Comparison of Properties of Wood-Plastic Composites Based on Alternate Degradation in Seawater and Acid Rain

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To investigate the change of the service performance of wood-plastic composites degraded by sea water and acid rain, three types of wood-plastic composite materials were prepared with sorghum straw reinforced with high-density polyethylene (SS/HDPE), polypropylene (SS/PP), and polyvinyl chloride (SS/PVC). Under the extreme alternate degradation conditions simulated by seawater (salinity 3.5%, temperature 55 °C) and acid rain (pH 2.5, temperature 55 °C), the effects on the mechanical and wear properties and the chemical structures of the composites were determined. The exposure to the alternate sea water and acid rain deteriorated the fiber/matrix bonding quality of the composites; the mechanical and wear properties decreased accordingly. Before and after degradation, the three composites were sorted in descending order of the mechanical and wear properties as follows: SS/PVC composites > SS/PP composites > SS/HDPE composites. Sorghum straw /PVC had the best resistance to degradation and sorghum straw /HDPE composite had the least resistance. The matrix molecular chains of the SS/HDPE under the conditions of exposure were broken after 12 days.

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Keywords: Sea water and acid rain; Alternate corrosion; Wood-plastic composites; Mechanical properties; Wear properties; Chemical structures

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INTRODUCTION

Wood-plastic composite materials are made of plant fiber reinforced with thermoplastics or thermoset plastics; they are widely used in outdoor construction sites including ports, wharves, planks, and bridge decks. High-density polyethylene (HDPE), polypropylene (PP), and polyvinyl chloride (PVC) are the most commonly used thermoplastics for the preparation of wood-plastic composites (Schirp and Su 2016).

The effect of outdoor environmental factors such as light (Chaochanchaikul *et al.* 2013), bacterial erosion (Kositchaiyong *et al.* 2014; Srimalanon *et al.* 2016), freezing (Srubar 2015), and soil exposure (Kositchaiyong *et al.* 2014) on the service performance of wood-plastic composites has been discussed extensively. Water determines the durability of wood-plastic composites, as it can accelerate the photodegradation process and the growth of fungi. However, the service performance of wood-plastic composites under aggressive water environments such as sea water and acid rain is not well studied. Xiao *et al*. (2023) prepared wood plastic composite by poplar veneer and reclaimed high density polyethylene (HDPE). It was found that the hydrogen bonding between the cellulose and the molecular crosslinking network was strengthened, carbonized lignin was

coated on the surface of cellulose, and the composite has high strength (tensile strength 198.9 MPa). It is also waterproof, corrosion resistant, flame retardant, and has good heat insulation properties. Jiang *et al*. (2020) mixed three inorganic pigments, ferric oxide red, ferric oxide yellow, and ferric oxide blue, into wheat straw fiber reinforced polyvinyl chloride (PVC) composite material, carried out an artificial seawater accelerated degradation test, and found that wheatgrass fiber reinforced PVC composite material exhibited better resistance to seawater degradation, including better fiber/matrix interface interaction. The composites also showed low total fading rate, high surface hydrophobicity, stable mechanical properties, and good thermal stability. Duigou *et al*. (2014) studied the resistance of flax/polylactic acid composites to sea water degradation. The results reflected that the sea water exposure deteriorates the tensile strength and Young's modulus of flax/polylactic acid composites, and the loss of mechanical properties is relevant to the splitting of fiber bundles due to fiber bundle glue dissolving. Mazuki *et al.* (2011) studied the resistance of kenaf/polyester composites to distilled water, sea water, and acid rain. The three kinds of water degraded the energy storage and energy dissipation modulus of the kenaf/polyester composite, and the loss of dynamic mechanical properties can be linked to the degradation of cellulose and the hydrolysis of ester groups. A sea water and acid rain alternate exposure environment was built through orthogonal experiments that significantly degraded the service performance of wood-plastic composites, where seawater salinity was 3.5%, seawater temperature was 55 °C, acid rain pH value was 2.5, and acid rain temperature was 55 °C (Jiang 2018a). The service performance of sorghum straw/PVC composites has been studied in this alternate corrosive environment and extrusion molding process. The results indicated that the four methods, namely alkali treatment, stearic acid/palmitic acid treatment, silica powder/ASA modification, and paraffin-based Pickering emulsion impregnation, can strengthen the resistance to aggressive aqueous media and abrasion of sorghum straw/PVC composites (Jiang 2018a,b,c; 2019a,b). In order to compare the service performance of different matrix materials, sorghum straw was used together with HDPE, PP, and PVC to prepare wood-plastic composites to test various properties, providing theoretical reference for the preparation of wood-plastic composites resistant to seawater and acid rain corrosion.

EXPERIMENTAL

Raw Materials

The HDPE and PP used in this work are produced by Dongguan Huachuang Plasticization Co., Ltd. The PVC is produced by Xinjiang Tianye (Group) Co., Ltd. Sorghum straw (SS) was collected from local farmland in Nanjing, and they were ground to a particle size of 149 μm. The silane coupling agent KH-550 is produced by Nanjing Chuangshi Chemical Auxiliary Co., Ltd. The calcium-zinc compound stabilizer is produced by Shanghai Wenhua Chemical Pigment Co., Ltd.

Sample Preparation

Fiber silane treatment

First, KH-550 with 3% of the straw mass was diluted with absolute ethanol (volume ratio 1: 5), and the fiber was sprayed evenly with the diluted solution. The fiber was air-dried for 12 h at room temperature and then oven-dried at 90 °C for 12 h. The finished materials were sealed.

Sample compression molding

Each of the three plastics was three-dimensionally blended with the silanized fiber (mass ratio 1:1, the stabilizer should be added when blending PVC, and the amount of stabilizer should account for 8% of the fiber mass). The XLB-D400×400×2-Z flat vulcanizer (Shanghai Qi Cai Hydraulic Machinery Co., Ltd.) was used to mold the mixture. The molding parameters temperature, pressure, and time, were as follows: 155 °C, 9.7 MPa, and 10 min to prepare sorghum straw/HDPE composites (Jiang 2019b); 180 °C, 12.5 MPa, and 12 min for the preparation of sorghum straw/PP composite materials (Liu *et al.* 2016); and 160 °C, 10 MPa, and 15 min for the preparation of sorghum straw/PVC composite materials (Yuan *et al.* 2017).

Corrosion Environment Design

NaCl (Analytical Reagent, weight percentage ≥ 99.5%) was used to adjust the salinity of deionized water to acquire the sea water with the salinity of 3.5%; deionized water was used to dilute the mixed solution of H_2SO_4 and HNO_3 (molar ratio: SO_4^{2-} / NO_3^- = 5 / 1) to prepare the simulated acid rain solution with the pH value of 2.5.

The exposure process consisted of three cycles, and each cycle included the following steps: sea water for 2 days, followed by acid rain for 2 days, during which the water temperature was maintained at 55 ± 1 °C. At the end of each cycle, samples were dried at the room temperature until the mass change was less than 1% after 24 h, and then their performance was characterized.

Performance Characterization

The measurement of tensile and bending properties referred to GB/T 1040.1 (2006) and GB/T 9341 (2008), respectively. The tests were completed with a CMT6104 electronic universal testing machine (MTS Industrial Systems (China) Co., Ltd.). The test speed was 2 mm·min^{-1}, and the testing result was the average value of five repeated tests.

The wear performance measurement were according to GB/T 3960 (2016). They were completed using an M-2000A ring/block wear testing machine (from Zhangjiakou Xuanhua Kehua Testing Machine Manufacturing Co., Ltd.). The smooth wheels were made of Quenching steel 45, working as counterparts. The wear parameters including load, sliding speed, and duration of each pass, were set to 100 N, 200 r·min^{-1}, and 120 min, respectively.

The average friction coefficient (μ) was measured by the built-in sensors, and the specific wear rate (WS) was calculated using Eq. 1,

$$W_S = \frac{\Delta M}{L \cdot F \cdot \rho} \quad (1)$$

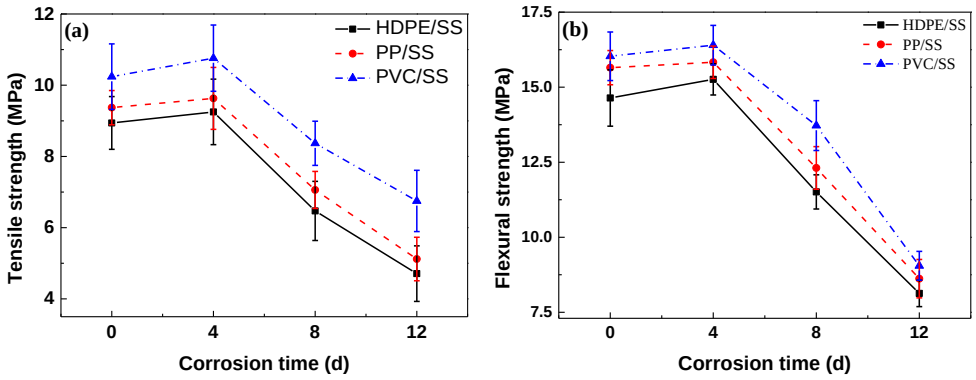
where ΔM represents abrasion loss weight (mg), L represents sliding distance (m), F represents applied load (N), and ρ represents sample density (g·cm^{-3}). The test result is the average value of 3 repeated tests.

The microscopic morphology observation of the tensile section and the wear surface were imaged using an S-4800 field emission scanning electron microscope (Hitachi, Japan). An E-1010 ion sputtering instrument (Hitachi, Japan) was used to spray gold on the observation surface before image acquisition.

RESULTS AND DISCUSSION

Mechanical Properties

The tensile and bending properties of three wood-plastic composite are illustrated in Fig. 1. With the extension of the exposure cycle, the tensile and flexural strength of the three wood-plastic composite materials increased first and then decreased. It is believed that a few fibers sucking water and swelling can partially reduce the crack defects of the two phases (that is the fiber and the matrix phase) so that the two phases are more closely attached, the stress transmission is more continuous, and the tensile and flexural strengths increase slightly in the early stage of corrosion. Excess fiber water swelling can greatly increase the two-phase crack defects so that the distance between the two phases becomes farther, stress transmission becomes more difficult, and the tensile and flexural strength decreases significantly in the late stage of corrosion. The three wood-plastic composite materials in descending order of the tensile and flexural strength were sorghum straw/PVC, sorghum straw/PP, and sorghum straw/HDPE composites. This result is consistent with the conclusion provided by scholars such as Mazzanti *et al.* (2016). After 12 days of exposure, the tensile and flexural strength of the three wood-plastic composite materials decreased. The decreases in sorghum straw/HDPE composite materials were 47.3% and 44.5%, respectively; in sorghum straw/PP composite materials, 45.4% and 44.9%, respectively; and in sorghum straw/PVC composite materials, 34.1% and 43.5%, respectively. The three composites sorted in descending order of the decrease in tensile and bending strength were sorghum straw/PVC, sorghum straw/PP, and sorghum straw/HDPE. The decrease in tensile and bending strength can be attributed to increased two-phase crack defects.

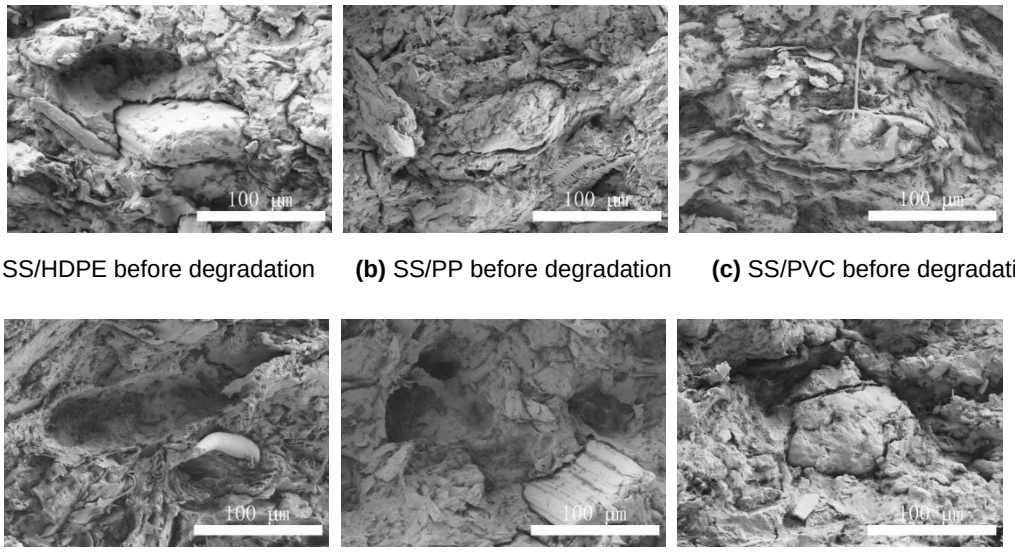


(a) Tensile strength **(b)** Flexural strength

Fig. 1. Tensile and flexural properties of the three types of wood-plastic composites

The SEM micrographs of the tensile sections of the three wood-plastic composites are displayed in Fig. 2. As shown in Fig. 2(a) to (c), the two-phase interfaces of sorghum straw/HDPE and sorghum straw/PP composites were clear (the difference was not significant) before exposure, while the two-phase interface of sorghum straw/PVC composites was blurred. The analysis suggests that the boding quality of sorghum straw/PVC composite material was higher than that of sorghum straw/HDPE and sorghum straw/PP composite material, which can be associated with the weak polarity of PVC (the polarity comes from its internal C-Cl bond). Compared with non-polar HDPE and PP, PVC is more compatible with the strongly polar sorghum straw.

Figures 2(d) through (f) show that overall fiber flaking, fiber extraction cavities, and two-phase interface cracks arose in sorghum straw/HDPE, sorghum straw/PP, and sorghum straw/PVC composites, respectively, after 12 days of exposure (defect grading: peeling> pulling out> crack). There was a link between the decrease in the quality of the two-phase bonding and the self-swelling of fibers caused by water absorption, where swelling stress led to a decrease in the locking strength of the matrix. The two-phase bonding quality of sorghum straw/PP composite material was higher than that of sorghum straw/HDPE composite material, which can be attributed to the stronger water stability of PP than HDPE, where water stability refers to the degree to which a substance is affected by water.



(a) SS/HDPE before degradation **(b)** SS/PP before degradation **(c)** SS/PVC before degradation

(d) SS/HDPE after 12 d degradation **(e)** SS/PP after 12 d degradation **(f)** SS/PVC after 12 d degradation

Fig. 2. SEM micrographs of the tensile fracture surfaces of three types of wood-plastic composites

Wear Performance

The friction coefficient and specific wear rate of the three wood-plastic composite materials are presented in Fig. 3. The friction coefficient and specific wear rate of the three wood-plastic composite materials all showed a tendency to ascend with the extension of the exposure cycle. The wear resistance of wood-plastic composites was mainly determined by the grip strength of the matrix to the fiber (that is the two-phase mechanical interlocking). The tighter the matrix holds the fiber, the higher was the resistance to load deformation of the matrix and the load-bearing capacity of the fibers, and the less the fibers debonded into free abrasive particles. Thereby, lower friction coefficient and specific wear rate were obtained. Thus, it is inferred that the deterioration of the abrasion resistance caused by the alternating corrosion can be associated with the damage of the fiber holding by the matrix, which has been confirmed in the above. The three wood- plastic composite materials sorted by the abrasion resistance from high to low were sorghum straw/PVC, sorghum straw/PP, and sorghum straw/HDPE composites. This sequence was highly consistent with the high and low distribution of the two-phase locking strength and matrix deformation variables (that is mechanical properties) of the three wood-plastic composite materials.

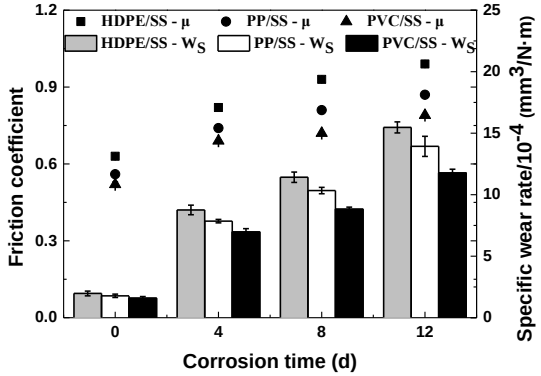
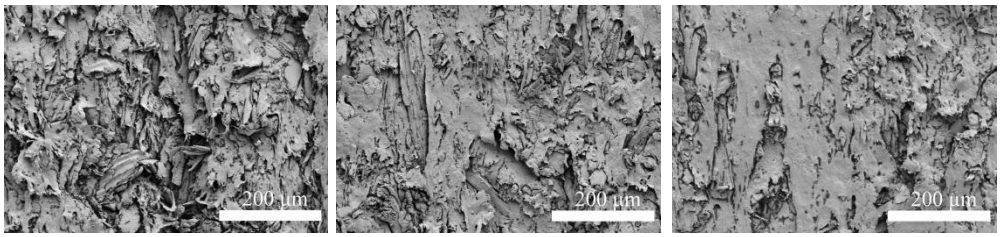
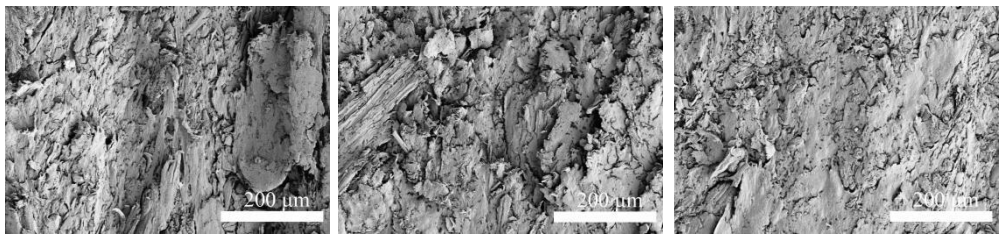


Fig. 3. Friction coefficients and specific wear rates of three types of wood-plastic composites

Figure 4 shows the SEM micrographs of the wear surfaces of three wood-plastic composite materials. Figures 4(a) through (c) show that the wear surfaces of the three wood-plastic composite materials were mainly characterized by melt wear and abrasive wear before exposure. Abrasive wear can be classified as either hard abrasive wear or soft abrasive wear (Jiang *et al.* 2019c). Hard abrasive wear mainly originates from the micro-protrusions on the surface of the mating parts, while soft abrasive wear mainly originates from fiber fragments peeled from the matrix by hard abrasive wear. When soft abrasive wear is happening, the fiber fragments at the friction interface (the interface between the two phases being in high-speed sliding contact under high temperature and high load conditions) become work-hardened, and the hard matrix melts and softens, so the fiber fragments driven by the counterparts can be embedded and plough the wear surface.



(a) SS/HDPE before degradation **(b)** SS/PP before degradation **(c)** SS/PVC before degradation



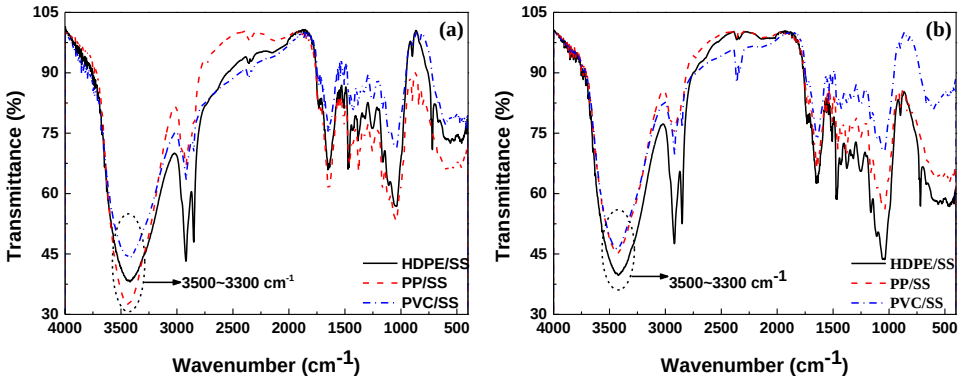
(d) SS/HDPE after 12 d degradation **(e)** SS/PP after 12 d degradation **(f)** SS/PVC after 12 d degradation

Fig. 4. SEM micrographs of the worn surfaces of three types of wood-plastic composites

Figures 4(d) through (f) show that the melting and abrasive wear characteristics of the three wood-plastic composite materials were more obvious after 12 days of exposure, which could be relevant to a decrease in the thermal resistance of the matrix caused the fracture of the two-phase heat transfer bridge (that is the two-phase bonding interface) and an increase in the probability of fiber peeling caused by the mechanical interlocking of the two phases and the decrease of fiber strength (water acting as a plasticizer for the fiber).

The three wood-plastic composite materials sorted by descending order of the wear surface roughness were sorghum straw/PVC, sorghum straw/PP and sorghum straw/HDPE composite materials, which corresponds to the distribution height of the wear resistance of the three wood-plastic composite materials.

Figure 5 shows the FTIR spectra of the three wood-plastic composite materials. The vibrational absorbances of the three wood-plastic composite materials were the strongest in the wave band of 3500 to 3300 cm^{-1} before exposure, where the vibration originates from the hydrophilic hydroxyl group contained in the fiber. It is indicated that the three wood-plastic composites inherited the strong hydrophilicity of the sorghum straw (Wu *et al.* 2013). Serving as a control, Fig. 5(b) shows that the hydroxyl vibration of the three wood-plastic composite materials was obviously weakened after 12 days of exposure, which can be associated with the chemical and hydrothermal synergistic modification of the sea water and acid on the fiber, by which hydroxyl can be removed. Except for hydroxyl groups, other characteristic absorbance peaks of sorghum straw/PP and sorghum straw/PVC composites did not fluctuate significantly, but the characteristic absorbance peaks of HDPE matrix in sorghum straw/HDPE composites such as the in-plane shear vibration (1471.8 cm^{-1}) and the in-plane rocking vibration (719.1 cm^{-1}) of methylene-CH_2 are obviously strengthened, indicating that the HDPE molecular chain was broken by 12 days of exposure. It is inferred that the alternate exposure to seawater and acid rainwater mainly acts on the implanted fiber, while the plastic matrix is free from such effects (excluding the HDPE matrix) (Kai *et al.* 2017; Jiang 2022).



(a) Before degradation **(b)** After 12 d degradation

Fig. 5. FTIR spectra of three types of wood-plastic composites

CONCLUSIONS

1. Alternate corrosion of seawater and acid rain deteriorate the surface quality of sorghum straw/HDPE, sorghum straw/PP and sorghum straw/PVC composite materials, resulting in the different mechanical and wear properties of three wood-plastic composites.
2. Before and after the alternate corrosion of seawater and acid rain, the mechanical and abrasion properties in descending sort are as follows: sorghum straw/PVC, sorghum straw/PP and sorghum straw/HDPE composites
3. According to the evaluation of mechanical and wear properties, sorghum straw/PVC composite has the best alternate corrosion resistance to the sea water and acid rain.

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