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Thermal transformation of bamboo sawdust for its advanced cementitious composites

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ABSTRACT

This paper investigates a vacuum heat treatment (VHT) technology at 160℃, 200℃ and 240℃ for 6–14 h to modify bamboo sawdust (BS) and then BS/cement composites for the development of low carbon construction materials. The hydration process, thermal stability, micro-morphology and crystallinity, and chemical and mechanical changes for both VHT BS and composites are examined by FTIR, TG-DTG, XRD and SEM analyses. The mechanism of improving the mechanical properties of modified BS on composite materials is further elaborated together with the physical and mechanical properties and durability. The results show that the flexural strength and compressive strength of the modified BS/cement composites after VHT at 200℃ for 10 h are increased by 61.2% and 13.8%, respectively, compared with those in the untreated group, and the composites have better durability in the modified group. VHT resulted in cellulose and hemicellulose degradation to certain degrees, lignin undergoes cross-linked condensation reaction and cellulose crystallinity increases. These changes reduce the number of BS hydrophilic groups and result in changes in BS microstructure and surface topography, providing favorable conditions for the bonding and interface development of BS/cement composites. The impact of BS/cement composites on the carbon footprint in the production stage was analyzed, showing that the carbon emissions of BS/cement composites after VHT were reduced by 5.7% compared with that of the corresponding OPC composites.

1. Introduction

Cement-based material is a common building material which has the characteristic of fast setting and high compressive strength, but there are serious drawbacks, such as low flexural strength, poor crack resistance and fracture toughness [1–3]. The improvement is conventionally to use steel bars to enhance the toughness of cement-based materials. Fber reinforced cement-based composites can also effectively improve the flexural strength of cement-based materials by compounding a certain number of discontinuous short fibers or continuous long fibers with cement [4]. Numerous studies have proved that the addition of fibre can improve the flexural and cracking resistance of cement-based materials, delay the development of cracks, reduce the number of cracks, and thereby improve its toughness [5–7]. Some commonly used fibre reinforcements include metal fibre, carbon fibre, glass fibre, asbestos fibre, polymer fibre and natural fibres [4,8,9]. Among them, applying natural fibres to the construction field and developing new green building materials, such as adding wood sawdust, wheat straw, rice straw, bamboo sawdust and other plant fibres in cement-based materials to obtain cement bonded fibreboard [8,10–12], which not only improves the utilization efficiency of biomass resources, but also effectively alleviates the shortcomings of cement-based materials that are easy to crack and poor toughness [10,13,14]. For example, Jarabo et al. [15] used corn stalk fibre as reinforcement for fibre-cement materials. Wang et al. [16] by mixing waste wood and cement had developed thermal/noise insulation cement-bonded particleboards with high strength and light weight successfully. Rodier et al. [17] obtained biochar from bagasse by thermochemical transformation (slow pyrolysis), and prepared insulating cement-based composites by mud dehydration. Bamboo has much shorter rotation length than wood, with high strength and carbon sequestration capacity [18]. The study showed that the carbon sequestration capacity of bamboo was higher than that of Chinese fir, Japanese

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cedar and red cypress [19]. The use of bamboo and derivatives with low carbon footprint to replace carbon-intensive cement-based materials has become an effective strategy to achieve the goal of "replacing wood with bamboo" and carbon neutrality [20,21].

Bamboo sawdust (fibers) retain the characteristic of natural bamboo, has high strength and large elongation at break, and can be added to cement to connect the matrix microcracks, thereby improving the mechanical properties of composite materials. Vasudevan [22] studied the physical and mechanical properties of bamboo sawdust Portland cement composites, and the results showed that with the increase of the mixing ratio of bamboo sawdust, the compressive and flexural strength of composites at 28d decreased first and then increased, reaching the maximum value when the amount of addition is 15%, which is 5% higher than that of the control group, which may be caused by the volcanic ash and aggregate filling effect of the bamboo sawdust in the cement matrix. Terai and Minami [23] using bamboo fibre as raw material, the flexural strength, tensile strength and compressive strength of the specimens strengthened by 0.01%, 0.02% and 0.03% fibre content all increased significantly. However, as a natural fibre, there is a compatibility problem between bamboo fibres and cementitious materials, which also directly affects the strength of cementitious composites [21]. Some researchers [24–26] founds that that plant fibers can dissolve a large amount of extracts, which may hinder the setting and hardening of cement in alkaline cement environments and negatively affect the interface compatibility of fibers with cement matrix. To improve the compatibility of plant fibers with cement, the main method is to physically or chemically modify plant fibers. Ban et al. [27] evaluated the performance of glycerin, aluminate and silane modified bamboo fibre-reinforced cement composites through a series of mechanical and durability tests. Arsène et al. [28] found that the composite material was prepared by adding 2 wt% pyrolysis (2 h at 200 °C) bagasse fiber to cement, and its tensile strength (7 MPa) was significantly improved, the value is greater than twice the strength of plain cement paste. Ballesteros et al. [29] explored the effect of accelerated carbonation and hornification treatments on fibre-cement composites, the results indicate the hornification treatment yields greater dimensional stability improving the fibre–matrix interface and greater Specific Energy of the composites, while accelerated carbonation generates denser matrices, which increases Modulus of Rupture. The authors of reported that at heat treatment temperatures at 200 °C, the moisture content of natural fibres reduces, the hydroxyl group on the surface of the fibre decreases, and the hemicellulose is degraded, and the lignin is partially dehydrated so that it is rearranged to improve the bond strength between the fibre and the cement matrix [2,28]. However, the literature generally lacks a focus on the in fluence of heat treatment temperature and time on the mechanical properties of cement composites materials reinforced with plant fibres.

Thus, this study prepared the modified bamboo sawdust (BS) /cement matrix composites by modifying the surface of BS by vacuum heat treatment (VHT), and the effects of different heat treatment temperatures and times on the mechanical properties of BS/cement composites were introduced. Finally, the durability and carbon emission of composite materials are evaluated by optimizing and improving screening methods, their bonding mechanism is discussed, and the feasibility of their application is clarified.

2. Materials and methods

2.1. Materials

Moso bamboo (Phyllostachys heterocycla) sawdusts (BS) were purchased from Weihua Incense Factory (Guangdong). The length was 6 mm–10 mm and the diameter was 0.6 mm–0.85 mm. Oher basic characteristic is shown in Table 1. Ordinary Portland cement (OPC), P. O42.5, was purchased from Fujian cement company limited, Fuzhou, polycarboxylic acid superplasticizer (SP), CQJ-JSS, from Shanghai Shenqi Chemical Technology Co., Ltd., hydroxypropyl methyl cellulose ether (HPMC), 40 ~ 200 thousand molecular weight, from Shanghai Shenqi Chemical Technology Co., Ltd. and calcium chloride, AR, from Xilong science co., Ltd.

Table 1
Physical properties of BS.

Apparent density (g/cm^3)	Water absorption of 24 h (%)	Water contact angle (°)	Thermal expansivity (μm/m·℃)	Thermal conductivity (W/m·K)
0.40	83.7	54.2	28	0.092

2.2. Vacuum heat treatment (VHT) of BS

The BS were put into a vacuum drying box, and the targeted temperature was set at 160℃, 200℃, 240℃ and kept at different temperatures for 6 h, 8 h, 10 h, 12 h and 14 h, respectively. The dryer program is set as follows: (1) The pressure in the drying oven is reduced to −0.1Mpa, and from room temperature to 100℃; (2) Keep at 100℃ for 1 h; (3) From 100℃ to the target temperature, the heating rate is set to 1℃/min; (4) maintain the corresponding time at the target temperature; (5) Drop the temperature from the target temperature to 40℃, and the cooling rate is set to 1℃/min. After the heat treatment, take out the BS and put them in the dryer to cool to room temperature. Then use the vibrating screen to screen the BS of 20 ~ 28 mesh for use.

2.3. Preparation of modified BS/Cement matrix composites

The composition of composite materials is shown in Table 2, where the content of BS, HPMC, $CaCl_2$, SP and defoaming agent is the percentage of the cement mass. The blank control groups included OPC and UM, where "CG" represents the specimens with Ordinary Portland cement (OPC) and "UM" represents the specimens with untreated BS, and "MO" represents all the specimens with modified BS. The preparation steps are as follows: firstly, the designed quantity of cement, BS and water were fed into a mixer and stirred for 3 min. Then, the mixture was evenly mixed and poured to 40 mm × 40 mm × 160 mm cement sand triplet test mold, which was placed in room temperature for 24 h before demolding. Finally, the specimen is placed in a conditioning temperature and humidity chamber according to the "GB/T 50081-2002″ standard maintenance for 28d.

2.4. Characterization

2.4.1. Thermal stability test of BS

The synchronous thermal analyzer was used to carry out the experiment in N_2 atmosphere, and the dried bamboo powder of 200–250 mesh was placed on the balance in the thermogravimetric analyzer to test the thermal weight loss rate of the sample during the heating process. The test conditions are as follows: the heating rate is 20℃/min, the temperature ranges between 20℃ and 900℃, and the injection weight is lower than 10 mg.

2.4.2. Water absorption of BS

2 g (M1) dried BS are put into a small beaker and 20 mL ultra-pure water is added to the beaker. After 24 h soaking, BS are filtered out

Table 2
Mixture design of BS/Cement composites.

Number	Cement (g)	W/C	BS (%)	HPMC (%)	$CaCl_2$ (%)	SP (%)	Defoaming agent (%)
OPC	1250	0.3	0	0	0	0	0
UM	1250	0.3	3	0.03	2	0.5	0.15
MO	1250	0.3	3	0.03	2	0.5	0.15

with Brinell funnel and absorbent paper is used to absorb excess water on the surface of BS. Then the mass of BS (M2) is measured. The water absorption of BS is calculated according to the Eq. (1) and the average value of three repeated tests is used.

$$\text{Water absorption} = \frac{M_2 + M_1}{M_1} \times 100\% \quad (1)$$

2.4.3. Micro-morphology test of BS

The micro-morphology of BS and cross-section of composite were observed by scanning electron microscope (SU8010, Hitachi High-tech Group), and the high vacuum mode and working voltage 15 kV were selected. The samples were firstly measured on a copper table bonded to the conductive adhesive and gently pressed the samples so that they adhered firmly to the conductive adhesive, and then the samples were treated with vacuum gold plating. The samples were finally put into the instrument and the power was switched on for testing.

2.4.4. Infrared spectroscopy measurement

The infrared spectrum of BS was measured by Pekin-Elmer Fourier transform attenuated total reflection infrared spectrometer, and the samples were prepared by KBr pressing method. The test procedure is as follows: 200 ~ 250 mesh of BS and KBr are mixed in an agate mortar and ground into a homogeneous, and pressed into a tablet. The resolution of the instrument is 4 cm^{-1}, the scanning range is 4000 ~ 400 cm^{-1}, and the scanning times are 32 scans/min.

2.4.5. Crystallinity measurement

Take an appropriate amount of 200–250 mesh BS on the glass slide, flatten it with a glass sheet, and put the glass slide into an X-ray powder diffractometer for testing. Cu-Kα target, operating voltage 40 kV, working current 40 mA, 2θ scanning was performed at 10°~ 50°, the scanning speed was 10°/min, and the scanning step angle was 0.02°. The relative crystallinity (CI%) of BS is calculated by Segal et al empirical method, as shown in Eq. (2).

$$CI\% = \frac{I_{002} - I_{am}}{I_{002}} \times 100\% \quad (2)$$

Where, I002 is the maximum diffraction intensity of 002 crystal plane; Iam is the diffraction intensity at the trough 2θ≈18° represents the diffraction intensity in the amorphous region.

2.4.6. Mechanical properties of BS cement composites

Using WDW-H microcomputer controlled electronic pressure testing machine to test the flexural and compressive strength of composites according to "Cement mortar strength testing method (ISO method)" (GB/T17671-1999). The size of the flexural specimen is 40 mm × 40 mm × 160 mm. Three specimens were taken from each group and their average was taken as the final results. The compression specimens are two half-section specimens after the end of the flexural test, the size is 40 mm × 40 mm, each group of six specimens, the final result is the average of the six specimens.

The flexural strength test was carried out by placing the composite materials on the roller with a span of 100 mm and loaded evenly at the loading speed of 50 N/s until the sample is broken. The flexural strength Rf (MPa) was calculated according to Eq. (3)

$$R_f = \frac{1.5F_f L}{b^3} \quad (3)$$

Where, Rf is the flexural strength (MPa), Ff is the failure load of specimen when it is broken (N), L is the distance between supporting cylinders (mm) and b is the side length of the pressure square section of the specimen (mm).

The compressive strength test was carried out by placing the half test block after the flexural test in the middle of the compression clamp. The test block was exposed about 10 mm outside the platen, and then the load was uniformly applied at a loading rate of 2400 N/s until the specimen failed. The compressive strength RC is calculated in Newtons per square millimeter (MPa) according to Eq. (4)

$$R_c = \frac{F_c}{A} \quad (4)$$

Where, RC is compressive strength (MPa), FC is the maximum load of the specimen during failure (N) and A is the bearing area of specimen (mm^2).

2.4.7. Hydration temperature

In order to explore the compatibility between BS and cement, the hydration characteristic, maximum hydration temperature (MHT) and time to reach this temperature, and fitness coefficient (CA) were used as the evaluation index of compatibility. CA is calculated according to the Eq. (5). The hydration process of the composites is examined by using the experimental scheme in Table 3. The mixture is produced by firstly mixing cement and BS in a plastic cup, then adding water and additives, and finally stirring the mixture evenly. The whole mixing process is completed in 3 min. Then the plastic cup is put into the hydration measurement device. The probe of the temperature recorder is inserted into the centre of the mixture and the temperature recorded at a rate of 20 s interval. The whole recording is taken for 24 h.

$$c_A = \frac{A_{wc}}{A_{nc}}/100 \quad (5)$$

Where, Awc is the hydration calorific value of bamboo shavings and cement mixture within 24 h after the start of hydration (h·℃), Anc is the hydration calorific value of pure cement within 24 h after the beginning of hydration (h·℃).

2.4.8. Durability of composites

Both the wet-dry cycle and freeze–thaw cycle were carried to examine the durability of the developed composites. The principle of the dry-wet test method follows the test procedure proposed by Filho [30], and 10 and 20 dry-wet cycles were carried out on the composites, respectively. The experimental group was soaked in water at 25 ℃ for 20 h, then dried at room temperature for 4 h, then dried in an oven at 70 ℃ for 20 h, and finally cooled at room temperature for 4 h for a total of 48 h. After completing 10 and 20 cycles respectively, the mechanical strength of the test group is tested.

The freeze–thaw cycle test is carried out in accordance with the Standard of Test methods for long-term performance and durability of ordinary concrete (GB/T50082-2009). The slow freezing method was used in the freeze–thaw cycle. Three groups of specimens were prepared before the experiment. One group is for testing the strength after the saturated water absorption by soaking the specimens in water for 48 h. The other two groups were soaked in water at 20 ± 2 ℃ for 4 days and put into a high and low temperature test chamber for freeze–thaw cycle test, in which the freezing temperature was −10 ℃ for 4 h, the melting temperature was 25 ℃ for 4 h. The number of designed freeze–thaw cycles is 45 and 90 respectively. At the end of 45 cycles, the flexural strength and compressive strength are tested. After 90 cycles, the remaining group is taken out for strength test.

Table 3
Mixtures for hydration heat measurement.

number	Modification mode of BS	Cement (g)	W/C	BS (g)	SP (%)
RBS	Untreated	140	0.3	10	0.5
200℃-10 h	Vacuum heat treatment at 200 ℃ for 10h	140	0.3	10	0.5

3. Results and discussion

3.1. Mechanical properties of composites

3.1.1. Effect of heat treatment on mechanical properties of BS/Cement composites

The effect of heat treatment time on the mechanical properties of the composites at 160℃, 200℃ and 240℃ were shown in Fig. 1. From the results, compared with OPC (Fig. 1a), the compressive strength of cement matrix composites with BS decreased to different degrees. Among them, the compressive strength of the untreated fibre is lowest with 49.3 MPa, and the compressive strength of BS/cementitious composites is higher than that of untreated groups after heat treatment of BS under different conditions. The possible reasons are that the BS has higher porosity and lower strength than the cement matrix, and the untreated fibre is more prone to agglomeration than the VHT fibre [27], which will be further verified in the subsequent analysis. Compared with OPC (Fig. 1b), the flexural strength of cement matrix composites with BS increased to different degrees, and showed a trend of normal distribution with time at 200℃. Among them, the flexural strength reached the maximum value of 11.33 MPa at 200℃ for 10 h, which was 130.28% and 61.2% higher than OPC and UM, respectively. The reason may be that low molecule sugars degrade with a longer VHT and hence greater loss of the BS strength, which leads to the BS being easily broken and destroyed in the cement matrix, thereby the flexural strength of the composites decreases. Furthermore, the change in the ratio of flexural to compressive strength is similar to that of flexural strength or compressive strength (Fig. 1c). The maximum ratio of flexural to compressive strength reached 0.202 at 200℃ for 10 h heat treatment, which was 162.3% higher than that of the OPC and 41.3% higher than that of the UM. Comparing the mechanical properties of composites under different heat treatment conditions indicates that the bending strength is the lowest at 160 °C, and the mechanical strength and toughness of the composites treated at 200 °C and 240 °C are higher, but the mechanical strength of BS is easy to decrease due to high temperature and long time. Therefore, to comprehensively compare the mechanical properties of the specimens in each group, and considering the low-energy-consuming treatment process, 200 °C for 10 h was selected as the appropriate treatment condition and the compressive and flexural strength were 56.11 MPa and 11.33 MPa, respectively.

3.1.2. Effect of heat treatment on the durability of BS/Cement composites

While adding natural fibres to cementitious materials could play a significant role in improving the flexural strength and brittleness, the biomass material itself is easy to degrade in the alkaline cement matrix, leading to a poor durability of the composites [31]. Therefore, the effect of VHT (200℃-10 h) on the durability of BS/Cement composite is investigated by simple dry-wet cycle test and freeze–thaw cycle test.

The frost resistance of cement-based materials refers to the ability to maintain good mechanical strength after many freeze–thaw cycles in the saturated state, and frost resistance is one of the important indexes to measure the durability of cement-based materials. In the process of freezing and thawing, when the internal temperature of the cement-based material falls below the freezing point, the pore water will freeze, the volume will increase and the expansion pressure increase [32]. The resulting tensile stress or compressive stress may gradually destroy the crystal structure of hydration products. When the expansion pressure reaches a certain degree, cement-based materials will cause strength damage due to more micro-cracks. It can be seen from Fig. 2a that with the increase of freeze–thaw cycles, the compressive strength of OPC, UM and MO increase gradually. After 90 cycles, the compressive strength of OPC increases by 19.9% compared with that before freezing and thawing. The changes of UM and MO are smaller, which are 13.1% and 12.4% higher than those before freezing and thawing, respectively. It is considered that after the specimen is saturated with water can play a role similar to water curing and promote the continuous development of cement strength, while the negative effect of short-term freeze–thaw cycle on strength loss is less than the positive effect of water curing.

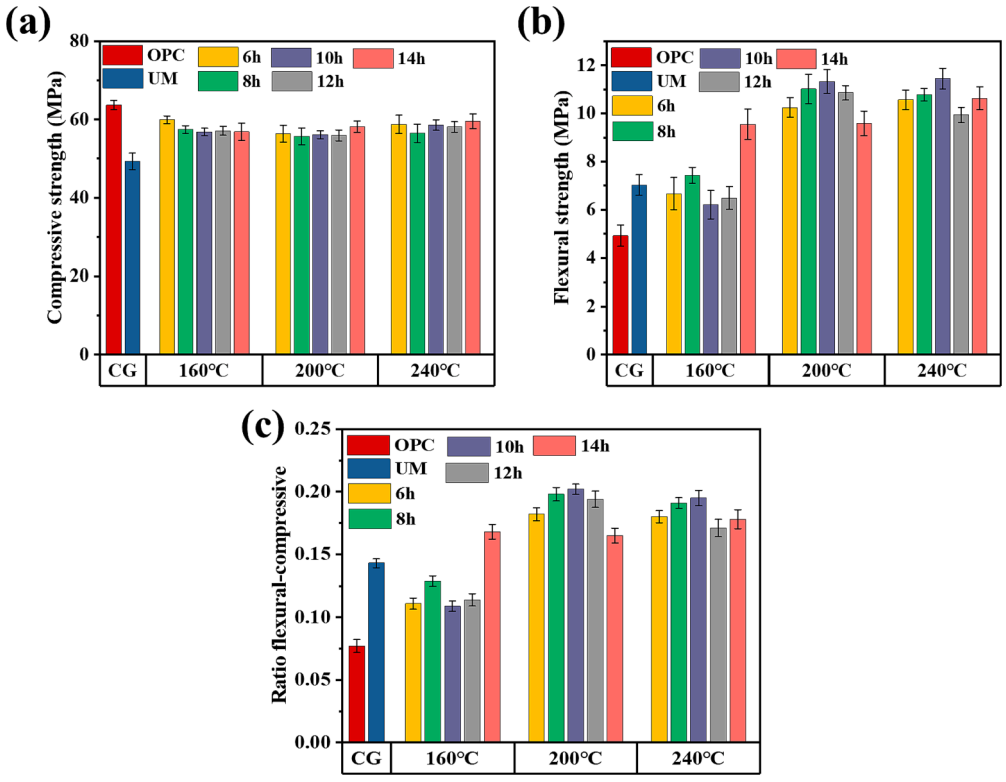

Fig. 1. Mechanical properties of composites at 160 ℃, 200 ℃, 240 ℃ and various VHT times (“ UM ”refers to untreated group): (a) compressive strength, (b) flexural strength, (c) ratio of flexural -compressive strength.

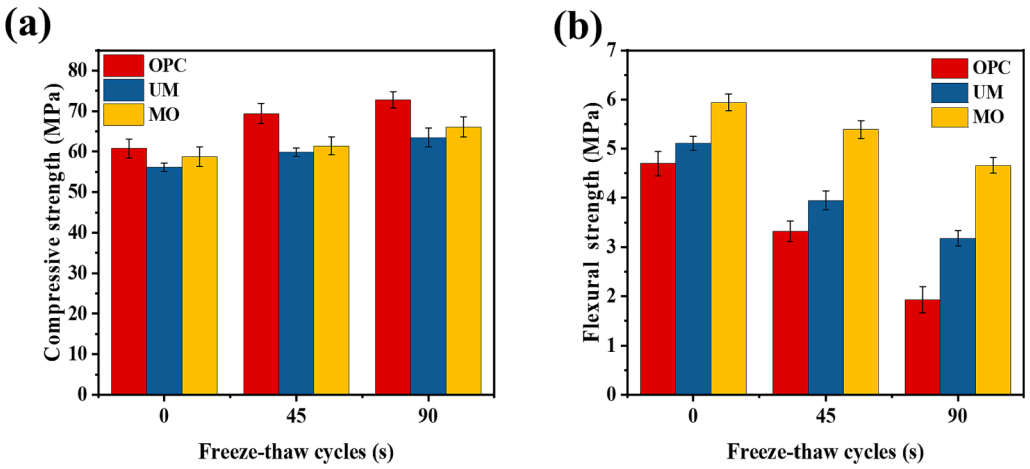

Fig. 2. Mechanical properties number of freeze–thaw cycles: (a) compressive strength and (b) flexural strength.

Therefore, the compressive strength of the specimen after freezing and thawing is higher than that before freezing and thawing; The low molecular weight sugar in BS will hinder the formation of hydration products, so the strength of the specimen mixed with BS is lower than that of the OPC, and the compatibility between BS and cement is improved because the heat treatment degrades part of cellulose and removes a large of anticoagulant components [31]. The cement strength is well developed, the matrix is denser, and the expansion stress caused by water freezing during freezing and thawing has less impact on the strength. Therefore, the strength of composites after the freeze–thaw treated group is higher than that of the UM, indicating that heat treatment can indeed improve the durability of BS cement matrix composites. As can be seen from Fig. 2b, the flexural strength of the three groups of specimens decreased to different degrees with the increase of the number of freeze–thaw cycles, indicating that freeze–thaw cycles would weaken the flexural strength of composite materials. Among them, after 90 cycles, the OPC strength accounted for 41.1% before freeze–thaw, 62.2% of that before freezing and thawing in the UM, and 78.5% of that before freezing and thawing in the MO, indicating that the frost resistance of the composite material was improved after heat treatment.

The alternation of drying and wetting exposure makes the cement-based materials either in the state of water saturation or drying. The loss of water at high temperature could lead to shrinkage cracks in the cement matrix and the deterioration of mechanical properties [33]. Therefore, the drying-wetting cycle is also one of the main factors affecting the durability of cement-based materials. Fig. 3 shows the effect of wet-dry cycle on the mechanical strength of composite materials. As can be seen from Fig. 3a, with the increase of dry and wet cycles, the compressive strength of the OPC, UM and MO all increase in different degrees. As afore discussed for freezing and thawing cycles, the strength of cement matrix continues to develop after saturated water absorption, and the positive effect of strength increase is greater than the negative effect caused by dry and wet cycles. In addition, the compressive strength of the MO is higher than that of the UM, because heat treatment removes some soluble sugar, which not only improves the interface compatibility between bamboo sawdust and cement, but also improves the alkali corrosion resistance of BS, thus improving the overall resistance of the modified group to wet and dry aging. As can be seen from Fig. 3b, the dry-wet cycle has a significant weakening effect on the flexural properties of cement-based materials. The flexural strength after 20 cycles is only 32.1% for the OPC, 37.0% for the UM and 46.8% for the MO that before the cycle, indicating that the durability of BS cement-based composites has been significantly improved after heat treatment.

3.2. *Compatibility of modified of Bamboo sawdust and Cement*

Fig. 4a shows the hydration-temperature of the cement-RBS – water mixed system and the cement-VHT modified BS-water mixed system. The hydration characteristic values of the mixture of VHT modified bamboo sawdust and cement are shown in Table 4. It can be observed from Fig. 4a and Table 4 that the hydration temperatures of the two mixed systems first increased and then decreased with the increase of time, but the two mixed systems have different temperature peak values. The hydration reaction of cement is delayed and the highest hydration temperature is reduced obviously because of the addition of BS. BS heat treated at a temperature of 200 °C for 10 h initiates the hydration

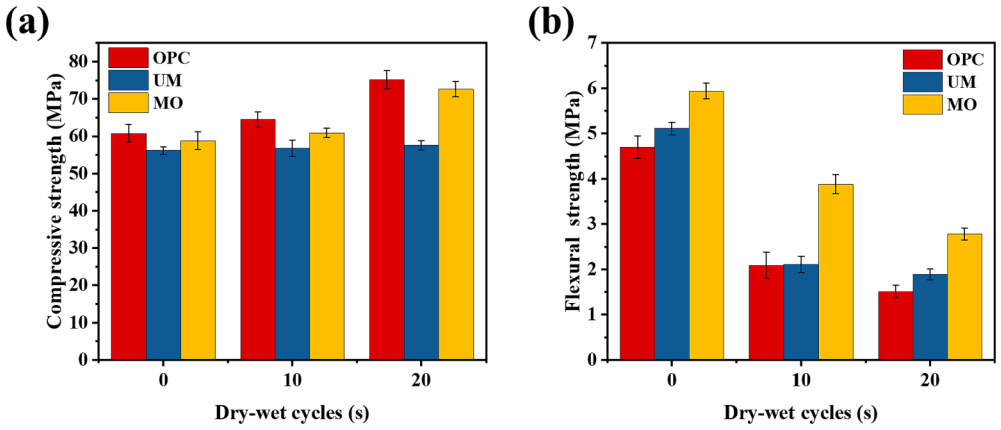

Fig. 3. Mechanical properties vs number of dry-wetting cycle: (a) compressive strength and (b) flexural strength.

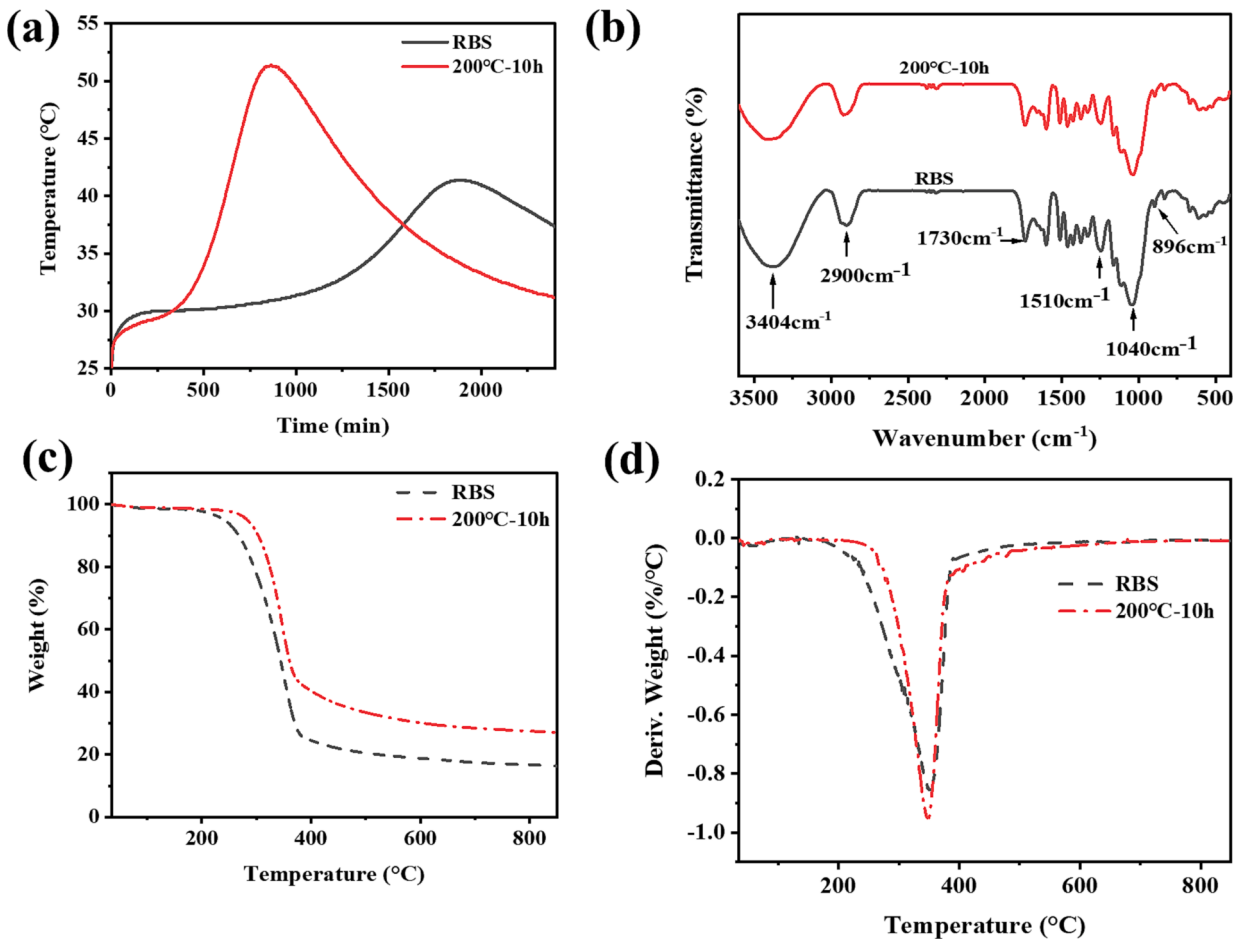

Fig. 4. Compatibility of VHT BS and cement: (a) Hydration exothermic curve of mixtures, (b) FTIR patterns of modified BS, (c) TG curves of modified BS and (d) DTG curves of modified BS.

Table 4
Hydration characteristic of VHTBS-cement mixture.

Number	Maximum hydration temperature (Tm/°C)	Time to reach the highest hydration temperature (t/min)	conformity coefficient (CA/%)	indoor temperature (T/°C)
RBS	40.1	1859	67.8	25 ± 1
200°C-10 h	51.4	860	95.7	25 ± 1

process much earlier than RBS, which reaches the acceleration stage faster. During the acceleration period, tricalcium silicate and dicalcium silicate reacted more intensively, releasing more heat and giving rise to much higher maximum hydration temperature (MHT), the slope of the heat release curve was steeper. Compared with RBS composite, the MHT of 200°C-10 h composite was increased by 11.3°C, the time to reach the temperature was about 16 h earlier, the fitness coefficient was increased by 27.9% that indicating VHT significantly improved the compatibility between BS and cement and hence cement hydration. This may be mainly due to the degradation of a large number of hemicellulose and oligosaccharides by heat treatment, which reduces the slow coagulation component in the water extract and affects the hydration rate of cement clinker. The functional changes of the VHT modified BS show that as amount of free water is removed from cellulose and hemicellulose (Fig. 4b) and hemicellulose partially pyrolyzes to generate gases such as acetic acid and furfural, or form esters [34], the hydroxyl groups of BS are reduced, so that the intensity of the –OH absorption peak of VHT modified BS at 3404 cm^{-1} is weakened. The weakening of the expansion and contraction vibration absorption peak intensity of C=O at 1730 cm^{-1} is caused by the thermal degradation of hemicellulose. There was no significant change in the intensity of the corresponding lignin characteristic absorption peak at 1634 cm^{-1}, 1510 cm^{-1} and 1256 cm^{-1}, which was mainly due to the desorption water and partial ether bond fracture of lignin at 200°C, accompanied by the cross-linking condensation reaction of some lignin. The intensity of the absorption peak of C–O stretching vibration and –OH flexural vibration at 1040 cm^{-1} decreases, indicating the number of volatile aliphatic compounds is reduced. The absorption peak near 896 cm^{-1} belongs to the stretching vibration of β-glycosidic bond, and the strength of this absorption peak decreases after heat treatment, which may be caused by the cracking of the glycoside bond as hemicellulose and cellulose degrade during heat treatment [35].

In addition, from the TG and DTG curves of BS before and after VHT modification (Fig. 4c and d), it can be seen that the initial pyrolysis temperature of the modified sawdust moved to the high temperature zone by 70°C, this is because the VHT degrades part of cellulose and improves the heat resistance of BS. The maximum pyrolysis rate temperature of the modified material is the same as that of RBS by the carbonization phase, but the maximum pyrolysis rate of the former is greater than that of the latter, which is caused by more intense cellulose pyrolysis in the modified material. TG/DTG characteristic parameters of BS before and after VHT modification show (Table 5) that the residual mass of modified BS is 10.55% higher than that of RBS, because the aromatic substances produced by lignin cross-linking condensation in modified BS could inhibit the pyrolysis of fibre. However, part of lignin

Table 5
TG/DTG Characteristic of BS before and after VHT modification.

number	Initial pyrolysis temperature (℃)	Maximum pyrolysis rate (%/℃)	Maximum pyrolysis rate temperature (℃)	Residual weight rate (%)
RBS	160	−0.85	350	15.97
200℃-10 h	230	−0.95	347	26.25

distributed on the surface of bamboo fibre after heat treatment could be combined with cellulose or hemicellulose to form a cross-linked structure, which reduces the leaching amount of lignin and can also promote the hydration of cement to a certain extent.

The above analysis also shows that VHT modification can degrade hemicellulose and remove the polar groups on the surface of bamboo fibre, and lignin could react with cellulose or hemicellulose to form a hydrophobic network structure with heat treatment, thereby the water absorption of modified materials decreased. The water absorption of VHT modified BS decreased by 15.2% compared RBS (Fig. 5), which is beneficial to the strengthening effect of BS on cement, which is also shown in the results of the mechanical strength test in Fig. 1.

3.3. Crystal structure and interface microstructure of BS/Cement composites

3.3.1. XRD analysis

To further understand the compatibility of modified BS with cement, the XRD analysis of the modified BS and cement composites materials is carried out (Fig. 6). It can be seen that the VHT at 200℃ for 10 h did not change the cellulose type of BS (Fig. 6a) and the relative crystallinity of modified BS calculated from the equation (2) was 58.3%, which was 9.1% higher than that of untreated BS. It is explained that the VHT may pyrolyze part of the hemicellulose, increasing the relative content of cellulose, and the degradation of various sugar groups in hemicellulose may produce crystalline structure, resulting in the increase of relative crystallinity of BS. Among them, hemicellulose in BS and volatile oligosaccharides, and high temperature for cross-linking condensation reaction of lignin with cellulose, make the water extract of monosaccharide anticoagulating ingredients, such as reduction of lignin content. All these promoted the formation and development of cement hydration products, and improved the compatibility of BS and cement. Therefore, it can be seen from Fig. 6b that the diffraction peak of calcium hydroxide at $2\theta = 18.2^\circ$ and 26.8°, and the diffraction peak of calcium silicate hydrate at $2\theta = 29.6^\circ$ in the XRD spectrum of vacuum heat treatment group is stronger than those of unmodified group. The above analysis shows that the number of crystal products in the modified specimens is more and the strength is more fully developed, which is beneficial to the interfacial bond strength between BS and cement matrix, improving the mechanical properties of the composites.

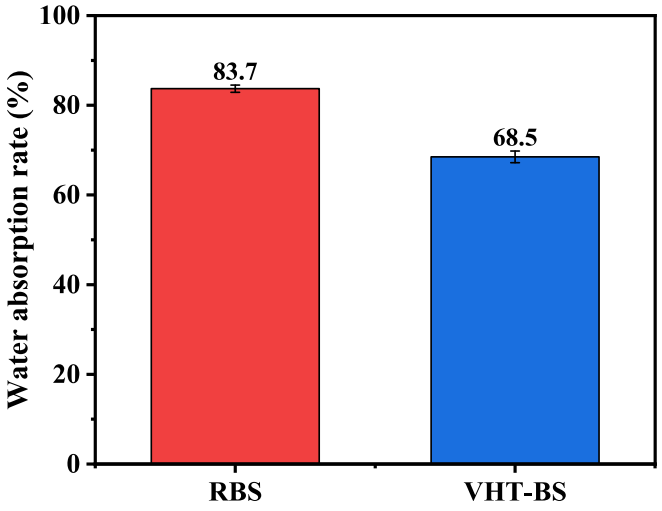

Fig. 5. Water absorption rate of BS by VHT modification.

3.3.2. Microstructural analysis

Change in microstructure of BS could make a significant influence on the bonding and interface structure of BS/Cement composites. It can be seen that due to the decomposition of some waxy, extractable and hemicellulose of BS by heat, the cell wall of bamboo fibre has produced some cracks and the surface of the fibre has become rough (Fig. 7a and b). Moreover, hemicellulose pyrolysis produces acetic acid, CO, CO_2 and volatile low molecular weight sugars [36], and the spillover of these components may create a pressure gradient, and together with the oven-drying under vacuum condition makes the opening of inner wall of the fibre cavity, which helps cement matrix form "a glue nail" to the BS.

The observation of Fig. 7c and d shows that after adding unmodified BS, it was observed that untreated fibre tended to agglomerate, the hydration of cement is hindered, and the hydration products are underdeveloped, especially the structure of the interface transition zone between BS and matrix is loose and porous and there is a wide gap, which results in low bond strength between BS and cement and reduces the effectiveness of BS strengthening. By contrast, the bonding strength between VHT modified BS and cement is much improved (Fig. 7e and f), the crack in the interface area is minimized. The compactness of cement matrix near BS is significantly higher than that of untreated composites. In addition, a large number of granular, plate or cluster hydration products can be observed on the surface of modified BS. These could be explained as follows: firstly, the pyrolysis of the chemical components of BS reduces the content of unfavorable components that inhibit the setting of cement, such the hydration of cement can be carried out smoothly, and the crystallization products develop well, so that the cement becomes dense; Secondly, VHT causes some cracks in the cell wall of BS and the surface becomes uneven, which is favorable for hydration products to grow on the surface of bamboo fibre in large quantities and beneficial for cement paste to enter the cell cavity to form a glue nail, forming a complete gel structure with high bonding strength with the external cement matrix [17].

3.4. Carbon footprint assessment

As an important building material, the global production of ordinary Portland cement (OPC) 3.5 billion tons annually [37], accounting for about 8% of global carbon dioxide emissions [38]. As the largest developing country, China's annual cement production accounts for about 60% [39]. According to the "China Building Energy Consumption Research Report (2020)", the energy consumption of cement production stage is 130 million tce (ton of standard coal equivalent), and the carbon emission is as high as 1.11 billion tCO_2. Driven by the strategic goal of carbon neutrality in China, cement has transitioned to low-carbon green. Among them, the raw material substitution method is an effective way to achieve the transformation, such as kaolin [40], carbon nanotubes [41], waste bamboo wood or derived biochar [38,42,43], to replace part of the cement to achieve the same performance requirements. As a traditional building material, bamboo has excellent carbon sequestration ability and sustainability, and the application rate in China's construction field has reached more than 20% [44].

Reducing CO_2 emissions is another important feature of this development of BS/cementitious composites. This section refers to the basic carbon accounting method (emission factor method) provided by IPCC, and calculates the carbon emissions of OPC, UM and MO production stages according to Eq. (6). The results are shown in Table 6.

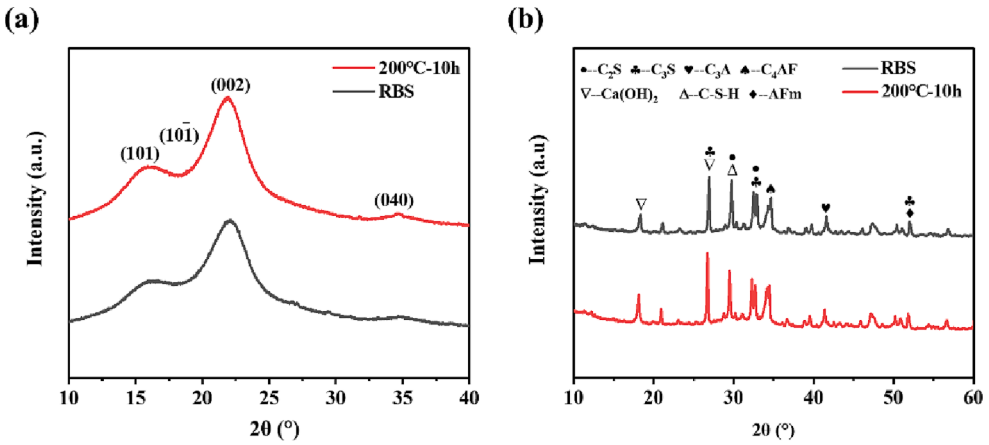

Fig. 6. XRD of modified BS and cement composites: (a) the RBS and the VHT modified BS; (b) the composites in the VHT modified group and the unmodified group.

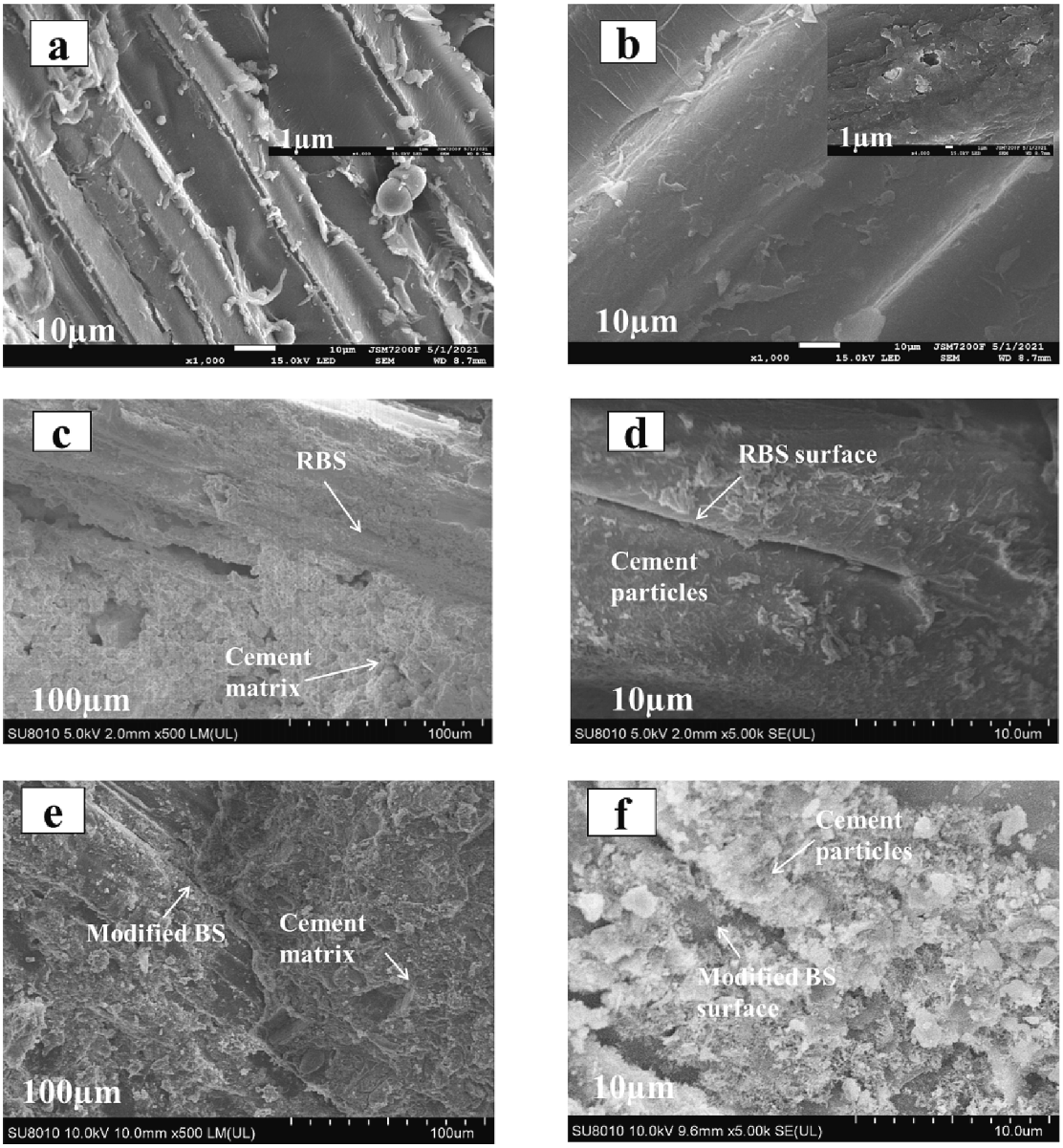

Fig. 7. SEM of BS and composites: (a) RBS, (b) 200℃-10 h; (c–d) Unmodified group of composites (RBS); (e–f) modified group of composites (200℃-10 h).

Table 6
Calculated data on carbon emissions during the preparation of 1 m^3 OPC, UM and MO.

The project	Carbon emission factor (kg/t)	OPC		UM		MO	
		Dosage (t/m^3)	Carbon emissions ($kgCO_2/m^3$)	Dosage (t/m^3)	Carbon emissions ($kgCO_2/m^3$)	Dosage (t/m^3)	Carbon emissions ($kgCO_2/m^3$)
Cement	631	1.43	902.33	1.35	851.9	1.35	851.9
Water	0.91	0.43	0.39	0.41	0.37	0.41	0.37
BS	−200	0	0	0.04	−8	0.04	−8
Power consumption	0.714	0.18	0.13	0.25	0.18	8.69	6.2
Sum up			902.85		844.45		850.47

$$C_P = \sum_{j=1}^{n} M_j F_j \quad (6)$$

Where, CP is the carbon emission during the block production stage ($kgCO_2/m^3$); Mj is the amount of the j raw material(t); Fj is the carbon emission factor of the j raw material ($kgCO_2$/ number of units).

The power consumption in Table 6 includes the total power consumption of the mixer and the vacuum drying oven during operation, which is not included here because the amount of each admixture is relatively too small. As can be seen from the table, the carbon emissions of OPC, UM and MO are 902.33 $kgCO_2/m^3$, 844.45 $kgCO_2/m^3$ and 850.47 $kgCO_2/m^3$, respectively, which are 6.4% and 5.7% lower than OPC. Considering that the incorporation of 3% modified bamboo fiber does not affect the mechanical properties of the composite material, the reduced amount of cement per unit volume of the composite material can reduce the carbon emissions of the product. Since bamboo is a sustainable carbon negative material with a carbon sequestration amount of (8.13 ± 2.15 $Mg{\cdot}ha^{-1}{\cdot}year^{-1}$) on the ground [45], the actual carbon emission will be much less than the calculated results in Table 6, when it is used in cement-based composite materials in construction projects, which needs further research in the future.

4. Conclusions

Vacuum heat treatment (i.e., 160 ℃, 200 ℃ and 240 ℃ heat treatment 6–14 h) has been successfully developed to modify the bamboo fibre for an improved BS/cement composite. The VHT modification degraded a large amount of hemicellulose and extractives into volatile gases, and leads lignin to cross-linked condensation reaction, such increased the relative crystallinity of bamboo fibre, reduced the water absorption of BS, and made the surface of bamboo fibre uneven, which could effectively increase the mechanical meshing force and hence interface bonding and structure between bamboo fibre and cement. The mechanical properties of VHT modified BS and cement composites were much improved compared to those of the unmodified group, and the optimal mechanical strength was achieved for the composites with BS treated at 200℃ for 10 h was the best. The flexural and compressive strength were 11.33 MPa and 56.11 MPa, respectively, which were 61.2% and 13.8% higher than those of the unmodified group. The developed composites depredated less under the freeze–thaw cycle and dry-wet cycle test; After 90 freeze–thaw cycles, the flexure retention value of specimens in Group UM was only 62.2%, while that in Group MO was 78.5%. After 20 dry and wet cycles, the flexural strength of UM and MO specimens is 32.1% and 46.8% of that before the cycle test, respectively. The carbon emissions of BS/cement composite production with and without VHT were 844.45 $kgCO_2/m^3$ and 850.47 $kgCO_2/m^3$, respectively, which were 6.4% and 5.7% lower than that of OPC composite production.

CRediT authorship contribution statement

Peixian Zuo: Methodology, Writing – original draft. **Zhong Liu:** Methodology, Investigation. **Hua Zhang:** . **Amende Sivanathanb:** . **Dasong Dai:** Supervision, Methodology. **Mizi Fan:** Conceptualization, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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References

[1] X. Mingjun, Z. Yijin, L. Zheng, L. Fanghua, J. Zhengwu, Study on alkylsilane-incorporated cement composites: hydration mechanism and mechanical properties effects, Cem. Concr. Compos. (2021).
[2] Q. Li, L. Ibrahim, W. Zhou, M. Zhang, Z. Yuan, Treatment methods for plant fibers for use as reinforcement in cement-based materials, Cellulose (2021).
[3] L. Mercedes, L. Gil, E. Bernat-Maso, Mechanical performance of vegetal fabric reinforced cementitious matrix (FRCM) composites, Constr. Build. Mater. (2018).
[4] O. Onuaguluchi, N. Banthia, Plant-based natural fibre reinforced cement composites: a review, Cem. Concr. Compos. (2016).
[5] A.K. Sinha, S. Bhattacharya, H.K. Narang, Abaca fibre reinforced polymer composites: a review, J. Mater. Sci. (2020).
[6] S.S. Munawar, K. Umemura, S. Kawai, Characterization of the morphological, physical, and mechanical properties of seven nonwood plant fiber bundles, J. Wood Sci. (2007).
[7] H. Savastano, P.G. Warden, R.S.P. Coutts, Brazilian waste fibres as reinforcement for cement-based composites, Cem. Concr. Compos. (2000).
[8] M. Ardanuy, J. Claramunt, R.d. Toledo Filho, Cellulosic fiber reinforced cement-based composites: a review of recent research, Constr. Build. Mater. (2015).
[9] C. Mehdi, G. Seyed Hamidreza, S. Pawel, M. Ewa, K. Wojciech, S. Dietmar, Boosting Portland cement-free composite performance via alkali-activation and reinforcement with pre-treated functionalised wheat straw, Ind. Crop. Prod. (2022).
[10] X. Shang, J. Yang, Q. Song, L. Wang, Efficacy of modified rice straw fibre on properties of cementitious composites, J. Clean. Prod. (2020).
[11] L.K. Aggarwal, Studies on cement-bonded coir fibre boards, Cem. Concr. Compos. (1992).
[12] M. Li, V. Nicolas, M. Khelifa, M. El Ganaoui, V. Fierro, A. Celzard, Modelling the hygrothermal behaviour of cement-bonded wood composite panels as permanent formwork, Ind. Crop. Prod. 142 (2019).
[13] A. Bourmaud, D.U. Shah, J. Beaugrand, H.N. Dhakal, Property changes in plant fibres during the processing of bio-based composites, Ind. Crop. Prod. (2020).
[14] M.S. Islam, S.J.U. Ahmed, Influence of jute fiber on concrete properties, Constr. Build. Mater. (2018).
[15] R. Jarabo, M.C. Monte, E. Fuente, S.F. Santos, C. Negro, Corn stalk from agricultural residue used as reinforcement fiber in fiber-cement production, Ind. Crop. Prod. 43 (2013) 832–839.
[16] L. Wang, S.S. Chen, D.C.W. Tsang, C.S. Poon, K. Shih, Value-added recycling of construction waste wood into noise and thermal insulating cement-bonded particleboards, Constr. Build. Mater. (2016).
[17] L. Rodier, K. Bilba, C. Onésippe, M.A. Arsène, Utilization of bio-chars from sugarcane bagasse pyrolysis in cement-based composites, Ind. Crop. Prod. 141 (2019).
[18] H. Chen, J. Wu, J. Shi, W. Zhang, H. Wang, Effect of alkali treatment on microstructure and thermal stability of parenchyma cell compared with bamboo fiber, Ind. Crop. Prod. (2021).

[19] N. Yuan, E. Wang, S. Lv, X. Tang, T. Wang, G. Wang, Y. Zhou, G. Zhou, Y. Shi, L. Xu, Degradation reduces greenhouse gas emissions while weakening ecosystem carbon sequestration of Moso bamboo forests, Sci. Total Environ. (2023).
[20] X. Luo, X. Wang, H. Ren, S. Zhang, Y. Zhong, Long-term mechanical properties of bamboo scrimber, Constr. Build. Mater. (2022).
[21] Y. Wu, J. Wang, Y. Wang, J. Zhou, Properties of multilayer transparent bamboo materials, ACS Omega (2021).
[22] G. Vasudevan, Performance using bamboo fiber ash concrete as admixture adding superplasticizer, IOP Conf. Ser.: Mater. Sci. Eng. 216 (2017).
[23] M. Terai, K. Minami, Fracture behavior and mechanical properties of bamboo reinforced concrete members, Procedia Eng. 10 (2011) 2967–2972.
[24] M. Yilmaz, M. Tokyay, I.O. Yaman, Cement production by cement-bonded wood particleboard wastes, Adv. Cem. Res. (2016).
[25] M. Fan, M.K. Ndikontar, X. Zhou, J.N. Ngamveng, Cement-bonded composites made from tropical woods: compatibility of wood and cement, Constr. Build. Mater. (2012).
[26] H. Junfeng, J. Yongming, C. Wenbo, Y. Youming, Value-added utilization of wood processing residues into cement-bonded particleboards with admirable integrated performance, Constr. Build. Mater. (2022).
[27] Y. Ban, W. Zhi, M. Fei, W. Liu, D. Yu, T. Fu, R. Qiu, Preparation and performance of cement mortar reinforced by modified bamboo fibers, Polymers (2020).
[28] M.A. Arsène, A. Okwo, K. Bilba, A.B.O. Soboyejo, W.O. Soboyejo, Chemically and thermally treated vegetable fibers for reinforcement of cement-based composites, Mater. Manuf. Process. 22 (2) (2007) 214–227.
[29] J.E.M. Ballesteros, G. Mármol, R. Filomeno, L. Rodier, H. Savastano, J. Fiorelli, Synergic effect of fiber and matrix treatments for vegetable fiber reinforced cement of improved performance, Constr. Build. Mater. 205 (2019) 52–60.
[30] R.D. Tolêdo Filho, K. Ghavami, G.L. England, K. Scrivener, Development of vegetable fibre–mortar composites of improved durability, Cem. Concr. Compos. (2003).
[31] E.P. Aigbomian, M. Fan, Development of wood-crete from treated sawdust, Constr. Build. Mater. 52 (2014) 353–360.
[32] B. He, M. Xie, Z. Jiang, C. Zhang, X. Zhu, Temperature field distribution and microstructure of cement-based materials under cryogenic freeze-thaw cycles, Constr. Build. Mater. (2020).
[33] F. Ren, C. Zhou, Q. Zeng, Z. Zhang, U. Angst, W. Wang, Quantifying the anomalous water absorption behavior of cement mortar in view of its physical sensitivity to water, Cem. Concr. Res. (2021).
[34] C. Croitoru, C. Spirchez, A. Lunguleasa, D. Cristea, I.C. Roata, M.A. Pop, T. Bedo, E. M. Stanciu, A. Pascu, Surface properties of thermally treated composite wood panels, Appl. Surf. Sci. (2018).
[35] F. Zhou, Z. Fu, X. Gao, Y. Zhou, Changes in the wood-water interactions of mahogany wood due to heat treatment, Holzforschung (2020).
[36] X. Zhou, W. Li, R. Mabon, L.J. Broadbelt, A mechanistic model of fast pyrolysis of hemicellulose†, Energ. Environ. Sci. (2018).
[37] P.S. Fennell, S.J. Davis, A. Mohammed, Decarbonizing cement production, Joule 5 (6) (2021) 1305–1311.
[38] K. Tan, Y. Qin, J. Wang, Evaluation of the properties and carbon sequestration potential of biochar-modified pervious concrete, Constr. Build. Mater. 314 (2022).
[39] C. Tan, X. Yu, Y. Guan, A technology-driven pathway to net-zero carbon emissions for China's cement industry, Appl. Energy 325 (2022).
[40] A. Ababneh, F. Matalkah, R. Aqel, Synthesis of kaolin-based alkali-activated cement: carbon footprint, cost and energy assessment, J. Mater. Res. Technol. 9 (4) (2020) 8367–8378.
[41] S. Licht, X. Liu, G. Licht, X. Wang, A. Swesi, Y. Chan, Amplified CO2 reduction of greenhouse gas emissions with C2CNT carbon nanotube composites, Mater. Today Sustain. 6 (2019).
[42] W. Liu, K. Li, S. Xu, Utilizing bamboo biochar in cement mortar as a bio-modifier to improve the compressive strength and crack-resistance fracture ability, Constr. Build. Mater. 327 (2022).
[43] B.A. Akinyemi, C. Dai, Development of banana fibers and wood bottom ash modified cement mortars, Constr. Build. Mater. 241 (2020).
[44] L. Shen, J. Yang, R. Zhang, C. Shao, X. Song, The benefits and barriers for promoting bamboo as a green building material in China—an integrative analysis, Sustainability (2019).
[45] L. Xu, Y. Shi, G. Zhou, X. Xu, E. Liu, Y. Zhou, C. Li, H. Fang, X. Deng, Temporal Change in Aboveground Culms Carbon Stocks in the Moso Bamboo Forests and Its Driving Factors in Zhejiang Province, China, Forests (2017).