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Hydration Behaviour and Infrared Spectroscopy of Pre-treatments Effect on Portland Cement-*Eremospatha macrocarpa* and *Laccosperma secundiflorum* Systems

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Abstract: The effects of cold water extraction, incorporation of calcium chloride ($CaCl_2$) and aluminium sulphate ($Al_2(SO_4)_3$) on the setting time (t_{max}), maximum hydration temperature (T_{max}), time ratio (t_R) and surface chemistry of *Eremospatha macrocarpa* and *Laccosperma secundiflorum* particles mixed with Portland cement was investigated. The mixtures were placed in thermally sealed thermos flasks for 24 h after which t_{max}, T_{max} and t_R were measured. The t_{max}, T_{max} and t_R were 12.4 and 11.9 h, 59.1 and 58.3°C, 1.1 and 1.1, respectively for untreated *E. macrocarpa* and *L. secundiflorum* and ranged from 5.2 to 10.7 h, 57.7 to 83.7°C and 0.5 to 0.9, respectively when treated with cold water and chemical additives. Cold water extraction and chemical additives significantly improved the hydration parameters of rattan-cement system. $CaCl_2$ performed better as a chemical accelerator than $Al_2(SO_4)_3$ while *L. secundiflorum* inhibited cement setting more than *E. macrocarpa*. Infrared spectroscopy showed that incorporation of $CaCl_2$ to *L. secundiflorum* particles helped expose cellulose to advance participation thereby enlarging its surface area for interpenetration networking with cement.

Key words: *Eremospatha macrocarpa, Laccosperma secundiflorum*, cold water extraction, chemical additives, cement, hydration temperature, setting time, infrared spectroscopy

INTRODUCTION

Production of Cement Bonded Boards (CBB) from untreated fibrous raw materials is faced with the problem of inhibitory effects of sugars, extractives and lignin in lignocellulosic materials (Moslemi and Lim, 1984; Hong and Lee, 1986). The disadvantages of inhibition include delayed setting, relatively lowered hydration temperature and prolonged time to attain maximum temperature (Moslemi and Lim, 1984). Addition of an accelerator into a mixture of cement-water paste could enhance the speed of hydration process to occur earlier (Nazerian *et al*., 2011). Several attempts have been made to overcome this challenge using cold or hot water extraction and/or incorporation of chemical additives such as calcium chloride ($CaCl_2$), aluminium sulphate ($Al_2(SO_4)_3$), magnesium chloride ($MgCl_2$) prior CBB production (Hong and Lee, 1986; Olorunnisola, 2007). The chemical additives are usually added in quantity of less than 4% (by cement weight) and have been found to enhance many of the boards' properties such as increased density, improved appearance, bending and compressive strength, dimensional stability and improved wood-cement bond due to its effect of accelerating the hydration of wood-cement mixtures (Olorunnisola, 2007). $CaCl_2$ is the most commonly used among various available chemical additives. It accelerates the hydration of cement particularly the tri-calcium silicate phase (C_3S), reduces the setting time and in some cases increases the maximum hydration temperature (Biblis and Lo, 1968; Moslemi *et al*., 1983; Lee and Short, 1989; Ramachandran, 1994; Olorunnisola and Adefisan, 2002). It improves the bending strength and dimensional stability attributable to increased board density and improved bonding between particles of lignocellulosics and cement (Badejo, 1989; Fabiyi, 2004; Olorunnisola, 2006). The internal bonding and direct screw withdrawal increased by 166 and 67%, respectively with the addition of $CaCl_2$ to coconut cement boards while those of density were 64 and 45%, respectively (Almwdia *et al*., 2002).

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However, $CaCl_2$ may not be effective in overcoming severe inhibitions of cement hydration due to heartwood polyphenols of some certain wood species. Compounds that can accelerate cement hydration and also chelate or chemically modify polyphenols are more effective than $CaCl_2$ at improving the cement compatibility of inhibitory wood species (Semple and Evans, 2000). Semple and Evans (2000) found that although $CaCl_2$ performed well as an accelerator in the presence of wood-wool of *Acacia mangium* wood, it was not as effective as other compounds like tin chloride ($SnCl_4$), aluminium chloride ($AlCl_3$) and sodium silicate ($Na_2O.3SiO_3$). This finding suggests that different lignocellulosics depending on their constituent would react differently when incorporated in cement mixes. Therefore, it is important to understand the effect of various chemical additives on different lignocellulosic fibres sources for making CBB.

In Nigeria, several studies have been conducted on the hydration of rattan canes (Dahunsi, 2000; Olorunnisola and Adefisan, 2002; Olorunnisola, 2005; Adefisan and Olorunnisola, 2007; Olorunnisola, 2007). The reason for this is because rattans have short rotation and can be harvested in less than seven years after planting and processed with simple and relatively cheap technology. Also, the assembly line from rattan harvesting to CBB production involves low capital investment (Olorunnisola and Adefisan, 2002; Olorunnisola, 2005; Olorunnisola, 2008). There are three major rattan species namely: *Eremospatha macrocarpa, Laccosperma secundiflorum* and *Calamus deerratus* that are found in Nigeria (Dahunsi, 2000). Adefisan (1999) reported that *E. macrocarpa* has diameter of 10-17 mm and stem length of 20-25 mm while *L. secundiflorum* has diameter of 10-20 mm and stem length of 10 mm. The sugar contents of both species differed with *L. secundiflorum* having the highest carbohydrate content (over 70%) which may cause it to have the highest probability of inhibiting cement hydration (Dahunsi, 2000).

These rattan species respond to pre-treatments differently. Olorunnisola and Adefisan (2008) reported that hot water extraction improved the compatibility of the *C. deerratus* while *L. secundiflorum* was more amenable to cold water extraction. Hot water extraction of *C. deerratus* cement mix had higher hydration temperature and lower setting time than those soaked in cold water. However, cold water extraction resulted in higher hydration temperature and lower setting time in the *L. secundiflorum* cement mix than hot water (Olorunnisola and Adefisan, 2008). Unfortunately, most of the hydration studies conducted on rattan canes by several researchers have centred on *L. secundiflorum* and *C. deerratus* while it is rare to find information on *E. macrocarpa*. Since both *E. macrocarpa* and *L. secundiflorum* are widely spread and common in Nigeria, it is very important to investigate the hydration behaviour of both rattan species under same laboratory conditions and experimental procedures. This step would enhance comparative analysis of hydration behaviour between both species. Apart from the traditional chemical pre-treatments that have been used so far, there is no available information on the use of $Al_2(SO_4)_3$ as chemical additive in relation to rattan canes.

The use of infrared spectroscopy to monitor the chemical structure of different polymers is widely explored. Its versatility is due to the fact that it requires minimum sample preparation, not tedious and not time consuming. However, its use for monitoring the changes that occur when cement, lignocellulosic fibres and chemical additives are mixed together is limited in literature. This study therefore aimed at investigating the effects of cold water extraction and incorporation of $CaCl_2$ and $Al_2(SO_4)_3$ on the hydration behaviour and infrared spectroscopy of *E. macrocarpa* and *L. secundiflorum* mixed portland cement.

MATERIALS AND METHODS

Matured stems of *E. macrocarpa* and *L. secundiflorum* canes were harvested from Gambari Forest Reserve located between longitude 50°44' E and latitude 7°14' N in Ibadan, Oyo state, Nigeria. The canes were converted into billets of about 6 cm and hammer milled. The milled particles were sieved using a set of 1.18, 0.85 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 and dried to 10% moisture content. These particles were divided into four sets with the first set mixed with cement but no additive incorporation (henceforth called untreated), the second set was soaked in distilled water for 30 min at room temperature, drained and dried to 10% moisture content (henceforth referred to as cold water treated), the third set pre-treated with $CaCl_2$ and the fourth set pre-treated with $Al_2(SO_4)_3$ before mixed with cement.

Hydration test: For the hydration tests, 15 g of the *E. macrocarpa* or *L. secundiflorum* particles, 200 g of Portland cement (purchased at a local hardware store, Moscow, Idaho state, USA) and 93 ml of distilled water were mixed in a polyethylene bag to form homogeneous slurry following the method developed by Adefisan and Olorunnisola (2007). The neat cement was mixed with 90 mL of distilled water while 3% $CaCl_2$ or $Al_2(SO_4)_3$

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Table 1: Cement compatibility assessment schemes

Parameters	Classification Index	Reference
Setting time (time to reach maximum temp., t_{max})	Suitable (<15 h) Unsuitable (> 20 h) Suitable (T_{max}>60°C)	Hofstrand *et al.* (1984)
Maximum hydration temp.	Intermediately suitable (T_{max} = 50-60°C) Unsuitable (T_{max}<50°C)	Sandermann and Kohler (1964)
Time ratio (t_R): ratio of setting time of wood/cement mix 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)

(by cement weight) was added. However, untreated and 30 min cold water extracted samples were mixed with the neat cement and 90 mL of distilled water only prior hydration characterisation. Hydration characterisation was performed in a set of well insulated thermos flasks. The temperature rise was monitored for 24 h using thermocouples (J-type) connected to an 8-channel datalogger (USB TC-08, Pico Technology). Three sampled specimens of each mixture were prepared. The compatibility of *E. macrocarpa* and *L. secundiflorum* with cement was assessed using the compatibility indices (Table 1).

Chemical characterization: Specimens for the chemical analysis were obtained from each of the untreated and pre-treated rattan/cement mixes and ground into fine powder using pestle and mortar. Fourier Transform Infrared (FTIR) spectra were measured directly from the powder (1% w/w basis) thoroughly dispersed in KBr (99% w/w basis). Spectra were recorded using a Thermo Scientific Nicolet 8700 spectrometer equipped with a DTGS detector. Each spectrum was taken as an average of 64 scans at a resolution of 4 cm^{-1}.

RESULTS AND DISCUSSION

Setting time of rattan-cement composites: The results of the hydration tests are presented in Table 2 and Fig. 1. The setting times of the *E. macrocarpa* and *L. secundiflorum* cement mixes without pre-treatment were 12.4 and 11.9 h, respectively. Based on the classification of Hofstrand *et al.* (1984), the untreated *E. macrocarpa* and *L. secundiflorum* were very suitable for Cement Bonded Board (CBB) production. Generally, the incorporation of chemical additives and 30 min cold water extraction of the two fibrous materials resulted in reduced setting time that ranged from 5.2 to 9.4 and 5.6 to 10.7 for the *E. macrocarpa* and *L. secundiflorum* cement composites, respectively. In addition, the setting time for 30 min. cold water extraction and 3% $Al_2(SO4)_3$ were very similar for the two rattan species (Table 2). The greatest improvement in the setting time was observed for rattan/cement/water mix treated with $CaCl_2$.

Rattan species (*E. macrocarpa* and *L. secundiflorum*) did not significantly affect the setting times of the rattan/cement/water mix but incorporation of different chemical additives significantly influenced the setting time of the rattan/cement/water mix (Table 3). $CaCl_2$ significantly reduced the setting time of the rattan/cement/water mix than $Al_2(SO_4)_3$. Olorunnisola (2008) reported the setting time of 10.3 h for 30 min cold water extracted *L. secundiflorum* (sieved) mixed with cement. This is agreement with 10.7 h obtained in this study for same condition (Table 2).

Maximum hydration temperature of the rattan-cement composites: The maximum hydration temperatures (T_{max}) attained by the untreated *E. macrocarpa* and *L. secundiflorum* cement mixes were 59.1 and 58.3°C (Table 2). The T_{max} for $CaCl_2$, $Al_2(SO_4)_3$ and 30 min cold water extraction pre-treated *E. macrocarpa*/cement mix were 83.7, 60.4 and 65.1°C, respectively. In addition, T_{max} for $CaCl_2$, $Al_2(SO_4)_3$ and 30 min cold water extraction pre-treated *L. secundiflorum*/cement mix were 78.6, 57.7 and 63.3°C, respectively (Table 2). Based on the Sandermann and Kohler (1964) index, the untreated *E. macrocarpa* and *L. secundiflorum* could be classified as intermediately suitable for the production of CBB. The chemical pre-treated *E. macrocarpa* and *L. secundiflorum* could be classified as suitable except the $Al_2(SO_4)_3$ pre-treated *L. secundiflorum* which ranked as intermediately suitable for the production of CBB. Hence, the addition of chemical additives significantly improved the T_{max} of the rattan/cement mixes with those treated with $CaCl_2$ having highest maximum hydration temperature than those pre-treated with $Al_2(SO_4)_3$ and 30 min cold water extraction.

In addition, *E. macrocarpa*/cement mix had higher T_{max} than *L. secundiflorum*/cement mix. This indicates that $CaCl_2$ was more effective than $Al_2(SO_4)_3$ or 30 min water extraction in minimising the inhibitory effects of sugars and extractives present in the rattan/cement mixtures. The practical implication of this study is that the use of $Al_2(SO_4)_3$ to pre-treat *E. macrocarpa* or *L. secundiflorum* is not economical since 30 min water extraction gave the same T_{max}; hence cold water extraction is preferred because water is readily available and affordable. In addition, *L. secundiflorum* particles however inhibited cement setting more than *E. macrocarpa* particles. Higher sugar contents in the *L. secundiflorum* canes may contribute to its low T_{max}.

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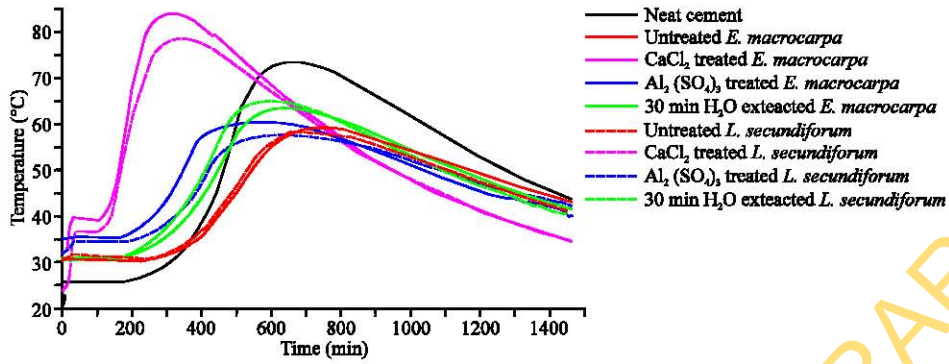

Fig. 1: Hydration behaviour of *Eremospatha macrocarpa* and *Laccosperma secundiflorum*/cement mixes

Table 2: Hydration parameters of *Eremospatha macrocarpa* and *Laccosperma secundiflorum*/cement mixes

Pre-treatment	Setting time maximum (t_{max}, h)	Maximum hydration (temperature T_{max}, °C)	Time ratio index (t_R)
E. macrocarpa/cement mix.			
None	12.4^{a}	59.1^{b}	1.1^{a}
30 min cold H_2O extraction	10.0^{c}	65.1^{bc}	0.9^{b}
3% $CaCl_2$	5.2^{d}	83.7^{a}	0.5^{c}
3% $Al_2(SO_4)_3$	9.4^{c}	60.4^{b}	0.9^{b}
L. secundiflorum/cement mix.			
None	11.9^{a}	58.3^{b}	1.1^{a}
30 min cold H_2O extraction	10.7^{b}	63.3^{bc}	1.0^{ab}
3% $CaCl_2$	5.6^{d}	78.6^{a}	0.5^{c}
3% $Al_2(SO_4)_3$	10.7^{b}	57.7^{b}	0.9^{b}

Means with the same letters in the same column for each of the rattan species are not statistically different

Table 3: Duncan's multiple range tests of the effects of pre-treatment and rattan species on the hydration parameters of rattan/cement mixes.

Factors	Setting time maximum (t_{max}, h)	Maximum hydration temperature (T_{max}, °C)	Time ratio index (t_R)
Pre-treatments			
None	12.2^{a}	58.7^{b}	1.1^{a}
30 min cold H_2O extraction	10.4^{b}	81.2^{a}	0.5^{c}
3% $CaCl_2$	5.4^{c}	81.2^{a}	0.5^{c}
3% $Al_2(SO_4)_3$	10.1^{b}	59.1^{b}	0.9^{b}
Rattan species			
E. macrocarpa	9.0^{a}	66.7^{a}	0.8^{a}
L. secundiflorum	9.4^{a}	64.9^{a}	0.8^{a}

Means with the same letters in the same column for either pre-treatment or rattan species are not statistically different

Olorunnisola (2008) reported that the maximum hydration temperature of 30 min cold water extracted *L. secundiflorum* (sieved) mixed with cement was 51°C. This is contrary to 63.3°C obtained in this study for same condition (Table 2). This contradiction may be due to differences in the sources of Portland cement used. Olorunnisola (2008) used Portland cement produced in Nigeria while Portland cement used in the present study was purchased at a local hardware store, Moscow, Idaho state, USA. The study conducted by Olorunnisola (2008) ranked 30 min cold water extracted *L. secundiflorum* as intermediately suitable while the present study conducted at Idaho ranked it suitable for CBB production.

The choice of any of these two rattan species (without pre-treatment) did not significantly affect the T_{max} of the rattan/cement mixes. However, the application of chemical additives significantly influenced the maximum hydration temperatures of the *E. macrocarpa* and *L. secundiflorum*/cement mixes (Table 3). This implies that different chemical additives had different effects on the hydration behaviour of the rattan/cement mixes.

Time ratio indices of the rattan-cement composites: The time ratio indices (t_R) of the rattan/cement mixes are presented in Table 2. The time ratio indices for both untreated rattan species cement mixes were the same (1.1). Similarly, the t_R for $CaCl_2$ pre-treated *E. macrocarpa*/cement mix and *L. secundiflorum*/cement mix were the same (0.5). The t_R for $Al_2(SO_4)_3$ and 30 min cold water were 0.9 and 0.9-1.0, respectively for pre-treated *E. macrocarpa*/cement mix and *L. secundiflorum*/cement mix. Therefore, pre-treating either of the two rattan species with $CaCl_2$, $Al_2(SO_4)_3$ or 30 min cold water extraction did not make any difference, hence t_R is not rattan species dependent but chemical

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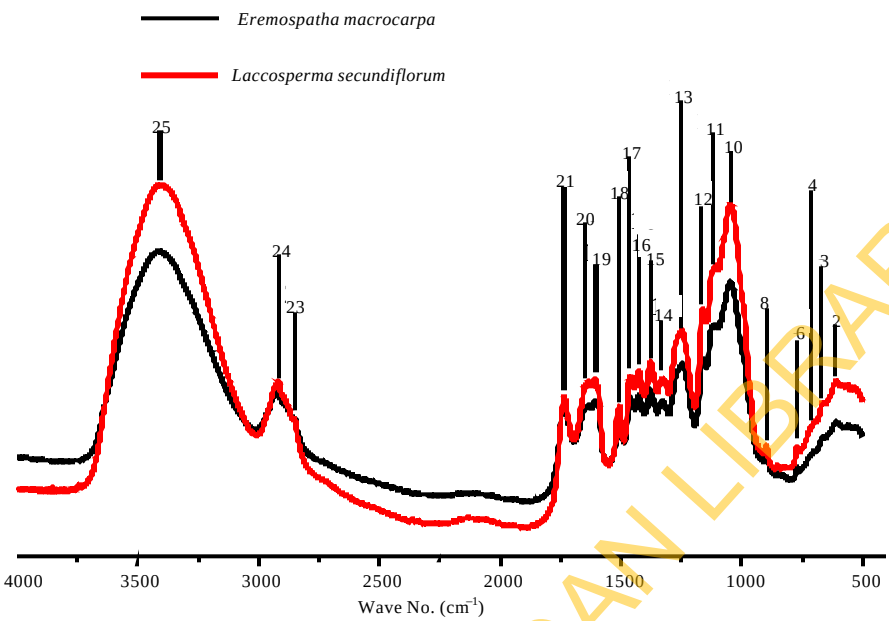

Fig. 2: FTIR spectra of two rattan species: *Eremospatha macrocarpa* and *Laccosperma secundiflorum*. Each spectrum is an average of spectra from two specimens

additive dependent. Based on the classification of Olorunnisola (2008), the untreated rattans are suitable for CBB production. The incorporation of chemical additives significantly improved the t_R of the rattan/cement mixes. The greatest improvement was observed for rattan/cement mixes pre-treated with $CaCl_2$ (Table 3). Therefore, it suggests that $CaCl_2$ improved the compatibility of the rattan/cement mixes more than $Al_2(SO_4)_3$ or 30 min cold water extraction.

Olorunnisola *et al.* (2005) reported that incorporation of 3% $CaCl_2$ to *L. secundiflorum*-cement system gave setting time and maximum hydration temperature as 9 h and 53.3°C, respectively. Their data showed that only the setting time support the suitability of 3% $CaCl_2$ pre-treated *L. secundiflorum*-cement system but the present study show that both the setting time and maximum hydration temperature ranked 3% $CaCl_2$ pre-treated *L. secundiflorum*-cement system as suitable for CBB production. The compatibility ranking of fibrous material based on the time ratio index shows 30 min cold water extracted *L. secundiflorum* is suitable for CBB production. Hence, the present study and the report of Olorunnisola (2008) support this finding.

Chemical characterisation: Figure 2 shows the FTIR spectra of *E. macrocarpa* and *L. secundiflorum* without cement. Infrared bands observed in the various treatments with their peak assignments and structural polymers are presented in Table 4 and 5. There are similarities and a few dissimilarities in the positions and intensities of the infrared spectra of the two rattan species investigated. Peaks numbered 2, 6, 8, 10, 14, 15, 17 and 20 have the same band frequencies for both *E. macrocarpa* and *L. secundiflorum* (Table 4, 5). However, the band frequencies for peaks numbered 3, 4, 11, 12, 13, 17, 18, 21, 23, 24 and 25 for *E. macrocarpa* differed from that of *L. secundiflorum*. Majorly, the carbonyl band for xylan differed by 3 cm^{-1} with *E. macrocarpa* occurring at 1737 cm^{-1} and *L. secundiflorum* at 1734 cm^{-1}.

The lignin assigned peak for *E. macrocarpa* and *L. secundiflorum* occurred around 1506/1608 cm^{-1}. However, some peaks occurred at higher frequency for *E. macrocarpa* than *L. secundiflorum*. Examples of these are peaks at 698, 1113, 1162, 1463 and 3412 cm^{-1} for *E. macrocarpa* compared with *L. secundiflorum* at 695, 1110, 1161, 1457 and 3407 cm^{-1}. The band at 3540-3000 cm^{-1} which was assigned to O-H groups in the rattans emerged due to the combination of cellulose, hemicelluloses and lignin (Faix, 1992). This band is broader with higher intensity for *L. secundiflorum* than *E. macrocarpa*. Likewise the intensities for peaks numbers 10, 11, 12, 13, 15, 17, 19 and 20 are higher for *L. secundiflorum* than *E. macrocarpa*. Generally, there is no difference in the chemical functional groups that were present in both rattan species. Therefore, the peak intensity, band width and b and frequency from the

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Table 4: Summary of infrared bands observed in *Eremospatha macrocarpa* and the untreated and pre-treated *E. macrocarpa*/cement mixes. The wavenumber of the 30 min cold water extraction is not presented because they are similar to that of $Al_2(SO_4)_3$

		Wavenumber (cm^{-1})			
Structural polymer	Peak assignment	Mix/$CaCl_2$	Mix/ $Al_2(SO_4)_3$	Erem/Cement mix	Erem
Cement	v_4 of Si-O bending	525	520	519	-
	Unknown	617	-	617	609
	Alkene C-H bending	650	662	-	662
Cellulose	Rocking vibration CH_2	-	-	-	698
Cement	v_4 of CO_3	713	-	713	-
Arabinogalactan		-	-	-	771
Cement	v_2 of CO_3	874	873	875	-
Cellulose	C1-H deformation of glucose ring	-	-	-	898
		991	988	986	-
Cellulose and hemicellulose	C-O stretch	-	-	-	1047
Polysaccharides and Lignin	Aromatic skeletal and C-O stretch	1113	1115	1112	1113
Cellulose and hemicellulose	C-O-C vibration	-	-	-	1162
Lignin	C-O of guaiacyl ring	-	-	-	1247
Syringyl	C_1-O vibration	-	-	-	1330
Cellulose and hemicellulose	C-H deformation	-	-	-	1377
Lignin	C-H in-plane deformation with aromatic ring stretching	1425	1421	1425	1425
Cellulose	CH deformation, asymmetry in CH_3 and CH_2	1472	1472	1472	1463
Lignin	Aromatic skeletal vibration (C = C), guaiacyl>5	-	-	-	1506
Lignin		-	-	-	1608
Extractives		1645	1645	1646	1635
Xylan in hemicelluloses	Conjugated C = O	-	-	-	1737
		-	-	-	-
		2853	2853	2853	2853
	C-H stretching	2923	2923	2923	2920
Rattan polymers	OH stretching	3445	3438	3433	3412
Cement	OH from $Ca(OH)_2$	3643	3643	3644	-

Table 5: Summary of infrared bands observed in *Laccosperma secundiflorum* and the untreated and pre-treated *L. secundiflorum*/cement mixes. The wavenumber of the 30 min cold water extraction is not presented because they are similar to that of $Al_2(SO_4)_3$

		Wavenumber (cm^{-1})			
Structural polymer	Peak assignment	Mix/$CaCl_2$	Mix/ $Al_2(SO_4)_3$	Laco/Cement mix	Laco
Cement	v_4 of Si-O bending	518	521	518	-
	Unknown	617	617	617	609
	Alkene C-H bending	-	-	665	664
Cellulose	Rocking vibration CH_2	-	-	-	695
Cement	v_4 of CO_3	713	-	713	-
Arabinogalactan		-	-	-	771
Cement	v_2 of CO_3	875	873	874	-
Cellulose	C1-H deformation of glucose ring	-	-	-	898
		996	984	984	-
Cellulose and hemicellulose	C-O stretch	1083	-	-	1047
Polysaccharides and Lignin	Aromatic skeletal and C-O stretch	1108	1114	1113	1110
Cellulose and hemicellulose	C-O-C vibration	-	-	-	1161
Lignin	C-O of guaiacyl ring	-	-	-	1248
Syringyl	C_1-O vibration	-	-	-	1330
Cellulose and hemicellulose	C-H deformation	-	-	-	1377
Lignin	C-H in-plane deformation with aromatic ring stretching	1420	1420	1426	1425
Cellulose	CH deformation, asymmetry in CH_3 and CH_2	1481	1466	1457	1457
Lignin	Aromatic skeletal vibration (C = C), guaiacyl>5	-	-	-	1507
Lignin		-	-	-	1609
Extractives		1636	1641	1636	1635
Xylan in hemicelluloses	Conjugated C = O	-	-	-	1734
Cement	$CaCO_3$	1789	-	1793	-
		2852	2852	2852	2852
	C-H stretching	2919	2919	2919	2919
Rattan polymers	OH stretching	3444	3433	3438	3407
Cement	OH from $Ca(OH)_2$	3643	3643	3643	-

spectra can only be used to differentiate the two rattan species under investigation.

Chemical changes that occurred due to the blending of untreated, 30 min cold water extracted, $Al_2(SO_4)_3$ or $CaCl_2$ pre-treated *E. macrocarpa* or *L. secundiflorum* mixed with cement after the hydration testing had been terminated are illustrated in Fig. 3 and 4. The addition of Portland cement caused the appearance of some peaks in

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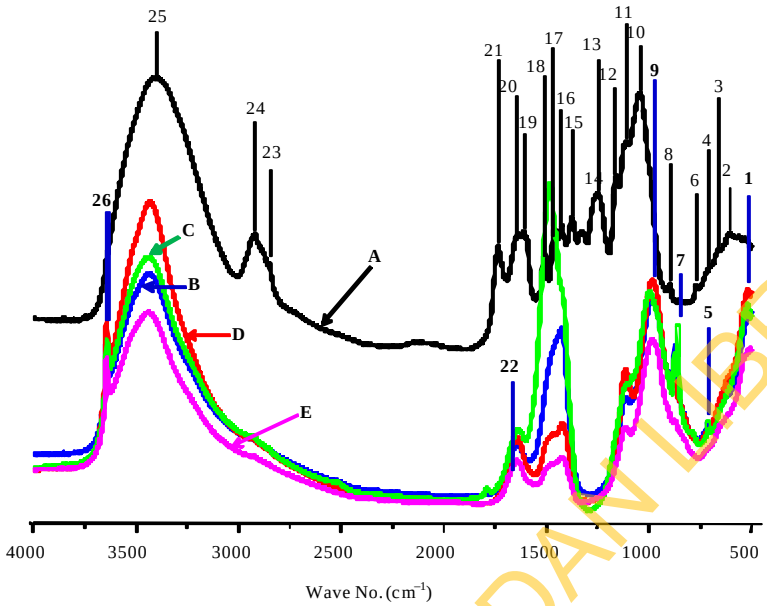

Fig. 3: FTIR spectra of (A) *Eremospatha macrocarpa*, (B) *E. macrocarpa*/cement mix, (C) *E. macrocarpa*/cement/$CaCl_2$, (D) *E. macrocarpa*/cement/$Al_2(SO_4)_3$ and (E) *E. macrocarpa*/cement/30 min cold water extraction. Each spectrum is an average of spectra from two specimens. Peak position and assignment as well as structural polymer for each peak are presented in Table 1

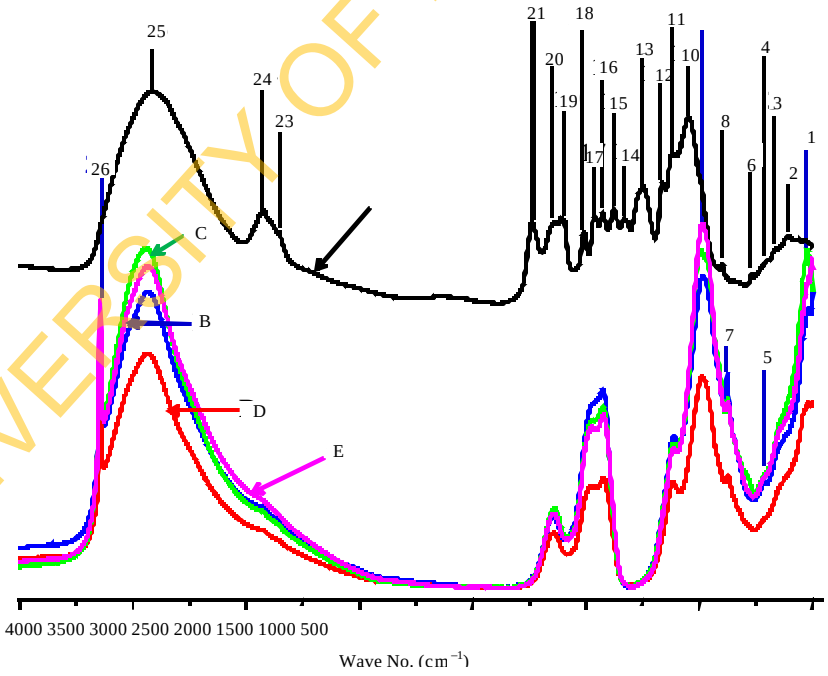

Fig. 4: FTIR spectra of (A) *Laccosperma secundiflorum*, (B) *L. secundiflorum*/cement mix, (C) *L. secundiflorum*/cement/$CaCl_2$, (D) *L. secundiflorum*/cement/ $Al_2(SO_4)_3$ and E) *L. secundiflorum*/cement/30 min cold water extraction. Each spectrum is an average of spectra from two specimens. Peak position and assignment as well as structural

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the spectra (numbers 1, 5, 7, 22 and 26). The formation of the band at 3643 cm^{-1} in the untreated, 30 min cold water extracted and chemically treated rattan/cement mixes remained unchanged; indicating that its emergence is due to the chemical constituent of cement. It was due to the metal-bonded hydroxide (Mollah *et al*., 1992). This indicates the OH band from $Ca(OH)_2$. The band at 3407/3414 cm^{-1} which was assigned to O-H groups in lignocellulosic materials, was affected by the pre-treatment and incorporation of cement to the rattan species. The blending of the rattan particles with cement and the incorporation of chemical additives and 30 min cold water extraction caused the band to be become narrower than in the ordinary rattan particles. In addition, peaks 23 and 24 at 2853 and 2926-2918 cm^{-1}, respectively drastically decreased due to the addition of cement. This implies that the cement suppressed the methylene and methyl stretching frequencies that occurred in the rattan species.

The lignin assigned peaks (1506/1507 and 1608/1609 cm^{-1}) did not appear in the rattan/cement mix but were masked due to the presence of broader band with peaks at 1426 and 1457 cm^{-1}. In addition, the peak at 1047 cm^{-1} disappeared when cement was mixed with rattan particles. There were many bands that disappeared due to the addition of cement namely: peaks numbers 21, 15, 14, 13 and 6 which are xylan in hemicelluloses, cellulose, syringyl, guaiacyl and arabinogalactan, respectively (Table 4, 5). Addition of $CaCl_2$ to *L. secundiflorum* particles helped expose cellulose to advance participation probably by enlarging its surface area for interpenetration networking with cement. Chemical reactivity of this peak (number 17) is rattan species dependent. The region between 1750 and 750 cm^{-1} was drastically affected (reduced the peaks' intensities) by the incorporation of $CaCl_2$ while $Al_2(SO_4)_3$ and 30 min cold water extraction had little effect on this region for *E. macrocarpa*. However, 30 min cold water extraction drastically reduced the peaks' intensities in the region between 1510 and 1300 cm^{-1} for *L. secundiflorum*.

CONCLUSIONS

The effects of cold water extraction and chemical additives on the setting time (t_{max}), maximum hydration temperature (T_{max}), time ratio (t_R) and surface chemistry of *Eremospatha macrocarpa* and *Laccosperma secundiflorum* particles mixed with Portland cement was investigated. Hydration behaviour showed that *E. macrocarpa* and *L. secundiflorum* canes are suitable for CBB production based on its setting time and time ratio index. However, maximum hydration temperature only ranked *E. macrocarpa* and *L. secundiflorum* as intermediately suitable. Cold water extraction (for 30 min) and chemical additives improved the hydration behaviour of the rattan cement mixes. Calcium chloride was a better chemical accelerator for the rattan cement mixes than aluminium sulphate. Cold water extraction had little advantage over aluminium sulphate for the species. *L. secundiflorum* inhibited cement setting more than *E. macrocarpa*. The surface chemistry studied using infrared spectroscopy showed that addition of cement to rattan fibre caused the suppression of methylene and methyl stretching frequencies that occurred in the rattan species. Addition of $CaCl_2$ to *L. secundiflorum* particles helped expose cellulose to advance participation probably by enlarging its surface area for interpenetration networking with cement.

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