany and Microbiology, University of Ibadan. The harvested canes were converted into billets of about 6 cm and hammer milled. The milled particles were collected and sieved using a set of 1.18 mm, 0.85 mm and 0.60 mm sieves. Particles that passed through the 0.85 mm sieve and were retained in the 0.60 mm sieve were collected, air dried to 10% moisture content and separated into two portions i.e. those to be used 'as is' and those to be subjected to chemical pre-treatments.

Hydration Test

For the hydration tests, 15g of the rattan particles, 200g of ordinary Portland cement and 93ml of de-ionized water were mixed in a polyethylene bag to form homogeneous slurry as in Adefisan and Olorunnisola (2007). The neat cement was mixed with 90 mL of de-ionised water. Calcium chloride ($CaCl_2$) and magnesium chloride ($MgCl_2$) used as chemical accelerators, were added by dissolving in the de-ionised water at two concentration levels, i.e. 0 and 3% (by weight of cement). The tests were performed in a set of well insulated thermos flasks. Temperature rise was monitored for 27 hours using a T-type thermocouple. Three replicates of each mixture were prepared. The compatibility of *C. deerratus* and *L. secundiflorum* with cement was assessed using the compatibility indices shown in Table 1.

Results and Discussion

The results of the hydration tests are shown in Table 2 and depicted in Fig 1.

Setting time of Rattan-Cement Composites

The setting time of the rattan-cement composites are presepted in Table 2. The setting time of the rattan composites without pre-treatment ranged from 25.7 to 26.5hrs. Based on the classification of Hofstrand *et al.* 1984, the untreated rattan particles are unsuitable for CBC production having t_{max} greater than 15hrs. The addition of chemical additives improved the t_{max} of the rattan-cement mixes. Composites pre-treated with $CaCl_2$ had between 56 to 72% improvement in setting time compared with 10 to 58% for $MgCl_2$ treated composites. What this suggests is that chemical additives rendered the inhibitory substances present in rattan particles inactive and enhanced compatibility of rattan particles with cement. This observation is in line with those of Semple and Evans (2002) that the application of chemical additives to wood-cement mixes remove / reduce cement inhibitors and enhance the hydration behaviour.

Also, while the application of different chemical additives did not have significant influence on the t_{max} of the *Calamus* composites, $CaCl_2$ was more effective than $MgCl_2$ in reducing the setting times of the *Laccosperma* composites. What this indicates is that particles of the *Laccosperma* canes inhibited cement setting more than *Calamus* (Table 3) due to higher sugar content (Dahunsi, 2000). The higher reactivity of calcium over magnesium (Bodner and Pardue, 1999) may have resulted in the ability of $CaCl_2$ to overcome the inhibitory effects of sugars and extractives in the cement mixes than $MgCl_2$.

Table 1: Compatibility Assessment Schemes

S / No.	Parameters	Classification Index	Reference
1	Time to Maximum Temperature (t_{max})	Suitable (<15hr) Unsuitable (> 20hr)	Hofstrand *et al.* 1984
2	Maximum Hydration Temperature	Suitable ($T_{max} > 60^0C$) Intermediately Suitable ($T_{max} = 50 - 60^0C$) Unsuitable ($T_{max} < 50^0C$)	Sandermann and Kohler, 1964
3	Time Ratio (t_R): Ratio of setting time of wood- cement composite to neat cement i.e. $t_R = t_{WC} / t_{NC}$	$1 \le t_R \ge 1.5$ (Suitable) $1.5 < t_R \ge 2.0$ (Acceptable) $t_R > 2.0$ (Inhibitory)	Olorunnisola, 2008

Table 2: Hydration Parameters of Rattan-Cement Composites

	Hydration Parameters		
Pre-treatments	Maximum Temperature (T_{max})	Setting Time (t_{max})	Time Ratio (t_R)
	Calamus deerratus		
None	46.6^{BC}	26.5^{A}	3.7^{A}
3% $CaCl_2$	65.7^{A}	7.4^{B}	1.0^{C}
3% $MgCl_2$	62.8^{A}	11.1^{B}	1.4^{C}
	Laccosperma secundiflorum		
None	43.1^{C}	25.7^{A}	3.6^{AB}
3% $CaCl_2$	60.9^{A}	11.3^{B}	1.6^{C}
3% $MgCl_2$	49.3^{B}	23.1^{A}	3.0^{B}

*Means with the same letters are not statistically different

Table 3: Duncan's Multiple Comparison of the Effect of Chemical Additives, Additive Concentration and Species on the Hydration Parameters of Rattan-Composites

	Hydration Parameters		
Factors	T_{max}	t_{max}	t_R
Additive Concentration			
0%	44.9^{B}	26.1^{A}	3.6^{A}
3%	59.7^{A}	13.2^{B}	1.7^{B}
Chemical Additives			
$CaCl_2$	54.1^{A}	17.3^{B}	2.5^{B}
$MgCl_2$	50.4^{B}	21.6^{B}	2.9^{A}
Species			
Calamus	55.4^{A}	17.9^{B}	2.5^{B}
Laccosperma	49.1^{B}	21.5^{A}	2.9^{A}

*Means with the same letters are not statistically different

Maximum Hydration Temperature of Rattan-Cement Composites

The maximum hydration temperatures (T_{max}) attained by the rattan composites without pre-treatment ranged between 43.1 to 46.6°C. Based on the Sandermann and Kohler (1964) classification, the untreated rattans are again unsuitable for CBC production. The addition of chemical additives to the rattan-cement mixes however resulted in 12 to 29% increment in T_{max} (Table 2). Composites pre-treated with $CaCl_2$ had higher T_{max} than those treated with $MgCl_2$. The application of $MgCl_2$ did not significantly improve the T_{max} of the *Laccosperma*-cement mixes in relation to the *Calamus* composites. What the foregoing suggests is that chemical additives removed / reduced the cement inhibitors present in the rattan-cement mixes and enhanced the hydration temperature in line with the observations of Ramachandran, (1994); Soriano *et al.*, (1998) and Semple and Evans (2002).

However, while calcium chloride seemed to perform better as a chemical accelerator for the rattan-cement mixes than $MgCl_2$ due to the higher reactivity of calcium over magnesium (Bodner and Pardue, 1999), particles of the *Laccosperma* canes inhibited cement setting more than those of the *Calamus* (Table 3). Again higher sugar content of the *Laccosperma* canes (Dahunsi 2000) may have retarded the T_{max} of the *Laccosperma* composites in comparison with those of the *Calamus* composites.

Time Ratio Indices of Rattan-cement Composites

The time ratio index (t_R) of the rattan-cement mixes are shown in Table 2. The t_R ranged from 3.6 to 3.7 for the rattan composites without pre-treatment and from

1.0 to 3.0 when treated with chemical additives. Based on Olorunnisola (2008) classification, the untreated rattans are again unsuitable for CBC production having a t_R greater than 2.0. Pre-treating the rattan composites with chemical additives generally improved the t_R indices and hence the compatibility of the rattan canes with cement.

The application of $CaCl_2$ improved the t_R indices of the rattan-cement composites more than $MgCl_2$ (Tables 2 and 3). As shown in Table 2, whereas rattan-composites pre-treated with $CaCl_2$ had t_R indices that ranged between "Acceptable to Suitable" for CBC production, *Laccosperma*-composites treated with $MgCl_2$ strongly inhibited cement setting. What this implies is that $CaCl_2$ again improved the compatibility of rattan canes with cement than $MgCl_2$. Hence, $CaCl_2$ can be regarded as a better chemical additive than $MgCl_2$ in the production of rattan-cement composites. Particles extracted from the *Laccosperma* canes again inhibited cement setting more than those of the *Calamus*.

Conclusions

The following can be deduced from this work:

i) The untreated particles of *Calamus deerratus* and *Laccosperma secundiflorum* canes are not compatible with cement.

ii) Particles extracted from the *Laccosperma* canes inhibited cement setting more than those of the *Calamus* canes.

iii) The addition of chemical additives enhanced the compatibility of the rattan particles when mixed with cement.

iv) Calcium chloride improved the hydration behaviour of the rattan cement composites more than magnesium chloride.

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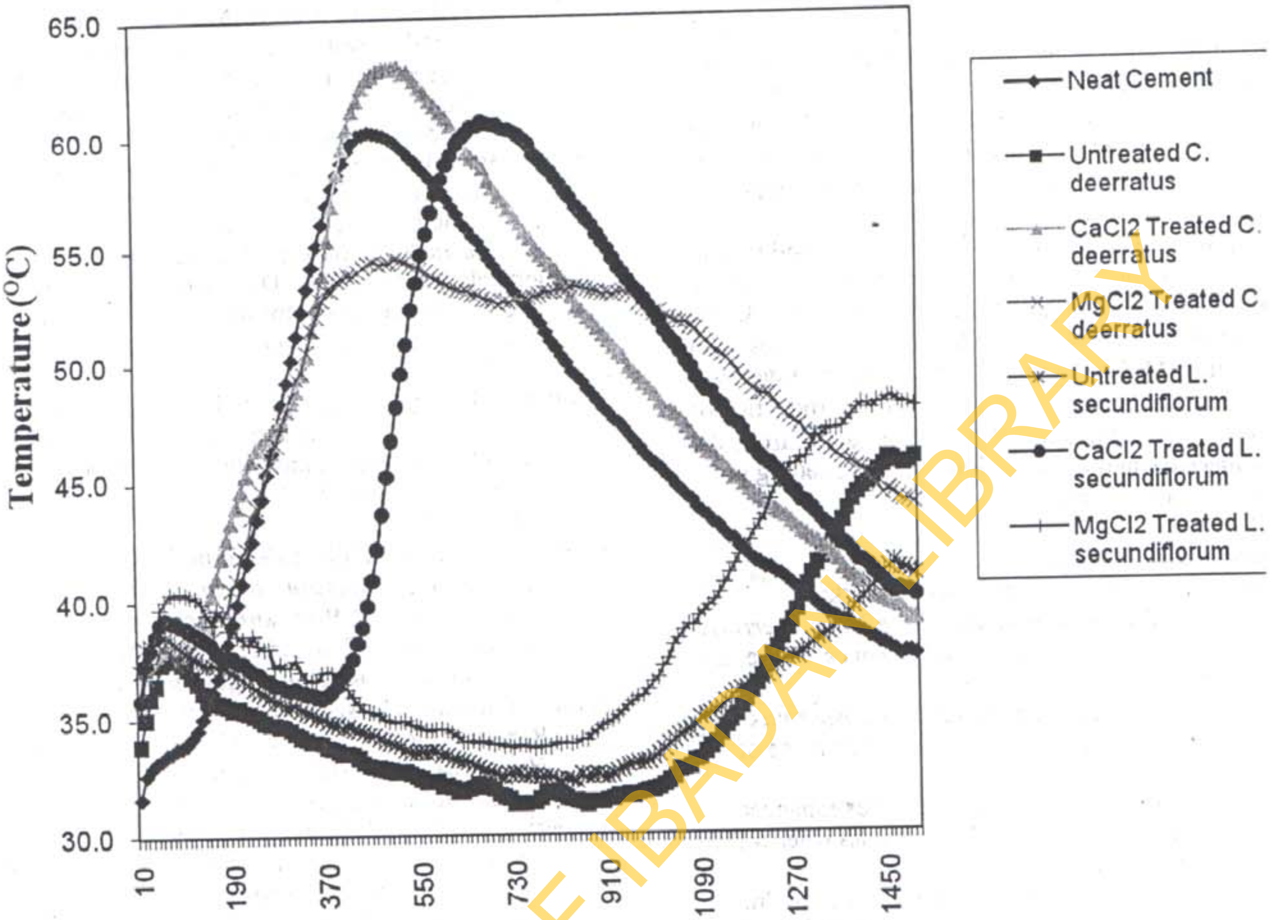

Fig 1: Hydration Behaviour of *C. deerratus* and *L. secundiflorum* Cement Mixes