



Surface modification of wood and its effect on the interfacial bonding properties of cement-based wood composites

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Abstract

In order to increase the service life of waste wood and improve its bonding ability with cement mortar, in this study, cement-based wood composites were prepared by the hydrostatic pressing method using waste wood chips as filler material and cement mortar as the binder, after the wood was modified with NaOH, A-171 silane coupling agent and acrylate copolymer emulsion, respectively, and compounded with cement mortar. The effects of the modifications on the surface properties of wood were analyzed by SEM (scanning electron microscopy), XPS (X-ray photoelectron spectroscopy), and capillary rise tests. The dimensional stability and mechanical properties of the composites were tested, and finally, the bonding work of the composites was calculated based on the surface free energy theory. The results showed that the three modifications improved the interfacial bonding properties of wood and cement mortar and increased the dimensional stability, mechanical strength, and bonding power of the composites while changing the morphology, chemical properties, and wettability of the wood surface. This research work can provide new ideas and reference experience for improving the interfacial properties of cement-based wood composites.

1 Introduction

About 60 million tons of waste wood was produced in China each year, so we need to keep exploring the recycling and utilization of waste wood. How to rationally use waste wood and the improvement of its added value have become a key research direction and focus of attention in the forestry and wood processing industry. In Europe, lignocellulosic waste is widely used as a low-cost, abundant, degradable biomass material for furniture and particleboard production (Klímek et al. 2018). Moreover, in Japan, waste wood has been innovatively applied to road paving materials and has achieved more widespread application (Cheng et al. 2014). Research by European and Japanese scholars has served as a good model for the reuse of waste wood, but it also raises new questions: the current production of wood composites mainly relies on resin-based adhesives, but resin-based adhesives may have substances such as formaldehyde that are not friendly to the human body and ecological environment (Kusumah et al. 2016; Mantanis et al. 2017). Furthermore,

the preparation process of resin-based adhesives is complicated and the economic cost is relatively high, which to some extent limits the production and application of wood composites. In contrast, cement mortar is ecologically friendly, has a simple production process, relatively low economic cost, and is more commonly used in civil engineering. As consequence, we used ordinary silicate cement mortar as a binder and reinforcing base to prepare cement-based wood composites (CWC for short), which is important for improving the recycling potential of wood waste and advancing the development of civil engineering materials.

Hasan and co-workers showed the presence of impurities such as tannins and glucose in wood, which hinder the hydration of cement and ultimately reduce the compatibility of wood with cement mortar (Hasan et al. 2021a, b, c, d). Hemicellulose also hydrolyzes in the cement lye to produce substances such as arabinose that hinder cement hydration, which requires to modify the wood in the preparation of CWC (Bilba et al. 2003; Chakraborty et al. 2013). The modification of biomass materials using NaOH is a classical approach, and some researchers have used this approach in their studies (Abdelrhman et al. 2015; Quiroga et al. 2016; Cabral et al. 2020). In addition, silane coupling agents can also improve the properties of composites, and Song et al. (2011) showed that the physical and mechanical properties

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of wood flour/HDPE composites were improved after modification with silane coupling agents, and concluded that "A-171" had the best modification effect. Applying a silane coupling agent on the surface of cement mortar, He (2011) found that this modification increased the bonding performance of cement mortar with hot asphalt. In recent years, extensive research has also been carried out in China and abroad on the modification of cement mortars by polymers such as acrylate copolymer emulsions and vinylidene chloride, and related studies have shown that this modification can improve properties such as the strength and durability of cement composites, but this method is mostly carried out by mixing polymer emulsions directly into cement mortars. Although the application of silane coupling agents and polymer emulsions in composites is relatively common, few studies have addressed the specific effects on CWC properties after direct modification of wood in these two ways.

The interface is a multilayer transition region formed by the contact among phases within the composite, and its bonding properties play an important role in the overall performance of the composite (Zhang 2016). The interfacial bonding properties of composites can be characterized by microscopic and macroscopic tests, among which microscopic tests are more direct, but are difficult to implement due to the limitations of current testing techniques in the field of materials science (Xu et al. 2021). Therefore, we indirectly characterized the interfacial bonding ability of CWC by its macroscopic properties, calculated the interfacial bonding work of CWC based on the surface free energy (SFE) theory, and investigated the changes of wood modification on the interfacial bonding performance of CWC from an energetic point of view.

In summary, this paper selected NaOH, A-171 silane coupling agent (SC), and acrylate copolymer emulsion (ACE) to modify the wood. Additionally, we explored the effects of the three modification methods on the microscopic morphology, chemical properties, and wettability of the wood surface by SEM (scanning electron microscopy), XPS (X-ray photoelectron spectroscopy), and other tests. Importantly, the modified wood was used to prepare CWC to test the dimensional stability and mechanical properties, and the reasons for the changes in interfacial properties and macroscopic properties of the composites caused by the changes in wood surface properties were compared and analyzed based on the test results.

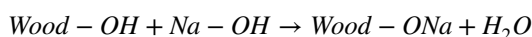
2 Materials and methods

2.1 Materials

The wood chips used in this test are from Harbin Tianan Lumber Factory. The sand is ordinary river sand with a particle size of 0.075–0.6 mm. P.O42.5 Ordinary Portland Cement was used, and the chemical composition of cement is shown in Table 1. Q8081 polycarboxylic acid system high-efficiency water reducing agent (PCA) and NaOH, etc. were commercially purchased. The test water is laboratory tap water.

2.2 Wood surface modification and chemical composition

NaOH modification: We first configured a 1 wt% aqueous NaOH solution, in which the dried wood chips were placed and processed for 3 h. The modified wood chips were washed with water to neutralize them, filtered, and then dried in a dryer at 105 °C until the mass no longer changed. The chemical reaction of wood with NaOH is shown below.



SC modification: First, we configured 95 wt% ethanol aqueous solution, then adjusted the PH of the solution to about 3 with concentrated hydrochloric acid, and finally, added vinyltrimethoxysilane while stirring to make a volume fraction of 4%. When the silane coupling agent had been hydrolyzed at room temperature for 2 h, we put the wood chips into the solution and then treated them by immersion at room temperature. After 2 h, the wood chips were modified and washed until neutral, filtered, dried at 120 °C under constant weight, bagged and sealed. The molecular model of vinyltrimethoxysilane is shown in Fig. 1.

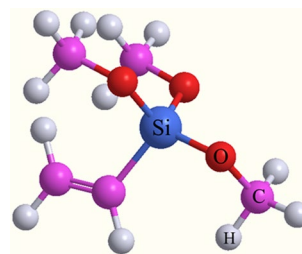


Fig. 1 Molecular model of vinyltrimethoxysilane

Table 1 Chemical composition of cement (%)

Composition	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃
Content	63.27	21.34	4.52	3.21	3.53	1.98

ACE modification: We configured an aqueous solution of 15 wt% acrylate copolymer emulsion at room temperature, and then added the dried wood chips to it while stirring, followed by processing it at room temperature for 3 h. After treatment, the wood chips were filtered, put in a 105 °C environment and dried by air to constant weight, and then sealed in bags for spare.

According to GB/T 2677.10 (Fibrous raw material—Determination of holocellulose) and GB/T 2677.8 (Fibrous raw material—Determination of acid-insoluble lignin), the chemical composition of wood before and after modification was determined. The results are shown in Table 2. The above method determines the relative content of lignin, cellulose, and hemicellulose in wood. NaOH treatment reduces the lignin and hemicellulose in wood. Therefore, the relative content of cellulose in wood increased after NaOH treatment.

2.3 Preparation of CWC

The matching ratios were determined through preliminary tests: water-cement ratio 0.8, sand-cement ratio 0.4, wood-cement ratio 0.3, and 0.2% PCA (all the above are mass ratios based on cement). Since Ca^{2+} is adsorbed to the wood surface thereby inhibiting the hydration of the cement (Jorge et al. 2004), we supplemented the Ca^{2+} in the system by adding 2% anhydrous CaCl_2 by mass of cement as an admixture in the preparation of CWC.

To ensure that the wood chips were evenly dispersed in the cement slurry, the weighed cement, wood chips, and sand were placed in a mixing pot with a planetary mortar mixer for 2 min of slow dry mixing. After the mixture was evenly mixed, it was stopped for 90 s, and then PCA with anhydrous calcium chloride aqueous solution was added for 4 min of rapid mixing. The homogeneous mixture was placed in the mold and hydrostatically formed by SYE-200D type pressure tester so that the forming size was 40 mm × 40 mm × 160 mm, and three parallel specimens were made in each group. After 24 h at room temperature, the mold was demolded and put into a standard maintenance box with humidity above 90% and temperature (20 ± 3) °C for maintenance.

Table 2 Relative content of chemical components before and after wood modification

Modification methods	Lignin	Hemicellulose	Cellulose
UT	27.47	28.39	42.40
1%NaOH	5.28	19.83	74.29
4%SC	32.30	26.21	40.28
15%ACE	28.13	28.36	42.46

2.4 Scanning electron microscopy (SEM) analysis

After evacuating the wood chips with gold spray, the microscopic morphology of the wood surface before and after the modification was observed with a scanning electron microscope of type EM-30plus at 13 kV in BE electron mode.

2.5 X-ray photoelectron spectroscopy (XPS) test

The surface chemistry of the wood before and after modification was analyzed by testing the content of elements and functional groups on the wood surface with a Thermo Scientific K-Alpha + type device. The tests were performed using a Mono AlK α (1486.6 eV) ray source, corrected for the binding energy of all elements by the binding energy of C1s at 284.8 eV. Data processing and analysis were performed using Avantage 5.948 software.

2.6 Wettability test of wood surface

The wettability of wood flour can be tested using the capillary rise test, based on Washburn's impregnation equation to calculate the contact angle information of wood chips before and after modification (Magalhães da Silva and Oliveira 2021). The calculation equation is as follows:

$$h^2/t = \gamma_L R_{eff} \cos\theta / 2\eta \quad (1)$$

where h is the liquid rise height, cm ; t is the impregnation time, s ; γ_L is the liquid surface tension, $mJ \cdot m^{-2}$; R_{eff} is the capillary effective radius, μm ; θ is the contact angle between the liquid and the solid, ($^\circ$); η is the liquid viscosity, $mPa \cdot s$.

The capillary tube with an outer diameter of 6 mm, wood powder with a 60 mesh sieve, and a layer of geotechnical filter paper wrapped around the bottom of the capillary tube were selected. The test solution was distilled water and formamide. The test was conducted at 25 °C. The liquid surface tension of hexane was selected as the calibration liquid to test the effective radius of the capillary R_{eff} . The specific steps are: (1) The filter paper was wrapped around the bottom of the capillary to prevent leakage of wood powder during the test; (2) Filling the capillary with a quantitative wood powder and shaking to a certain dense state, ensuring that the top of the dense wood powder from the bottom of the capillary is about 4 cm; (3) Immersing the bottom end of the capillary filled with wood powder into the glass dish containing the test solution, ensuring that the top edge of the filter paper is always above the test solution; (4) The rise of the test liquid in the capillary was continuously observed, the rise distance and

Table 3 Liquid surface tension parameters (25 °C)

Reagent	$\gamma_L/(mJ \cdot m^{-2})$	$\gamma_L^d/(mJ \cdot m^{-2})$	$\gamma_L^p/(mJ \cdot m^{-2})$	$\eta/(mPa \cdot s)$
Distilled water	72.8	21.8	51.0	0.89
Formamide	57.9	34.4	23.5	3.343
N-hexane	18.4	18.4	0	0.326

corresponding time were recorded. The physical properties of the test liquids are shown in Table 3, and the average of the three tests was taken as the final result.

During the test, it was found that: (1) Wood may appear hydrophobic after modification by ACE, and (2) the cement mortar will solidify and harden. The appearance of these problems led to the inability to obtain its contact angle information by capillary rise test. For this phenomenon, we tested its contact angle with distilled water and formamide (in Table 3) by video optical contact angle measuring instrument (OCA20). Finally, we took the average of 5 tests as the final result of the experiment.

2.7 Dimensional stability test

Referring to JC/T 411–2007 (Cement-bonded particle-board reinforced with fibrous wood particles), the 24 h water absorption (WA) and 72 h water absorption thickness expansion (TE) of the specimens placed in the room for 7 days were used as the evaluation indexes for the dimensional stability of CWC.

In order to test WA, we weighed the mass of the CWC specimens left in the chamber for 7 days with an accuracy of 0.1 g. The CWC specimens were placed in water at room temperature to make them completely immersed. After 24 h, the CWC specimens were taken out and the surface water was wiped off with absorbent paper, and then the sample mass was weighed. Each specimen was weighed 3 times and the average value was taken as the final result. It should be noted that the whole process needs to be completed within 10 min. The calculation formula is as follows:

$$W = \frac{m_2 - m_1}{m_1} \times 100\% \quad (2)$$

where W is the 24 h water absorption rate of the specimen (%); m_1 is the mass of the specimen before water immersion (g); m_2 is the mass of the specimen after water immersion for 24 h (g).

In the TE test, we measured the thickness of the CWC specimens before and after soaking in water, which was done with the help of vernier calipers. The specific process refers to the WA test; each specimen was measured five times to take the average value as the final result. The calculation formula is as follows:

$$T = \frac{h_2 - h_1}{h_1} \times 100\% \quad (3)$$

where T is the 72 h water absorption thickness expansion rate of the specimen (%); h_1 is the thickness before immersion (mm); h_2 is the thickness after 72 h immersion (mm).

2.8 Mechanical properties test

(1) Referring to GB/T 1449–2005 (Fiber-reinforced plastic composites–Determination of flexural properties), the mechanical properties of CWC were tested by using P-M universal material testing machine. In addition, the bending strength and bending modulus of elasticity were calculated.

We first placed the specimen on the support axis and then adjusted the support axis spacing to 100 mm. When the spacing had been adjusted, we started the instrument and controlled the loading rate of 10 mm/min. Finally, we plotted the load–deflection curve based on the load and deflection values. The bending strength and bending modulus of elasticity are calculated as follows:

$$\sigma_f = \frac{1.5F_f \cdot L}{bh^2} \quad (4)$$

where σ_f is the bending strength of CWC (MPa); F_f is the maximum load when the specimen is damaged (N); L is the span of the test (mm); b is the width of the specimen (mm); h is the thickness of the specimen (mm).

$$E_f = \frac{\Delta p \cdot L^3}{4bh^3 \cdot \Delta f} \quad (5)$$

where E_f is the bending modulus of elasticity of CWC (MPa); Δp is the load increment corresponding to the linear segment on the load–deflection curve (N); Δf is the deflection at the midpoint of the span corresponding to Δp (mm).

(2) Unfortunately, the CWC specimen undergoes large deformation and shows the characteristics of yield deformation when compressed, and there is no more obvious peak in its load–deflection curve. Therefore, its compression strength was determined by referring to the method specified in ASTM C165-2017. The loading rate was set to 2400 N/s, and the load–deflection data were recorded. The compression strength is calculated as follows:

$$\sigma_m = \frac{W}{A} \quad (6)$$

where σ_m is the compression strength of CWC (MPa); W is the load at 10% deformation of the specimen (N); A is the compressive area of the specimen (mm^2).

3 Results and analysis

3.1 Wood surface morphology analysis

Figure 2 shows the microscopic morphology of the wood surface before and after modification, where (a) is UT, (b) (c) is NaOH modified, (d) is SC modified, and (e) (f) (g) is ACE modified. As shown in Fig. 2a, the surface of the original wood is present with a texture, relatively flat and smooth, having a certain gloss. Figure 2b, c shows that after NaOH modification, the surface of the wood becomes rougher, and at a magnification of $\times 1000$, it is observed that there are

obvious folds and cracks on the surface. At the same time, the wood surface became duller and no longer had the glossy and bright texture of UT, probably because the NaOH modification reduced the wax content on the surface of the wood (Berger et al. 2020). Observing Fig. 2d, it was found that after SC modification, no significant difference compared to UT was still found at a magnification of $\times 5000$, which indicates that SC modification did not have a large effect on the wood microformat in this experiment.

The observation of Fig. 2e–g revealed that the modification of wood by ACE resulted in the generation of an extremely complex and irregular translucent film on its surface. The appearance of this film caused the grain pores on the surface of the wood to be covered to varying degrees. The film covering the wood surface will reduce the direct contact between wood and cement mortar, which may reduce the inhibition of cement hydration by extractives

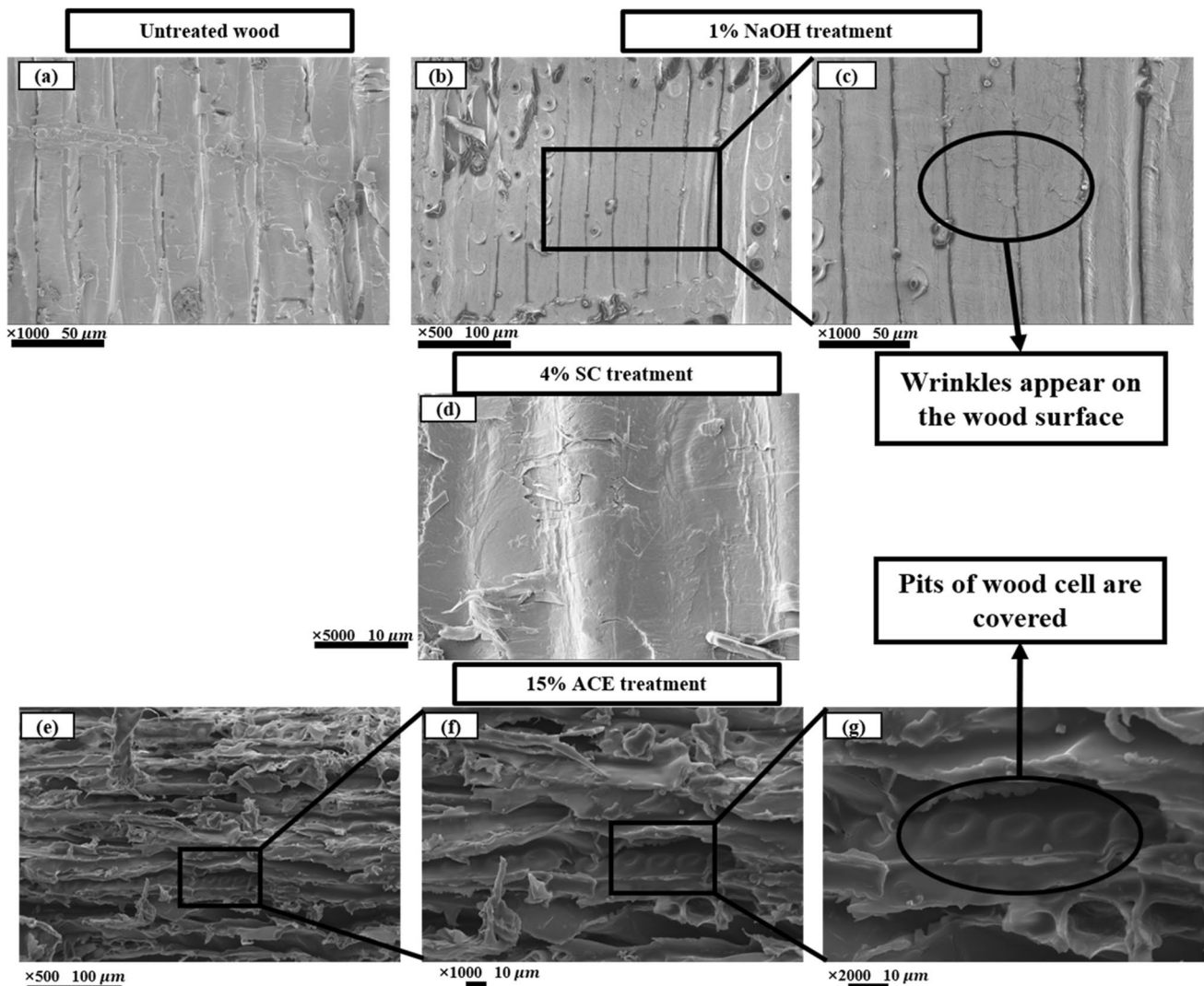


Fig. 2 SEM images of wood surfaces: a UT, b, c NaOH modified, d SC modified, and e–g ACE modified

and hemicellulose in wood, thus improving the compatibility and interfacial bonding between the two (Quiroga et al. 2016; Jorge et al. 2004). The experimental results showed that NaOH and ACE modification significantly changed the microscopic morphology of the wood surface.

3.2 Analysis of wood surface chemical properties

The main components of wood are lignin, cellulose, hemicellulose, and extractives, among which the rich hydroxyl functional groups in the three major elements make the surface of wood suitable for chemical modification. While the XPS test technique can probe the chemical information of the material at a depth of 10 nm (Kocaefe et al. 2013), which reflects the surface properties of the material, therefore, this study characterizes and analyzes the surface chemical properties of wood after modification by the XPS test.

The full spectrum and elemental content statistics of the wood are shown in Fig. 3 and Table 4, respectively. It is found in Fig. 3 that the main elements on the surface of the wood are C and O (H element could not be determined). After the NaOH and SC modifications, the characteristic peaks of Na and Si elements appeared on the surface, respectively, as shown in Table 4, indicating that the above

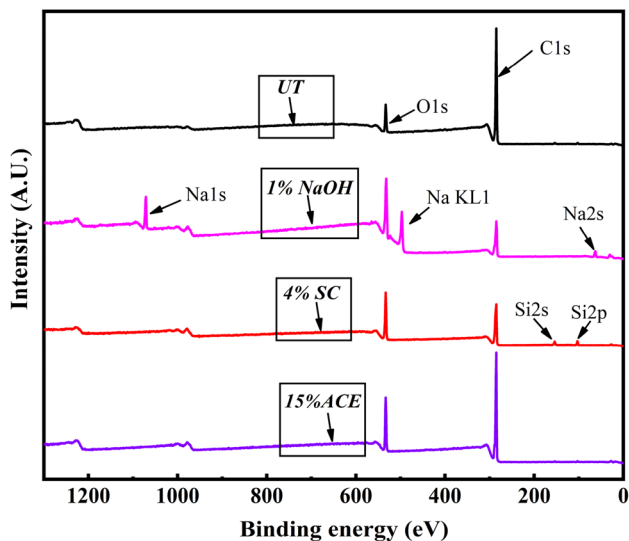


Fig. 3 XPS Survey

Table 4 Mole fraction of XPS spectrum

Modification methods	O1s/%	C1s/%	N1s/%	Si/%	Na/%	O/C
UT	9.65	89.39	0.96	–	–	0.11
1%NaOH	32.09	49.41	0.63	–	17.87	0.65
4%SC	25.90	68.00	0.65	5.44	–	0.38
15%ACE	17.88	80.99	0.42	0.71	–	0.22

modifications not only resulted in large changes in the elements on the surface of the wood but also in possible chemical reactions to produce new substances. After ACE modification, a small amount of Si elements was found on the surface of the wood, which may be due to the introduction of Si elements on the surface of the wood under the influence of the silicone emulsion in ACE.

The analysis of Table 4 shows that all three modifications resulted in a large change in the elemental content of C and O on the surface of the wood. Compared to UT, the O/C on the modified wood surface increased by about 5.9, 3.5, and 2.0 times, respectively, and the increase in O/C indicates that more oxygen-containing functional groups were produced on the wood surface which indicates an increase in the chemical activity of the wood surface (Avramidis et al. 2012). The content of elemental N on the wood surface did not change substantially after NaOH and SC modifications, which indicates that elemental N was less affected by the above two modifications, while the slight decrease in the relative content of elemental N after ACE modification may be due to the influence of the formation of a thin film on the wood surface, which caused a decrease in the relative content of elemental N in the wood surface. Kamdem et al. (1991) demonstrated that the high C content of wood indicates the presence of extractives on its surface, while the relative content of C1s on the surface of wood decreased by about 1.8 times after NaOH modification. This indicates that NaOH modification reduced the content of extractives on the wood surface.

Figure 4 and Table 5 show the C1s peak splitting fit and the test information. The presence of three peaks of elemental C on the surface of the wood was found by splitting the peaks, which indicates the presence of C atoms in three states on the surface of the wood. The positions of the C1, C2, and C3 peaks and the functional groups they represented are shown in Fig. 4. The absence of the C4 peak in the C1s spectrum may be due to the fact that such wood contains very few carboxylic acid groups. Analysis of the electron binding energy information in Fig. 4b revealed that peaks of metal carbides and metal hydrocarbons appeared on the surface of the wood modified by NaOH, which, combined with the analysis of the new characteristic peaks of Na elements in the full spectrum of Fig. 3, may be caused by the generation of Na_2CO_3 and NaHCO_3 on the surface of the wood.

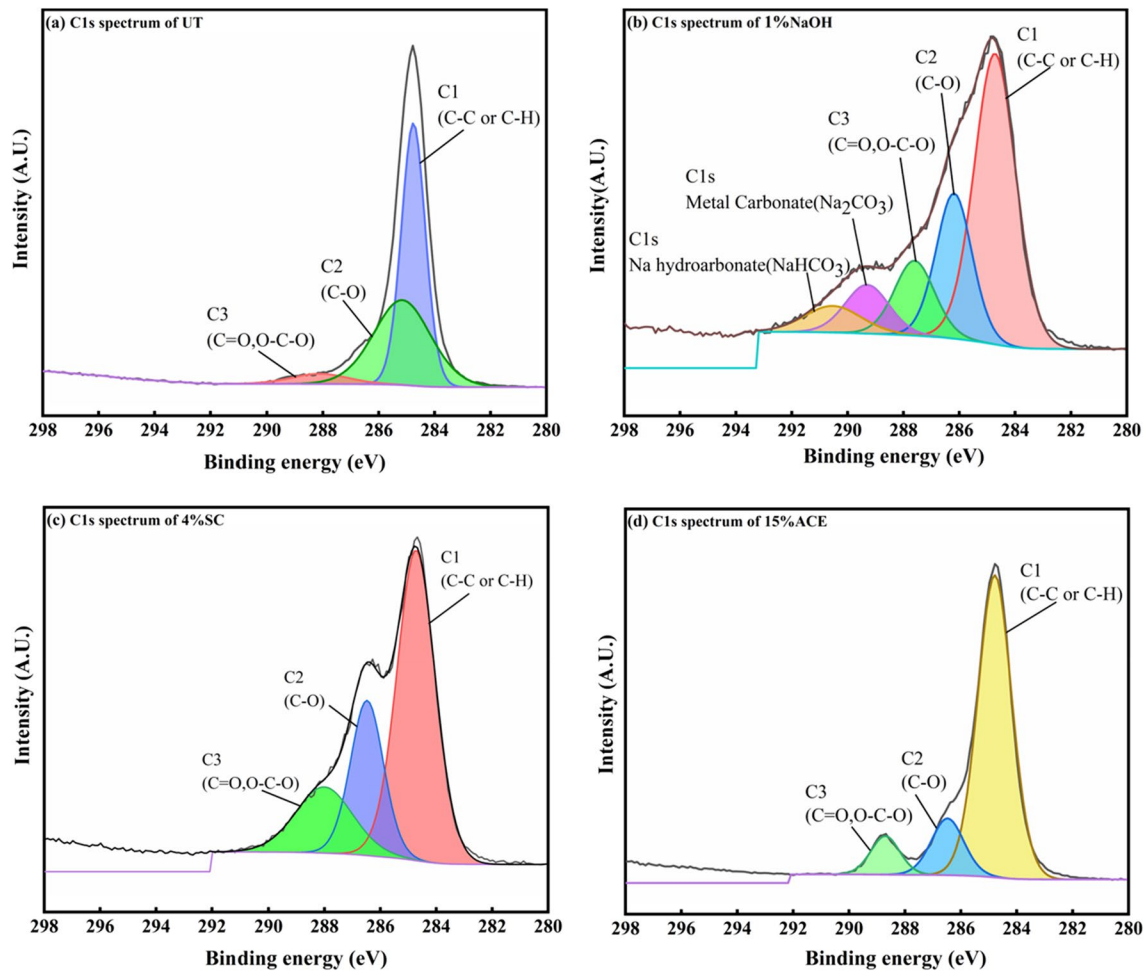


Fig. 4 C1s peak split diagram: **a** UT, **b** NaOH modified, **c** SC modified, and **d** ACE modified

Table 5 C1s test data on the surface of wood chips

Modification methods	Relative peak area/%			Binding energy/eV		
	C1	C2	C3	C1	C2	C3
UT	53.54	41.48	4.98	284.8	285.2	288.1
1%NaOH	50.22	21.86	12.55	284.7	286.2	287.6
4%SC	57.14	24.67	18.19	284.7	286.5	288.0
15%ACE	77.50	13.98	8.52	284.8	286.5	288.7

Related studies have shown that C1 peaks are mainly attributed to lignin and extractives in wood, C2 peaks are attributed to cellulose and hemicellulose, and C3 peaks are attributed to acetal structures in hemicellulose, carbonyl groups in lignin, and wood oxides (Altgen et al. 2016). Table 5 shows that the relative areas of C1, C2, and C3 peaks of the modified wood were changed, and the reasons for the changes were analyzed as follows: (1) NaOH modification: the presence of extractives on the wood surface increases the content of C1 (Kocafe et al. 2013). NaOH affects the chemical environment of α -carbon atoms by acting on acidic

α -hydrogen atoms, which affects the CH-O polar bonds, thus destroying hemicellulose and causing a decrease in the relative area of the C2 peak. The increase in C3 peak area could be attributed to the isomerization and condensation of unsaturated carbonyl compounds in some extracts by NaOH through saponification reactions, thus increasing the relative content of carbonyl (C=O) and acetal structures (O-C-O) (Fu et al. 2018; Sedan et al. 2007). (2) SC modification: The main active ingredient of A-171 silane coupling agent is $(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2$, which may introduce more hydrocarbon (C-H) groups in the process of wood modification,

thus causing the rise of the relative area of C1 peak. HCl is added to adjust the solution to an acidic environment in the process of configuring the silane coupling agent solution to promote the hydrolysis of the coupling agent. However, HCl destroys the structure of cellulose and hemicellulose and thus causes a decrease in the content of C–O groups, which may be the reason for the decrease in the relative area of the C2 peak. When cellulose and hemicellulose are destroyed, it causes an increase in the relative content of lignin, and the carbonyl group (C=O) in C3 is mainly attributed to the lignin molecule, which causes an increase in the relative area of the C3 peak (Fu et al. 2018). (3) ACE modification: ACE contains components such as $\text{CH}_2=\text{CHCOOH}$ and $\text{CH}_2=\text{CHCOO}(\text{CH}_2)_3\text{CH}_3$ (Zhang 2016). The modification of wood caused an increase in the relative content of C1 and C3 peaks, respectively, due to the introduction of the above-mentioned substances containing abundant hydrocarbon groups (C–H) and carbonyl groups (C=O). Through the analysis in Fig. 2e–g and Sect. 3.1, because the ACE modification method forms a film on the surface of the wood, and there were no C–O groups corresponding to the non-carbonyl C under the C2 peak in the components such as methacrylic acid, so it caused the decrease in both the content of C–O groups on the surface of the wood and the C2 peak area. The test and analysis results showed that NaOH, SC and ACE modifications all significantly changed the chemical properties of the wood surface.

3.3 Wood wettability analysis

The contact angle can characterize the hydrophilicity of the material, which exhibits hydrophobicity when the contact angle $\theta > 90^\circ$ and hydrophilicity when the opposite is true. Figure 5 reflects the trend of the contact angle of wood with

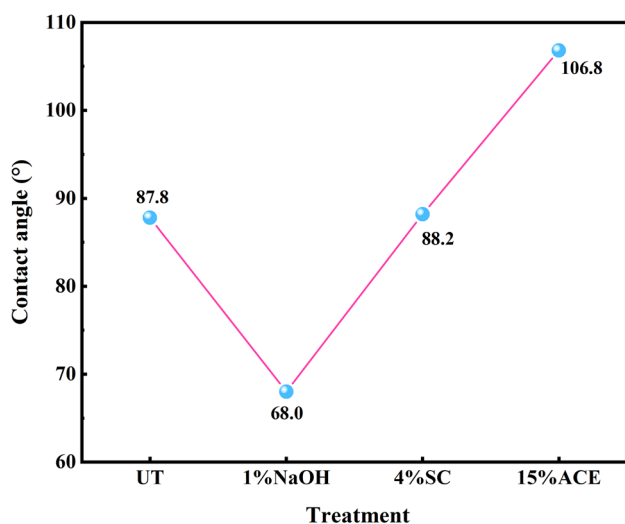


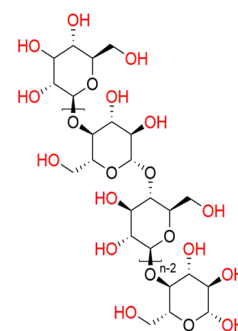
Fig. 5 Contact angle of wood flour and distilled water

distilled water before and after modification. After NaOH modification θ decreased to 68.0° , which may be due to: (1) Combined with the analysis in 3.2, the NaOH modification reduced the extractives and hemicellulose on the wood surface and increased the relative content of cellulose, while the cellulose molecule (as shown in Fig. 6) contains three hydrophilic hydroxyl (-OH) groups in each glucose group in addition to having two end groups, which makes the wood more polar, thus allows water to enter the non-crystalline region of the cellulose molecule, and increases the hydrophilicity of the wood. (2) The analysis in 3.1 showed that the NaOH modification caused wrinkles and cracks on the surface of the wood, which may have exposed hydrophilic groups such as hydroxyl (-OH) and carboxyl (-COOH) groups inside the wood and thus increased hydrophilicity. The slight increase in θ after SC modification of wood may be due to (1) the reaction of the hydrolysis group in A-171 with the hydroxyl group (-OH) on the wood surface, which reduces the polarity of the wood surface; (2) The silane coupling agent may act as a "protective layer" on the wood surface, thus reducing the water absorption of cellulose and hemicellulose in the wood; (3) The presence of non-N-atomic methyl (-CH₃) groups in $(\text{CH}_3\text{O})_3\text{SiCHCH}_2$ (vinyltrimethoxysilane), which also reflects some hydrophobicity and thus causes an increase in the contact angle between the wood and distilled water (Song et al. 2011; Lina Han et al. 2017; Koga et al. 2011). After 15% ACE modification, θ increased to 106.8° , which is 22% more than the original wood, showing a significant hydrophobicity, meaning that the surface of the wood will be more difficult to absorb water. This is caused by the fact that the ACE emulsion forms a thin film, which can prevent direct contact between the wood and the water to some extent. The test and analysis results showed that all three modifications changed the wettability of the wood surface.

3.4 Dimensional stability analysis of CWC

Figure 7 shows the WA and TE of CWC before and after wood modification. The WA values in descending order are NaOH modified, UT, SC modified and ACE modified. The NaOH modified wood increased the WA of CWC by

Fig. 6 Molecular formula of cellulose



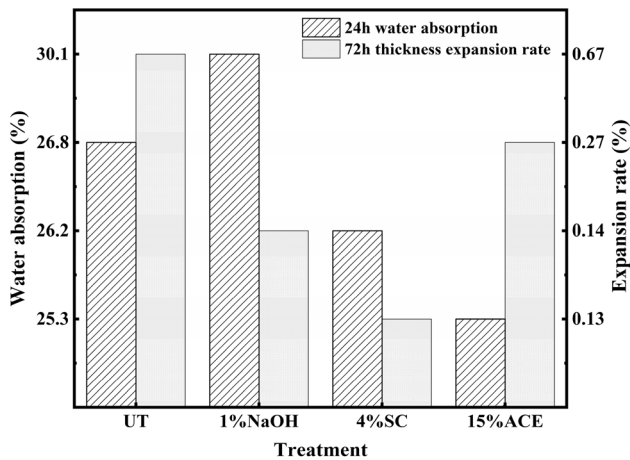


Fig. 7 Water absorption and thickness expansion rate of CWC

12.3%, but the WA decreased by 2.2% and 5.6% after SC and ACE modified wood compared to UT, respectively. The test results show that the trend of WA is consistent with the analysis of wood wettability in 3.3, i.e., the more hydrophilic the wood is, the higher the WA value of the prepared CWC and the better the water absorption. This indicates that the WA of CWC shows a positive correlation with the hydrophilicity of the wood within the scope of this test.

The TE of CWC modified by NaOH and SC decreased by 79.1% and 80.6%, respectively, where the NaOH modification increased the WA of CWC but showed a significant decrease in TE. This indicates that the change in interfacial binding properties of CWC caused by NaOH and SC modification of wood reduces its ability to absorb water and swell. The TE of CWC prepared by ACE modification also showed a decrease of 59.7% compared to that of unmodified. The reason for this change is due to multiple factors: (1) The

ACE modification produced a 5.6% decrease in the WA of CWC itself, the reduction in water absorption mass reduces the swelling of the composite under the same conditions; (2) The acrylate emulsion itself has excellent adhesion properties, which may enhance the bonding properties between wood and cement mortar and improve the interfacial bonding ability of CWC, thereby limiting the interfacial bonding ability of CWC to some extent, thus limiting the water absorption and swelling of CWC to a certain extent.

The test results show that, from the perspective of the dimensional stability of the composite, all three wood modification methods reduced the water absorption thickness expansion rate of CWC specimens, and the TE results all met the requirements of $\leq 1.5\%$ in JC/T 411–2007. Unexpectedly, NaOH modification is the most effective.

3.5 Mechanical properties analysis of CWC

Figure 8 shows the mechanical strength and flexural modulus of CWC before and after wood modification. Comparing to the control group, it was found that the changes in interfacial binding properties of modified CWC had a relatively significant effect on macroscopic mechanical properties.

The compressive strength of the composites gained 8.9% after the wood was modified with NaOH. However, the bending strength decreased by 30%, which is difficult to explain. The analysis in chapter 3.2 showed that wood modified by NaOH reduced extractives and hemicellulose that inhibit cement hydration, and several studies have demonstrated that NaOH-modified biomass materials increase their compatibility with cement (Ma and Chuangui 2012; Liang-ming et al. 2002). Figure 2c shows that the wood surface becomes rougher, which, based on mechanical interlocking theory, also increases its compatibility with the mechanical engagement of cement mortar. As consequence, the interaction of

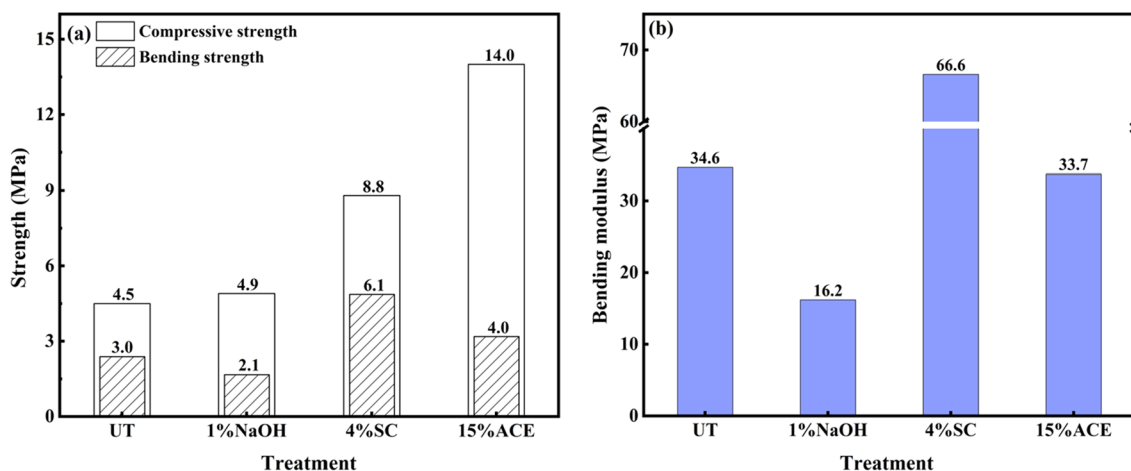


Fig. 8 Strength and modulus of CWC

these factors will enhance the interfacial bonding properties of CWC thereby increasing its mechanical strength. Our in-depth analysis suggests that there are multiple reasons for the decrease in bending strength: (1) The analysis in 3.2 shows that the NaOH modification reduces the compound content (mainly hemicellulose and extractives) on the wood surface, and the reduction of wood compounds reduces the tensile stress and tensile strength of wood (Cabral et al. 2020), which may be the main reason for the decrease in bending strength of CWC. (2) Another potential reason may be that the NaOH modification increases the hydrophilicity of wood and the high wood content in the ratio, which together lead to the wood absorbing more water and thus adversely affecting the hydration of cement, which may indirectly explain the smaller increase in CWC compressive strength. Combined with the experimental data and the above analysis, it shows that the change in the interfacial bonding properties of CWC caused by NaOH modification of wood is beneficial to its compressive strength but negatively affects the bending strength within the scope of this test.

The mechanical strength of CWC after wood modification by SC produced a large increase in both compressive and flexural strengths to 8.8 MPa and 6.1 MPa, which is an increase of 95.6% and 103.3%. The reasons regarding the causes of this change are manifold, as many theories can be used to explain this phenomenon, such as the chemical bonding theory, the physical action theory (He 2011), the surface infiltration theory, and the reversible equilibrium theory (Zisman 1969). Because the chemical bonding theory for silane coupling agent to enhance the interface mechanism is more common, this theory can be used to analyze the specific process and reaction mechanism as shown in Fig. 9: (1) Methoxy (-OCH₃) connected with Si hydrolysis to generate silanol containing silicon hydroxyl (Si-OH); (2) Dehydration and condensation of the silicon hydroxyl group (Si-OH) at one end of the silanol to form oligomeric silanols containing Si-O-Si covalent bonds; (3) The silicone hydroxyl group (Si-OH) in the oligomeric silanol reacts with the hydroxyl group (-OH) on the surface of the wood to form hydrogen bonds; (4) The hydrogen bond breaks during the heating and drying process and is accompanied by a dehydration reaction to form a C-O-Si covalent bond with the surface of the wood; (5) During the mixing process between the wood and the cement mortar, the silicone hydroxyl group (Si-OH) reacts with the hydroxyl group (-OH) in the cement mortar and dehydration condensation to generate Si-O-Si covalent bonds, which connects wood to cement mortar and improves the interfacial bonding properties between wood and cement mortar, thus causing the enhancement of macroscopic mechanical properties of CWC (Song et al. 2011; He 2011; Abdelmouleh et al. 2007). Of course, another possible reason is that the silanol molecule contains multiple hydroxyl groups (-OH), a silanol molecule undergoes a condensation

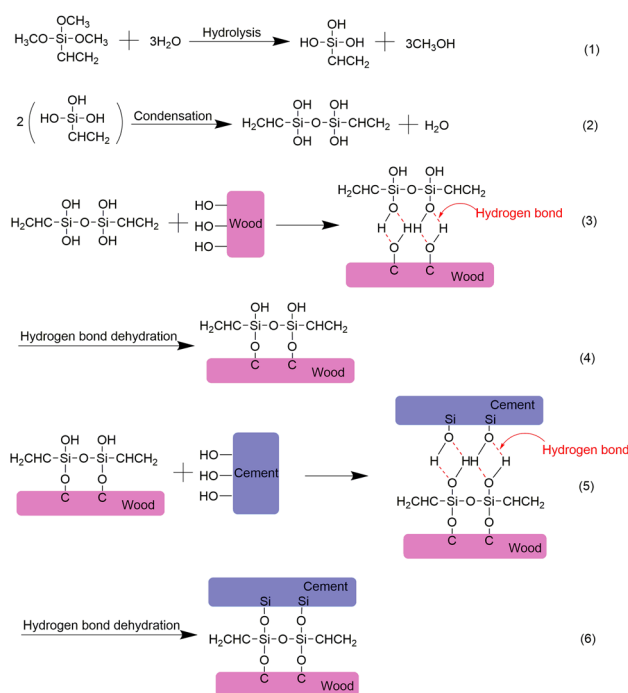


Fig. 9 Mechanism of action of A-171 silane coupling agent

reaction with multiple Si-O bonds inside the cement mortar, connecting multiple mortar particles and forming a spatial network structure, which will increase the compactness and energy absorption capacity of the cement mortar system to some extent, thus enhancing the mechanical properties of CWC (He 2011).

The compressive and flexural strengths of CWC were increased by 211.1% and 33.3%, respectively, after ACE modification of wood, which shows that the change in interfacial bonding properties of CWC caused by ACE modification is also very obvious in terms of its mechanical strength, especially the compressive strength. The reasons for these changes are the result of a combination of factors: (1) The film structure generated on the surface of the wood after ACE modification hinders its direct contact with cement mortar and reduces the release of inhibitory substances from wood into cement mortar, reducing the effect of wood on cement hydration (Quiroga et al. 2016). (2) The presence of reactive ester group (-COOR) groups in ACE, which can react with multivalent metal cations generated by cement hydration and form special bridge bonds with ACE through ionic bonds, which in turn improve the mechanical properties of CWC. (3) The presence of ACE films is equivalent to the addition of a transitional interfacial layer between wood and cement mortar, and the presence of this interfacial layer improves the bonding performance and strength between the composites (He 2011). (4) The extremely complex lamellar film structure generated on the surface of the wood can fill

the voids in CWC to a certain extent. It will improve its mechanical properties on a macroscopic level, of course, which may also be one of the reasons causing the reduction in the expansion of the water absorption thickness of CWC.

Figure 8b shows the change in the bending modulus of CWC, which characterizes the magnitude of the material's ability to resist bending deformation within the elastic limit. Modification of wood by NaOH, SC, and ACE decreased the bending modulus of CWC by 53.2%, enhanced it by 92.5%, and decreased it by 2.6%, respectively. This indicates that the modification of wood by NaOH and ACE reduced the ability of CWC to resist bending deformation, and combined with the load–deflection diagram in Fig. 10, it can be found that these two modifications significantly increased the value of the spanwise deflection corresponding to the maximum breaking load of CWC and improved its flexibility capacity. On the contrary, the bending modulus of CWC after modification by SC increased substantially; the change in Fig. 10 indicates that the maximum breaking load was increased while the mid-span deflection value was reduced, indicating that the SC-modified wood improved the resistance of CWC to bending deformation and increased its stiffness properties.

3.6 Interface bonding function analysis of CWC

The binding work can reflect the interfacial bonding performance of the composite from the energetic point of view. The larger the value of the binding work, the more energy is required for the separation of the composite, and then, the better the interfacial bonding properties of the composite material (Li et al. 2015; Lugscheider and Bobzin 2001).

In this experiment, the binding work was calculated by Eq. (7):

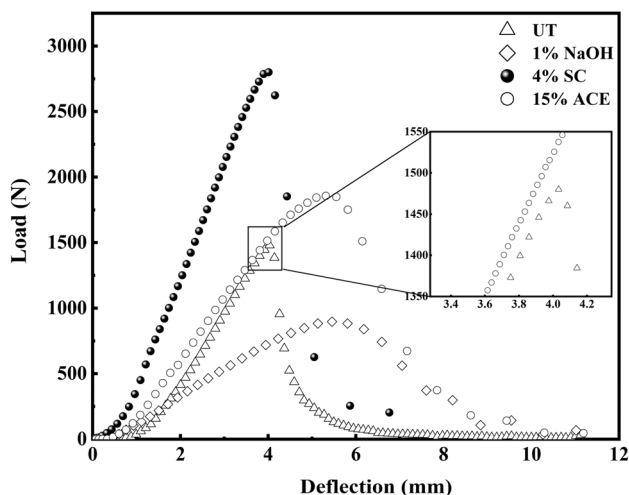


Fig. 10 Load–deflection curve of CWC

$$W_{AB} = \gamma_A + \gamma_B - \gamma_{AB} \tag{7}$$

where W_{AB} is the binding work of the composite material (mJ/m^2); γ_A and γ_B are the surface free energy of materials A and B, respectively (mJ/m^2); γ_{AB} is the interfacial energy on the contact surface of material AB (mJ/m^2).

The interface free energy can be expressed in Eq. (8):

$$\gamma_{AB} = \gamma_A + \gamma_B - 2 \left(\sqrt{\gamma_A^d \cdot \gamma_B^d} + \sqrt{\gamma_A^p \cdot \gamma_B^p} \right) \tag{8}$$

where γ_A^d and γ_B^d are the dispersion components of A and B, respectively (mJ/m^2); γ_A^p and γ_B^p are the polar components of A and B, respectively (mJ/m^2).

Substituting Eq. (8) into Eq. (7) yields Eq. (9):

$$W_{AB} = 2 \left(\sqrt{\gamma_A^d \cdot \gamma_B^d} + \sqrt{\gamma_A^p \cdot \gamma_B^p} \right) \tag{9}$$

For the dispersion and polarity components of the solid, the contact angle with the solid can be tested from liquids of two kinds with known surface properties and then calculated by the Owens–Wendt equation (Owens and Wendt 1969):

$$\gamma_L(1 + \cos\theta) = 2 \left(\sqrt{\gamma_S^d \cdot \gamma_L^d} + \sqrt{\gamma_S^p \cdot \gamma_L^p} \right) \tag{10}$$

where γ_L is the liquid surface tension; θ is the solid–liquid contact angle; γ_S^d and γ_S^p are the dispersion component and polar component of the solid, respectively; γ_L^d and γ_L^p are the dispersion component and polar component of the liquid, respectively.

The information on the contact angle measurements of distilled water and formamide with wood and cement mortar is shown in Table 6.

Figure 11 shows the interfacial binding work of wood and cement mortar in CWC calculated based on surface free energy (SFE) theory. The increase in the binding work of CWC after wood modification by NaOH, SC, and ACE compared to UT was 74.56%, 0.07%, and 82.29%, respectively, which indicates that energetically speaking within the scope of this test all three modifications improved the interfacial binding performance of CWC, with the ACE modification

Table 6 Contact angle measurement result

Samples	Contact angle $\theta/(^\circ)$	
	Distilled water	Formamide
UT	87.8	53.0
1%NaOH	68.0	62.4
4%SC	88.2	61.7
15%ACE	106.8	61.3
Cement mortar	26.6	22.7

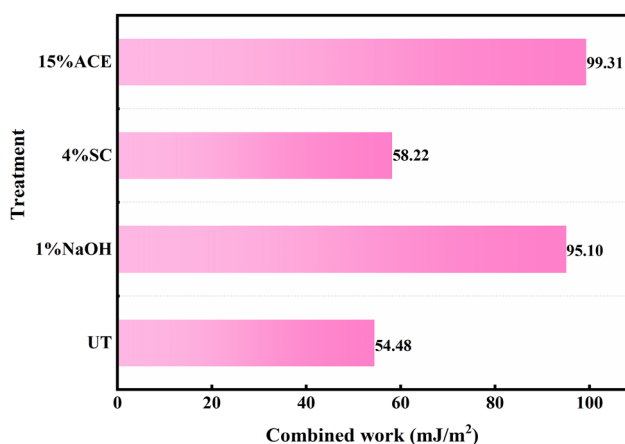


Fig. 11 Combined function of CWC

having the best enhancement effect. The enhanced interfacial bonding ability can enhance the mechanical properties of the composites, which is in agreement with the analysis of mechanical strength in 3.5. It is particularly noted that the dimensional stability of CWC, the analysis of interfacial bonding work, and the enhancement of compressive strength can prove that NaOH-modified wood enhances the interfacial bonding ability of CWC, but NaOH negatively affects the tensile stress and tensile strength of wood, so when the wood content in the composite is high, it reduces its bending strength instead under the interaction of various factors.

4 Conclusion

Based on the results of this study, the following conclusions can be drawn within the scope of this test:

- (1) The NaOH modification increased the surface roughness and reduced the surface gloss of the wood. The ACE modification produced a complex translucent film on the wood surface, the appearance of which covered the grain pores on the wood surface. In contrast, the SC modification did not have a large effect on the microscopic morphology of the wood. The three modifications changed the elemental content and chemical composition of the wood surface, increased the proportion of oxygen-containing functional groups and improved its surface activity.
- (2) NaOH modification enhanced the hydrophilicity of wood, while SC and ACE modification reduced its hydrophilicity, among which ACE modification was the most significant, resulting in an obvious hydrophobic property on the wood surface. WA of CWC was positively correlated with the hydrophilicity of wood. All three modifications reduced the TE of CWC,

where NaOH modification had the most significant reduction effect, with a reduction of 79.1%.

- (3) The changes in interfacial properties caused by the three modifications compared to UT resulted in no significant regular change in the macroscopic mechanical properties of CWC, i.e., NaOH modification improved the compressive strength and flexibility of CWC but reduced the bending strength by 30%. SC modification improved the compressive strength, bending strength and stiffness of CWC. ACE modification improved the compressive strength, bending strength and flexibility of CWC.
- (4) After using SFE theory analysis, it was found that NaOH modification, SC modification, and ACE modification increased the interfacial bonding power of CWC by 74.56%, 0.07%, and 82.29%, respectively. The three wood modifications enhanced the interfacial bonding ability of wood and cement mortar in CWC based on the energetics.

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Data availability Data will be made available on request.

Declarations

Conflict of interest No potential conflict of interest was reported by the authors.

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