Influence of Active Inorganic Fillers on the Physical and Mechanical Properties of Polyvinyl Chloride Wood-plastic Composites When Immersed

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Hydration-active steel slag and slag micropowder were used as inorganic fillers with silane coupling agent (KH550) to prepare wheat straw/polyvinyl chloride wood-plastic composites (WPCs) by extrusion molding. A 35-day immersion and a pre-immersion test were carried out to analyze the influence of steel slag and slag micropowder on the physical and mechanical properties of the WPCs under wet conditions. Results showed the following: (1) KH-550 exhibited a good surface modification effect on the activated steel slag and slag micropowder, (2) an increase in the activated steel slag and slag micropowder content could effectively reduce the percent water absorption of the WPCs by 20% to 25% and the expansion by 20% to 24%, respectively, compared with the control group, but had a limited effect on the tensile strength retention, and (3) pre-immersion could effectively induce the synergistic reinforcement effect of the active fillers, resulting in reaching the saturated water absorption within 20 days. The water absorption and tensile strength were respectively 18% to 25% lower and 1.5% to 3% higher than those of the composites without pre-immersion. The results of this study could provide experimental data and theoretical references for the influence of hydration-active inorganic fillers on WPC properties.

Keywords: Wood-plastic composite; Steel slag micropowder; Slag micropowder; Water absorption; Tensile strength

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INTRODUCTION

With the increase in the application of wood-plastic composites (WPCs) and the shortage of forest resources, the choice of composite filler material has gradually shifted to crop straws and various industrial waste residues (Yu 2013; Qi *et al*. 2019a). In the Xinjiang region of China, wheat is the main crop, with high straw yield and a low proportion of utilization. There are 19 steel and iron companies in Xinjiang, with a total crude steel production capacity of 24.1 million T. During industrial production, waste in the form of steel slag and slag are generated, each year totaling 13 million tons of solid waste (*e.g.*, steel slag, granulated convection furnace slag, desulfurization ash, fly ash, *etc.*) (Jin *et al*. 2019). Most of these wastes are discarded, occupying fertile soil and polluting the environment. Many existing waste utilization methods have low technical added values and low economic benefits. The search for high-value-added products using steel slag and slag is increasingly attracting attention. Therefore, developing methods to enable the secondary utilization of resources and the recycling of straw, steel slag, and slag is a key concern. The development of high-value-added utilization technologies that turn trash into treasure has practical importance in environmental protection and resource conservation (Wang *et al*. 2020).

When inorganic micropowders are used as WPC fillers, the increase in inorganic micropowders has varying effects on the composite's physical properties depending on the type of composite substrate (Buddi *et al*. 2018; Qi *et al*. 2019b). According to related studies, inorganic micropowders with relatively small particles usually have good filling effects, but such small particles may have poor dispersion, causing stress concentration. Moreover, the infiltration problem between the inorganic micropowder and the composite material substrate is likely to cause the composite material to undergo shear failure. Therefore, to use inorganic micropowder in composite materials, it is necessary to improve the micropowder's dispersion in the material and improve the interfacial bonding capability between the inorganic micropowder and the composite material (Lee *et al*. 2017). Appropriate modification of inorganic micropowders can increase the micropowder content in composite materials as well as enhance the processing and mechanical properties of the composite materials (Ismaeilimoghadam *et al*. 2016; Song *et al*. 2017).

Existing research mainly examines the use of inorganic materials as fillers and their corresponding mechanical properties, ultraviolet aging, and hygrothermal characteristics. There have been relatively few studies concerning the hydration activity of inorganic fillers and the effect that their hydration and hardening properties has on the macroscopic and microscopic properties of the WPCs. Steel slag and slag are used primarily as building materials, such as concrete. However, because of the complex composition of the material, it has a certain degree of expansion and poor volume stability in a water-rich state or high-humidity air (Jin *et al*. 2019). The f-CaO and f-MgO components react with water to form hydration products $Ca(OH)_2$ and $Mg(OH)_2$ (Yi *et al*. 2012), causing local swelling in the material and limiting the large-scale application of steel slag and slag as building materials. Many researchers have also studied the use of steel slag in the field of polymers, replacing part of the carbon black to combine with rubber. However, because steel slag and polymers have poor compatibility and poor dispersion, the products have reduced mechanical properties (Shen and Wang 2018). Yang *et al.* (2009) found that after modification by a coupling agent, composites made of steel slag and polyvinyl chloride (PVC) exhibited improved mechanical properties. Wu (2018) proposed that industrial solid wastes in the form of fly ash (FA), steel slag, and construction waste were added as plastic fillers to HDPE to prepare repair materials for pavement, and found that the gradation and type of steel slag had an impact on the compressive strength and abrasion resistance of the material. Ma (2004) applied physical and chemical methods to modify the surface of the steel slag micropowder to enhance its compatibility with rubber and improve its dispersibility, concluding that the dual modification method could effectively improve the interface bonding between the steel slag micropowder and the rubber. Sun *et al.* (2019) used slag as fillers to analyze the flame-retardant effect of PVC composite materials, and the results showed that it had a good flame-retardant and smoke-suppressing effect. The above-mentioned studies have carried out relevant studies on the application of steel slag and slag in organic and inorganic materials, but they have not conducted targeted research on its hydration activity in organic materials.

The current study used PVC and wheat straw as the substrates, hydrated active steel slag and slag micropowder as the inorganic fillers, and KH-550 as the modifier to analyzed the effects of steel slag and slag micropowder on the water absorption and mechanical properties of WPC materials under immersion conditions. Additionally, according to the hydration activity of steel slag and slag micropowder, the experiment studied the water absorption and mechanical properties of the composite materials after pre-immersion. The goal was to explore the influence of hydrated active inorganic fillers on the macroscopic and microscopic properties of WPCs through the above experiments, analyze the synergistic enhancement of the steel slag and slag micropowder on the properties of WPCs, and further develop new uses of steel slag and slag micropowder in the WPCs field.

EXPERIMENTAL

Main Raw Materials

The main raw materials used in this study were: PVC resin (SG-5, Xinjiang Tianye (Group), Shihezi, China); wheat straw fiber (WSF), particle size less than 180 μm (homemade, Xinjiang Wujiaqu Farm, Wujiaqu, China); silane coupling agent (KH-550, Nanjing Herun Coupling Agent, Nanjing, China); steel slag micropowder, a by-product of the steelmaking process, hot braised steel slag was selected in this experiment and ground with a ball mill for 20 min to reach a specified fineness (specific surface area was 425 to 500 m^2/kg) (Xinjiang Bayi Steel and Iron Co., Ltd. of Baosteel, Urumqi, China); slag micropowder, a by-product of the convection furnace ironmaking process, the steel-making pig iron quenching slag was selected in this experiment and ground with a ball mill for 30 min to reach a specified fineness (specific surface area was 400 ± 5 m^2/kg) (Xinjiang Bayi Steel and Iron Co., Ltd. of Baosteel, Urumqi, China). The main property indicators of steel slag and slag micropowder are shown in Table 1.

Table 1. Main Performance Indexes of Steel Slag and Slag Micropowder

Inorganic Powder	Activity Index	Specific Surface Area $(m^2 \times g^1)$	D_{10} (μm)	D_{50} (μm)	D_{90} (μm)	Water Absorption (%)	Chemical Components (%)					
							SiO_2	Al_2O_3	CaO	TFe	MgO	f-CaO
Steel Slag Micro-powder	0.75	429 ± 5	2.35	14.32	46.33	1.90	13.11	3.05	42.65	17.5	8.85	1.24
Slag Micro-powder	0.95	440 ± 5	2.52	16.47	66.84	2.30	36.37	10.29	41.5	0.25	7.43	/

Main Instruments and Equipment

The main instruments and equipment used in this study were: an electric heating constant-temperature convection oven (DHC-9053A, Nanjing Dongmai Technology Instrument, Nanjing, China) for drying; a laser particle size analyzer (LS-POP(6), Zhuhai Omec Technology, Zhuhai, China); a conical twin-screw extruder (RM200C, Harp Electric Technology, Harbin, China); a SANS microcomputer-controlled electronic universal testing machine (CMT6104, MTS Systems, Shanghai, China); a Fourier transform infrared (FTIR) spectrometer (NicoletiS10, DM Precision Instruments, Shanghai, China); an electric heating constant-temperature water bath (tank) (HH-600, Shangyu Daoxu Maoxiang Instrument and Equipment, Shaoxing, China); a low-temperature linear thermal dilatometer (PCY-D, Xiangtan Xiangyi Instrument, Xiangtan, China); and a field-emission environmental scanning electron microscope (Quanta FEG250, FEI Company, Hillsboro, Oregon, USA).

Sample Preparation

Material pretreatment

The selected wheat straw fibers were placed inside the electric heating-constant temperature convection-drying oven, and the temperature was adjusted to 90 °C. The samples were dried for 6 h to ensure the moisture content of the wheat straw fibers was less than 3%. Subsequently, the fibers were placed in a desiccator for later use. The inorganic filler micropowder was put into the electric heating constant-temperature convection-drying oven, the temperature was adjusted to 90 °C, and the sample was dried for 3 h and placed in a desiccator for later use. A solution of the KH550 silane coupling agent was prepared with absolute ethanol at a volume ratio of 1:5, and dried steel slag and slag micropowder were added to the solution and ultrasonically treated for 25 min. After the ultrasonic treatment, the slurry was allowed to stand for 5 to 8 min, and the steel slag and slag micropowder were filtered out using sucking filtration. The obtained micropowder was placed in the electric heating constant-temperature convection-drying oven at 90 °C and dried for 48 h. The dried micropowder was ground and passed through an 80-mesh sieve to obtain the steel slag and slag micropowder modified by a silane coupling agent.

Preparation of composite materials

According to the material mixing ratio in Table 2, the following materials were weighed and mixed: the steel slag and slag micropowder modified by the silane coupling agent, the dried wheat straw fiber, the PVC, and other additives. The prepared mixture was placed into a three-dimensional mechanical linkage mixer and mixed for 10 min. Next, the composite sample was extruded through a conical twin-screw extruder, and the temperature range of the extruder was adjusted to 175 °C to 185 °C. The temperature range of the four zones of the extruder was adjusted between 145 °C and 155 °C. The head pressure was 5 MPa, and the motor speed was adjusted to 15r/min. The sample size was 100 × 10 × 7 mm^3.

Table 2. Proportion of WPCs with Steel Slag and Slag Micropowder (wt%)

Specimen	PVC Wood-plastic Composites			
	Modified Steel Slag Micropowder	Modified Slag Micropowder	Wheat Straw Fiber	PVC
M#0	0	0	50	100
G#5	5	0	45	100
G#10	10	0	40	100
G#15	15	0	35	100
G#20	20	0	30	100
K#5	0	5	45	100
K#10	0	10	40	100
K#15	0	15	35	100
K#20	0	20	30	100

1. M material is PVC wood-plastic composite material without modified micropowder;
2. G material is PVC wood-plastic composite material with modified steel slag micropowder;
3. K material is PVC wood-plastic composite material with modified slag micropowder

Property Measurement and Structural Characterization

The tensile strength of composite materials was tested in accordance with GB/T 1040.4 (2006).The tests were conducted at room temperature (25 °C), and the result was an average of three measurements.

The water absorption property was determined as follows. After being dried to a constant weight, the composite material was transferred into a water tank and immersed completely. The water was at room temperature (23 °C ± 1 °C). Subsequently, the sample was removed according to the set time and was dried quickly using filter paper, followed by measurement. The mass and length of the specimen were measured using a balance (accuracy 0.001 g) and a vernier caliper (0.02 mm), respectively, and the data were inputted into the following equation to calculate the water absorption and water-absorbing expansion percent,

$$W = [(M_i - M_0) / M_0] \times 100\% \tag{1}$$

where W is the water absorption (wt%), M_0 is the mass (g) of the specimen before immersion in water, and M_i is the mass (g) of the immersed specimen in different time periods. The percentage of expansion during the adsorption of water was given by,

$$K = [(L_i - L_0) / L_0] \times 100\% \tag{2}$$

where L_0 is the length (mm) of the specimen before immersion in water, and L_i is the length of immersed specimen after different periods of immersion.

The linear thermal expansion coefficient of the composite materials was determined according to GB/T 2572 (2005). The temperature range was −30 °C to 60 °C, and the heating rate was 1 °C/min. Three samples were tested in each group, and the average value was used.

To conduct FTIR analysis, the sample was pressed into tablets, the spectral resolution was 4 cm^{-1}, the scanning wavenumber ranged from 4000 cm^{-1} to 400 cm^{-1}, and the number of scans was 16.

To determine the cross-section morphology, a field-emission environmental scanning electron microscope (Quanta FEG250; FEI Company, Oregon, USA) was used to analyze the micromorphology of composite materials.

RESULTS AND ANALYSIS

Analysis of Modification Effect on Steel Slag and Slag Micropowder

FTIR analysis

Figure 1a shows that the absorption peak intensity of the steel slag micropowder changed after modification. Before the modification of the steel slag micropowder, the stretching vibration peak of the intermolecular hydrogen bonds O–H appeared at approximately 3436 cm^{-1}. After the modification, the width of the O–H stretching vibration peak near 3440 cm^{-1} became narrower and the vibration peak intensity decreased, indicating that the hydroxyl group on the surface of the steel slag micropowder (–OH) had undergone a chemical reaction with KH-550. The O–H absorption peak narrowed, also indicating that the modified steel slag micropowder was less hydrophilic than the unmodified steel slag micropowder, that the water resistance had improved, and that the polarity of the micropowder had been reduced. The modified steel slag micropowder exhibited three symmetrical C–H stretching vibration absorption peaks: at 2930 cm^{-1}, 2965 cm^{-1}, and 2853 cm^{-1}, indicating that a new chemical bond had formed between the surface of the steel slag micropowder and KH-550. The Si–O–Si stretching vibration absorption peak of the modified steel slag micropowder at the wavenumber of 995 cm^{-1} was wider, indicating that the vibration absorption region of the R–Si–O–Si formed between KH-550 and the surface of the steel slag micropowder, and that of the Si–O–Si in the steel slag micropowder overlapped. According to Fig. 2(c), the silane coupling agent appeared to have been chemically coated on the surface of the steel slag micropowder. This was consistent with the results of the steel slag modification test described by Ma (2004).

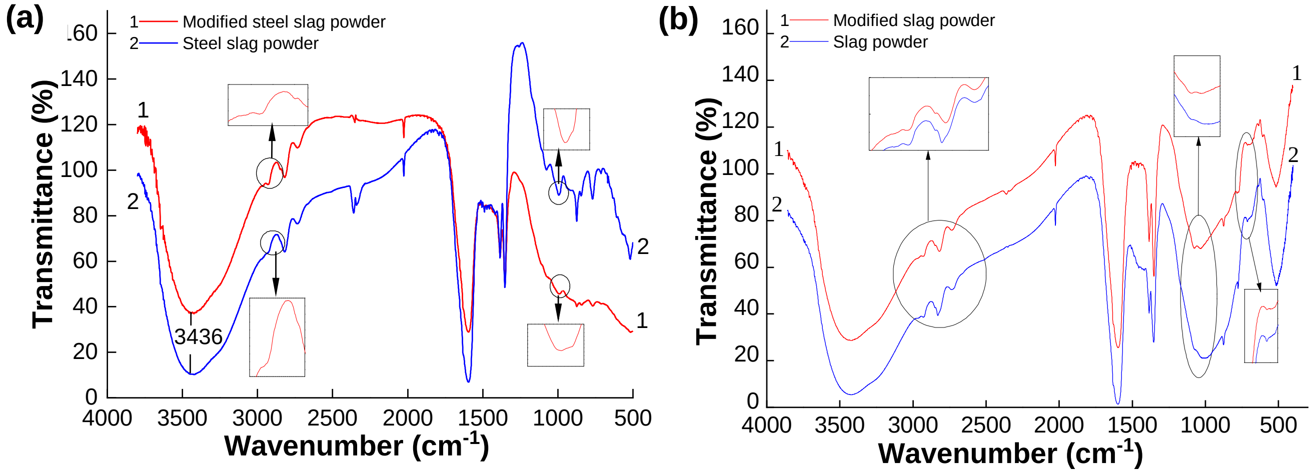
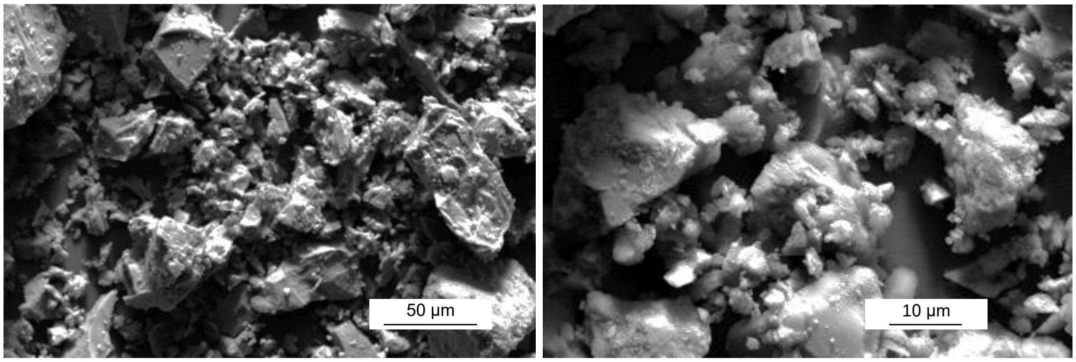


Fig. 1. FTIR spectrum of steel slag and slag powder: (a) FTIR comparison graph before and after steel slag powder modification; (b) FTIR comparison graph before and after slag powder modification

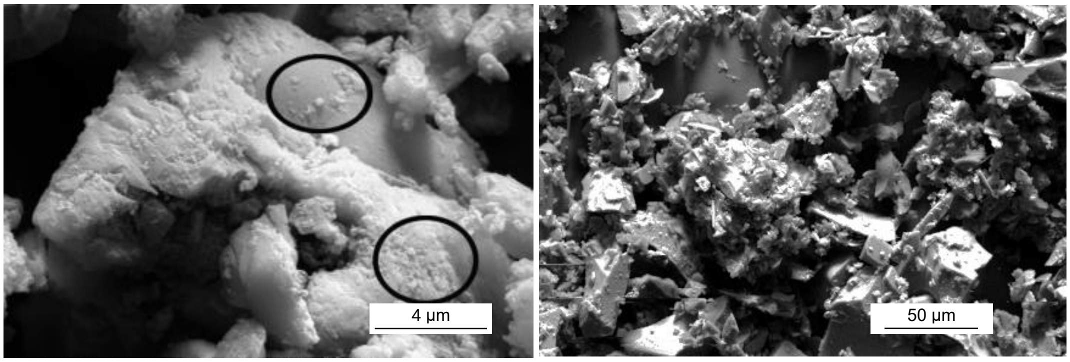
Figure 1b shows that the FTIR spectrum of modified slag micropowder was different from that of the modified steel slag micropowder (Fig. 1a). The absorption peak intensity between 950 and 1100 cm^{-1} increased, indicating that the stretching vibration of Si–O–Si overlapped with that of the surface groups of the slag micropowder. After modification, the width and intensity of the O–H stretching vibration peak near 3436 cm^{-1} did not change considerably, indicating that the water resistance of the slag micropowder modified by KH-550 was less improved; the peak change was only found at approximately 2810 cm^{-1}.

Scanning electron microscopy analysis

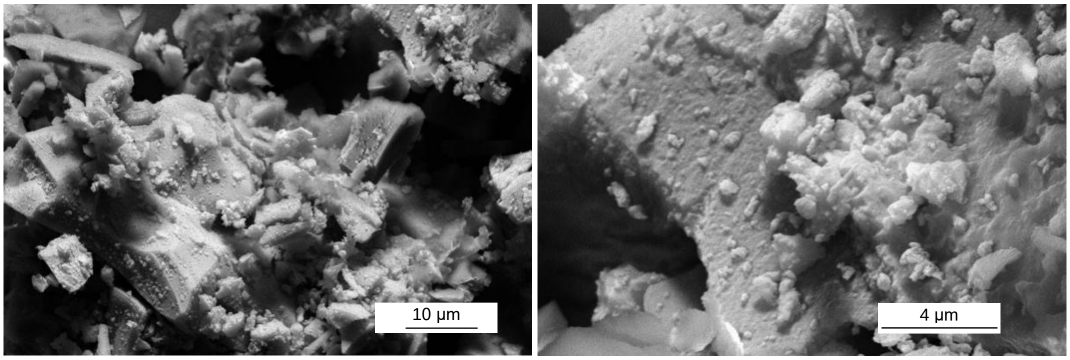
Figures 2a, 2b, 2d, and 2e show that, after KH-550 modification, the steel slag and slag micropowder showed good dispersion at 800x and 3000x magnifications. The analysis indicated that during the modification of the steel slag and slag micropowder by KH-550, alkoxy groups were hydrolyzed to form silanol, which then reacted with the hydroxyl groups on the micropowder surface to form hydrogen bonds and condense into SiO–M (M represents the surface of steel slag micropowder particles). This result reduced the surface polarity of the micropowder and improved the dispersion and compatibility. As shown in Figs. 2c and 2f, the surface of the steel slag and slag micropowder was covered with a layer of flocs. This layer was comprised of interwoven silanol groups of KH-550 silane molecules, forming a network film. This film layer improved the surface roughness of the steel slag and slag micropowder, enhancing the compatibility between the micropowder and the PVC substrate. The above results suggest that KH-550 had a good modification effect on steel slag and slag micropowder, and it featured good dispersibility and compatibility. The modification effect of KH-550 on steel slag micropowder was better than that on slag micropowder.



(a) Steel slag powder (800x) **(b)** Steel slag powder (3000x)



(c) Steel slag powder (12000x) **(d)** Slag powder (800x)



(e) Slag powder (3000x) **(f)** Slag powder (12000x)

Fig. 2. Micromorphology of modified steel slag and slag powder

Influence of Steel Slag and Slag Micropowder on the Water Absorption of WPCs

As shown in Fig. 3, as the content of active steel slag and slag micropowder increased, the water absorption of WPCs decreased. This relationship resulted because without the addition of micropowder, the wheat straw fibers in the composite material were entangled and thus were able to easily form a connection chain for water permeation (Srivabut *et al*. 2018). The active steel slag and slag micropowder, having relatively small size and large specific surface area of the particles, were distributed among the entangled wheat straw fibers after their addition (Ashori and Sheshmani 2010). Because of their distribution, the active steel slag and slag micropowder blocked the direct overlap between some wheat straw fibers, and the fibers were not able to form a complete long chain of wood water absorption. The steel slag and slag micropowder had low water absorption and hydraulic conductivity, hindering the formation of the network for transporting H_2O molecules and thereby reducing the water diffusion coefficient. Compared with activated steel slag and slag micropowder, wheat straw has a small bulk density, is a fluffy material, and cannot be easily coated and bonded by the PVC substrate. The steel slag and slag micropowder had small particles and a large specific surface area, and filled the gaps between the wheat straw fiber and the PVC substrate, reducing the available storage space for the H_2O molecules.

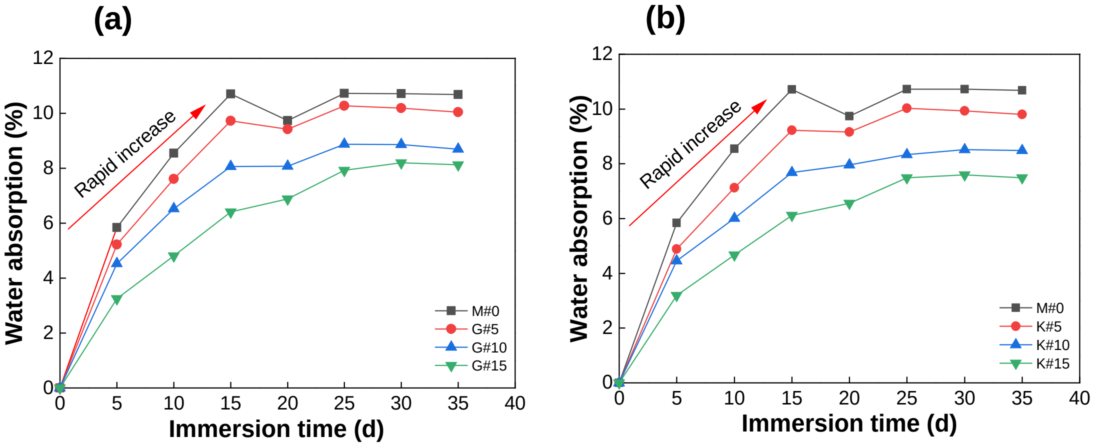


Fig. 3. Water absorption of PVC wood-plastic composites with different steel slag and slag powder content: (a) percent water absorption of G material and (b) percent water absorption of K material

Moreover, because the percent water absorption of activated steel slag and slag micropowder was lower than that of wheat straw, the overall water absorption of the material tended to decrease when the activated steel slag and slag micropowder content increased. Figure 3 also shows that with the same content of micropowder, the water absorption of the G material exceeded that of the K material. This may have resulted because the chemical components of steel slag contained f-CaO and f-MgO. When the composite material absorbed water, it reacted with water to form calcium hydroxide ($Ca(OH)_2$) and magnesium hydroxide ($Mg(OH)_2$) (Wang *et al.* 2020). Expansion stress was generated inside the material, reducing the interface bonding capacity between the filler and the PVC substrate and producing microcracks (Wu 2018).

In summary, the water absorption of the composite material during the 35-day immersion period showed a rapid increase and then a slow rise until saturation. An increase in the activated steel slag and slag micropowder content effectively reduced the water absorption of the composite material. In addition, with the same content of micropowder, the percent water absorption of the G material exceeded that of the K material. The comparison of the water absorption values of the composite material after immersion showed that K#15 and G#15 had lowest water absorption.

Influence of Steel Slag and Slag Micropowder on the Water-Absorbing Expansion of WPCs

As shown in Fig. 4, when the content of activated steel slag and slag micropowder increased, the water-absorbing expansion of the composite material showed a decreasing pattern. Under the same content of active steel slag and slag micropowder, the water-absorbing expansion of G material was greater than that of K material (Wu 2018).

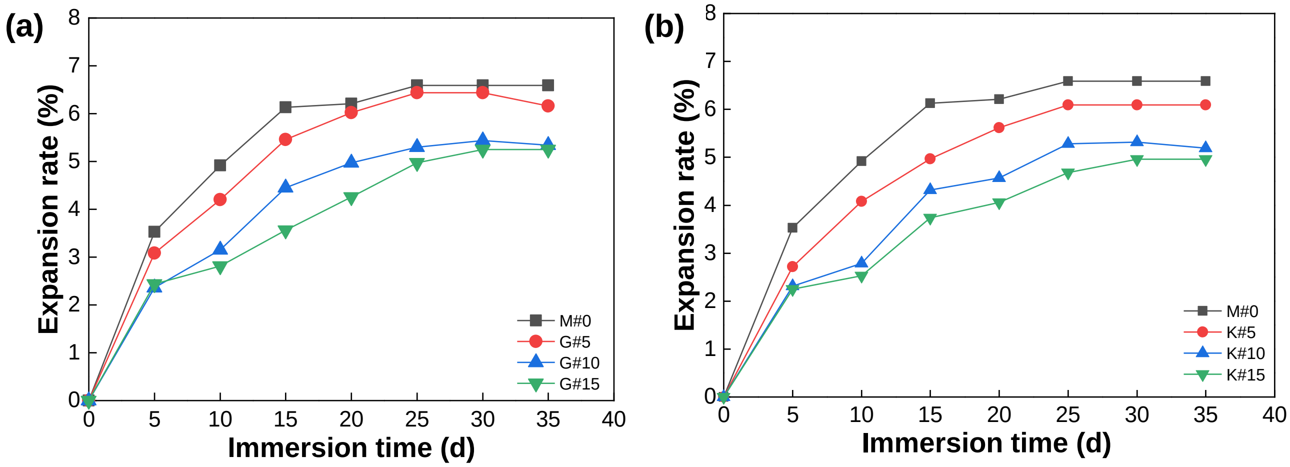


Fig. 4. Water-absorbing expansion of PVC wood-plastic composite: (a) water-absorbing expansion of G material; and (b) water-absorbing expansion of K material

In summary, during the 35-day immersion period of the composite material, an appropriate increase in the content of activated steel slag and slag micropowder effectively reduced the water-absorbing expansion of the composite material. In addition, under the same micropowder content, the water-absorbing expansion of the G material was higher than that of the K material. Comparing the water-absorbing expansion of the composite material after immersion showed that the expansion values of K#15 and G#15 were relatively low.

Influence of Steel Slag and Slag Micropowder on WPC Mechanical Properties

As shown in Figs. 3 and 4 combined with Table 3 and Fig. 5, the composite material absorbed a relatively large amount of water at a fast rising rate during the first 20 days of immersion. The high water absorption caused the filling material in the composite to rapidly absorb water and expand, causing microcracks to appear on the material surface. The appearance of microcracks further increased the water absorption and resulted in a quick decrease in the composite material strength (Srivabut *et al.* 2018). After 20 days of water absorption, the composite material's water absorption approached equilibrium, manifested by the slow development of cracks (or the absence of such development) and a slow decrease in the composite material strength. Regarding material microstructure, as the active steel slag and slag micropowder content increased, the coating effect of PVC on the filler improved, enhancing the composite material mechanical properties. With the same steel slag and slag micropowder content, the strength retention of the G material was lower than that of the K material; the water absorbed by the composite material reacted with f-CaO and f-MgO in the steel slag micropowder to form $Ca(OH)_2$ and $Mg(OH)_2$, which caused uneven expansion stress inside the material (Wang *et al.* 2020; Wu 2018). This uneven stress reduced the interface bonding energy of the filler and the PVC, produced microcracks, further deteriorated composite material properties, and reduced the composite material tensile strength.

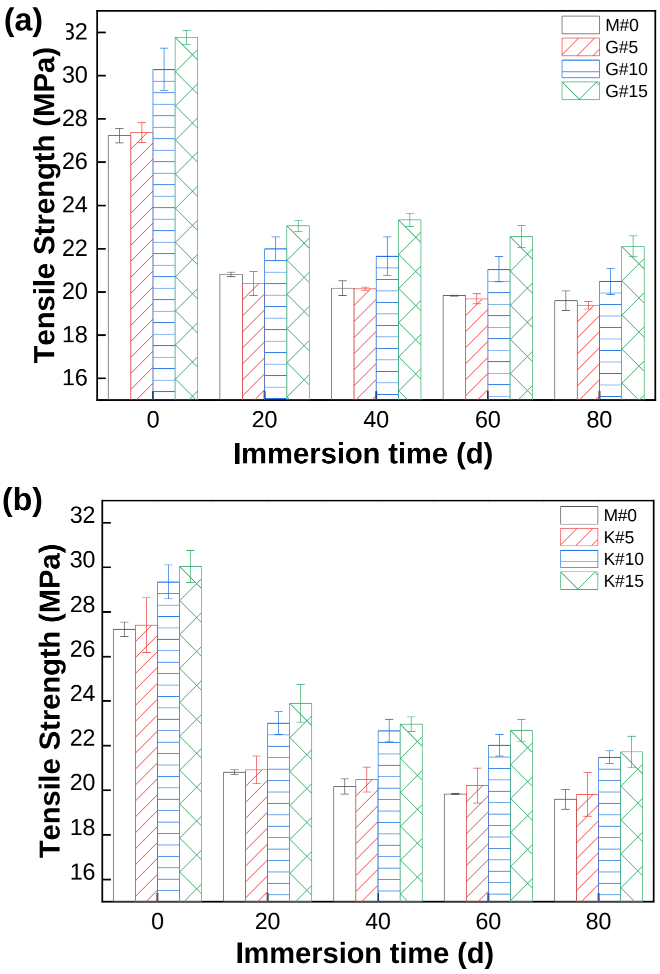


Fig. 5. Tensile strength of PVC wood-plastic composite with different immersion time: (a) tensile strength of G material before and after immersion; (b) tensile strength of K material before and after immersion

As shown in Fig. 6(a) and (b), most of the wheat straw fibers on the fractured surface were broken. The fractured surface was relatively flat without obvious holes and defects. The inorganic micropowder particles were better wrapped, and there were almost no micropowder particles at the cross section. In summary, after 80 days of immersion, the composite material tensile strength substantially dropped; G#15 and K#15 showed good properties under the immersion condition.

Table 3. Tensile Strength Retention of PVC Wood-plastic Composites with Different Immersion Times

Immersion Time (Days)	Tensile Strength Retention (%)						
	M#0	G#5	G#10	G#15	K#5	K#10	K#15
20	76.42	74.53	72.57	72.58	76.32	78.43	79.53
40	74.11	73.58	71.45	73.43	74.72	77.27	76.44
60	72.82	71.90	69.47	71.01	73.73	75.03	75.47
80	71.94	70.81	67.59	69.56	72.27	73.19	72.28

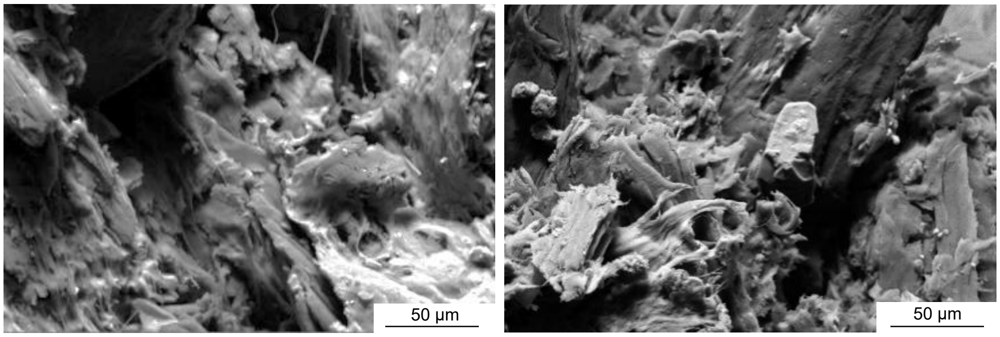


Fig. 6. Micro-morphology of tensile section of the composite materials: (a) G#15 (800x); (b) K#15 (800x)

Synergistic Enhancement of Steel Slag and Slag Micropowder Under Pre-immersion Conditions

The aforementioned immersion experiments performed linear measurement analysis mainly to determine the water resistance of the WPCs. The experimental results showed that the activated steel slag and slag micropowder improved the water resistance and mechanical properties of the composite. As the hydration activities of steel slag and slag varied, and likewise the condensation products, the following test schemes were set to determine the influence introduced by steel slag and slag. To fully reflect the hydration activity of the steel slag and slag micropowder and explore its beneficial effects, the test scheme was set as follows: when the water-absorption test method was used, the initial mass was first measured; after soaking for 3 days, the sample was removed and allowed to stand for 4 days. Subsequently, the test scheme for the original water absorption was used to measure the water absorption and tensile strength of the sample. The water absorption, tensile strength retention, and calculation results are shown in Fig. 7 and Table 4.

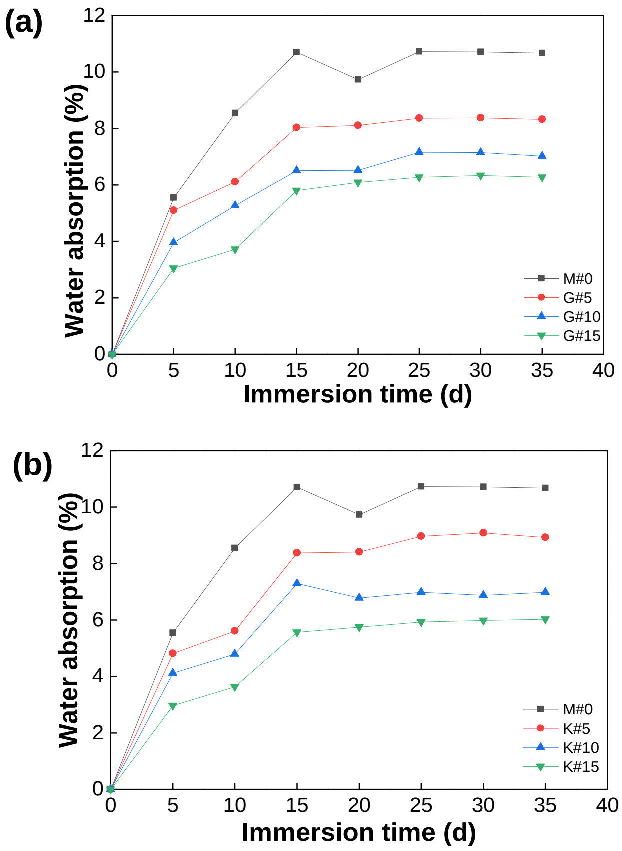


Fig. 7. Percent water absorption of PVC wood-plastic composite material after pre-immersion treatment: (a) percent water absorption of G material before and after immersion; (b) percent water absorption of K material before and after immersion

Table 4. Tensile Strength Retention of PVC Wood-plastic Composite Material after Pre-immersion Treatment

Immersion Time (d)	Tensile Strength Retention (%)						
	M#0	G#5	G#10	G#15	K#5	K#10	K#15
20	76.42	75.26	73.69	73.53	77.50	80.02	80.58
40	74.11	74.34	73.48	74.40	75.90	78.86	77.46
60	72.82	72.62	71.44	71.94	74.87	76.60	76.48
80	71.94	71.53	69.54	70.48	73.36	74.69	73.23

(a) G#15 apparent crack (20 d) **(b)** G#15 apparent crack (80 d) **(c)** K#15 apparent crack (80 d)

Fig. 8. Apparent cracks of pre-immersion composites with different immersion times

The comparison of Fig. 7 and Fig. 3 showed that the water absorption value of the composite material changed considerably after pre-immersion, and the percent water absorption after pre-immersion was between 18% and 25% less than that of the composite material without pretreatment. For both types of materials, the percentages of water absorption in the first 5 days were relatively high, but the water absorption and rate of rising of the pre-immersed specimens over a period of 5 to 15 days were considerably lower than those of the composite materials without pretreatment. The water absorption values of composite materials pre-immersed for 10 days were below 6%; moreover, the total water absorption values after 40 days were generally within 8%, while the water absorption values of composite materials without pretreatment were generally above 8%.

The comparison of Tables 4 and 3 shows that the tensile strength of the composite material after pre-immersion was higher than that of the composite material without pretreatment, with an average of 1.5% to 3% higher for each group. The tensile strength retention of slag micropowder WPCs was higher than that of steel slag micropowder WPCs.

Figure 8 shows the apparent cracks of pre-immersed composite materials at different immersion times. Microcracks appeared in the steel slag micropowder WPCs within 20 days of immersion (Figs. 8a and 8c) because the filler in this composite material absorbed water and expanded, destroying the interface bonding and causing micro-crack formation on the specimen surface. This phenomenon indicated that the water permeation would ultimately destroy the interfacial adhesion between the wood fiber and the plastic substrate, reducing the WPC properties (Zhao *et al*. 2020). The cracks under 80 days of immersion were compared with those under 20 days of immersion, and the results showed that at 80 days the cracks had exhibited slow growth since the 20-day mark. The water absorption of the composite material was close to saturation on day 20. The slow expansion of the material promoted the slow growth of cracks, which was consistent with the change trends of the water absorption, water-absorbing expansion, and tensile strength in the section “Influence of Steel Slag and Slag Micropowder on the Water Absorption of WPCs.” Cracks were found in the slag micropowder WPCs on day 80.

The main mineral phases of steel slag include C_3S, C_2S, RO, and C_2F, and f-CaO, f-MgO; other harmful chemical components are also important components that cause poor stability of steel slag. (Wang *et al.* 2020). The main mineral phase of slag is composed of C_2S, which has better activity than steel slag and a stable hydration process. The pre-immersion process of PVC-WPC material ensured that the steel slag and slag micropowder had sufficient hydration reaction time in water. At the beginning of the hydration reaction, the composite material’s hydration environment was mainly water; the lack of alkaline materials causes the hydration reaction to occur slowly. The resulting product (calcium-silicate-hydrate gel) wrapped the unreacted particles, weakening the bonding between gels. The resulting products mostly played a role of stacking. In the middle of the hydration reaction, C_3S and C_2S were excited to accelerate the reaction by some of the $Ca(OH)_2$ alkaline materials generated by the hydration. The extent of the reaction gradually increased, generating some products on the surface of the particles. On the one hand, $Ca(OH)_2$ combined with the surrounding gel to form a dense hardened body; on the other hand, the volume expansion squeezed out the tiny space occupied by straw fibers, which indirectly and directly impeded water transport. Regarding material microstructure, as the content of the active steel slag and slag micropowder increased, the microstructure of the PVC substrate became tighter, and the steel slag and slag hydration product improved the coating and filling effect of PVC on the straw. Thus, the composite material mechanical properties increased, and the water absorption decreased. This finding is consistent with the experimental results described by Srivabut *et al.* (2019) who found that the inorganic filler improved the coating and filling effect of PVC on straw.

When the steel slag and slag micropowder content was the same, the water absorption of steel slag micropowder WPCs was higher than that of slag micropowder WPCs. This difference was because the f-CaO and f-MgO hydration reaction products in the steel slag were large in volume and the reaction lagged, unable to synchronize with the C_3S and C_2S hydration and causing some stress concentration points inside the material. This hydration characteristic reduced the interfacial bonding capability between the steel slag and PVC, producing microcracks, thereby deteriorating the composite material properties, and reducing the composite material tensile strength. These findings were consistent with the presence of cracks on the composite material surface on day 20 (Fig. 8a).

CONCLUSIONS

1. The Fourier transform infrared (FTIR) and scanning electron microscopy (SEM) analysis results showed that: KH-550 still had a good surface modification effect on activated steel slag and slag micropowder. This improved its dispersion in composite materials and improved the compatibility between steel slag as well as slag micropowder and PVC substrate. The interfacial bonding force between steel slag as well as slag micropowder and PVC substrate were also improved. The modification effect of KH-550 on steel slag micropowder was better than that on slag micropowder.
2. The immersion test results of the activated steel slag and slag micropowder WPCs showed that the activated steel slag and slag micropowder not only had the filling effect, but also had a beneficial effect on the interface of the composite materials because of its appropriate amount of hydration active products. The macroscopic performance was that the water absorption and expansion of the composite materials showed a law of rapid increase first and then slow increase. Appropriate increase in the content of activated steel slag and slag micropowder could effectively reduce the water absorption and expansion of the composite materials, but had a relatively small impact on the tensile strength retention.
3. The results of the pre-immersion experiments showed that pre-immersion effectively induced the synergistic enhancement effect of the active fillers. The percent water absorption of the pre-immersed composite material changed substantially; the water absorption after pre-immersion was 18% to 25% lower than that of the composite material without pretreatment, and the initial water absorption and rising rates were considerably lower than those of the composite material without pretreatment. The water absorption of pre-immersion composite materials was below 6% in 10 days, and the saturated water absorption was basically reached in 20 days, while the composite materials without pretreatment were generally above 8%. Pre-immersion had a limited effect on the tensile strength of the composite materials, and the tensile strength retention of slag micropowder composite materials was higher than that of steel slag micropowder composite materials. Different hydration active products, morphology and their distribution inside the composite materials are the issues that research group will carry out later.

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REFERENCES CITED

Ashori, A., and Sheshmani, S. (2010). “Hybrid composites made from recycled materials: Moisture absorption and thickness swelling behavior,” *Bioresource Technology* 101(12), 4717-20. DOI: 10.1016/j.biortech.2010.01.060

Buddi, T., Rao, B. N., Singh, S. K., Purohit, R., and Rana, R. S. (2018). “Development and analysis of high density poly ethylene (HDPE) nano SiO_2 and wood powder reinforced polymer matrix hybrid nano composites,” *Journal of Experimental Nanoscience* 13(Supp. 1), S24-S30. DOI: 10.1080/17458080.2018.1426895

GB/T2572-2005 (2005) “Test method for average linear expansion coefficient of fiber reinforced plastics,” General Administration of Quality Supervision, Inspection and Quarantine of the People’s Republic of China, Beijing, China.

GB/T1040.4-2006 (2006). “Plastics—Determination of Tensile Properties,” General Administration of Quality Supervision, Inspection and Quarantine of the People’s Republic of China, Beijing, China.

Ismaeilimoghadam, S., Masoudifar, M., Nosrati, B., and Shamsian, M. (2016). “Effects of inorganic nanoparticles on mechanical and morphological properties of wood flour-polypropylene nano composites,” *Drewno* 59(196), 127-137. DOI: 10.12841/wood.1644-3985.127.09

Jin, Q., Zhu, L., and Hu, D. (2019). “The mechanical and erosion resistance properties of an alkali-activated steel slag cementitious system,” *Ekoloji* 28(107), 2203-2211.

Lee, D., Kim, S., Kim, B. J., Chun, S. J., Lee, S. Y., and Wu, Q. (2017). “Effect of nano-$CaCO_3$ and talc on property and weathering performance of PP composites,” *International Journal of Polymer Science* 2017(Special Issue), Article ID 4512378. DOI: 10.1155/2017/4512378

Ma, X. H. (2004). “Study of utilizing steel slag to develop high performance inorganic filler,” Master’s Thesis, Wuhan University of Technology, Wuhan, China.

Qi, R. G., He, C. X., and Jin, Q. (2019a). “Effect of acrylate-styrene-acrylonitrile on the aging properties of eucalyptus/PVC wood-plastic composites,” *BioResources* 14(4), 9159-9168. DOI: 10.15376/biores.14.4.9159-9168

Qi, R. G., He, C. X., Fu, J. J., Zhao, L., and Jiang, C. (2019b). “Effect of inorganic nanoparticles on the thermal and mechanical properties of wood fiber/HDPE composites,” *Journal of Shanghai Jiao Tong University* 53(3), 373-379. DOI: 10.16183/j.cnki.jsjtu.2019.03.016

Shen, H. Y., and Wang, Z. Z. (2018). “Research on surface modification of steel slag and its application in rubber,” *Materials Reports* 32(6), 1000-1003, +1019. DOI: 10.11896/j.issn.1005-023X.2018.06.027

Song, J. Q., Peng, H. S., Wang, G. S., and Wang, Y. (2017). "Study on applications of different inorganic fillers in polyethylene wood-plastic composites," *China Plastics* 31(1), 70-74.

Srivabut, C., Ratanawilai, T., and Hiziroglu, S. (2018). "Effect of nanoclay, talcum, and calcium carbonate as filler on properties of composites manufactured from recycled polypropylene and rubberwood fiber," *Construction and Building Materials* 162, 450-458. DOI: 10.1016/j.conbuildmat.2017.12.048

Srivabut, C., Ratanawilai, T., and Hiziroglu, S. (2019). "Response surface optimization and statistical analysis of composites made from calcium carbonate filler-added recycled polypropylene and rubberwood fiber," *Journal of Thermoplastic Composite Materials* (Online), 1-25. DOI: 10.1177/0892705719889988

Sun, Y. J., Yue, L., Zhang. X. Q., and Zhou, X. (2019). "Flame retardant and smoke suppression of iron ore residue used in soft polyvinyl chloride," *China Plastics* 48(02), 27-31.

Wang, X. H., Wang, J., Bai, J. F., Jin, Q., Zhu, L., and Yuan, Z. (2020). "Long-term drying shrinkage performance of steel slag cement mortar under unconstrained multi-condition," *Journal of Yangtze River Scientific Research Institute* 37(2), 153-158. DOI: 10.11988/ckyyb.20181053

Wu, T. T. (2018). *Preparation and Properties of Fly Ash and/or Steel Slag HDPE Composites,* Master's Thesis, Shanxi University, Taiyuan, China.

Yang, Q. L., Yao, Y. F., Gao, L., Yu, L. M., and Zhou, G. (2009). "Application of coupling agent on SlAG/GF /PVC composites," *Journal of Zhejiang Sci-Tech University* 26(1), 12-17.

Yi, H., Xu, G., Cheng, H. G., Wang, J. S., Wan, Y. F., and Chen, H. (2012). "An overview of utilization of steel slag," *Procedia Environmental Sciences* 16(4), 791-801. DOI: 10.1016/j.proenv.2012.10.108

Yu, H. J. (2013). *Study on Preparation and Performance of Wheat Straw/PVC Composite*, Master's Thesis, Nanjing Agricultural University, Nanjing, China.

Zhao, Z. H., Zhang, Q. F., and Wang, J. K. (2020). "Properties comparison of coextruded and un-coextruded wood plastic composites under high temperature accelerated water uptake," *Polymer Composites* 41(7), 2616-2624. DOI: 10.1002/pc.25560

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