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Seawater modification of lignocellulosic fibers: comparison of rice husk and rice straw fibers

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Abstract

Scientific investigations on the non-chemical modification of lignocellulosic fibers are important for engineers when they design green wood-plastic composites. Two types of lignocellulosic fibers, namely rice husk and rice straw fibers, were studied. The physicochemical and thermal properties of the fibers with and without seawater modification were compared. The results suggested that seawater modification improved the physicochemical and thermal properties of the fibers, and that it specifically increased the surface roughness, crystallinity, and pyrolysis temperature at 5% weight loss, and decreased the silicon, hemicellulose, and lignin content of the fibers. Compared with rice husk fibers, rice straw fibers exhibited a high growth ratio of crystallinity and pyrolysis temperature at 5% weight loss, and a high loss ratio of silicon. Seawater modification of rice husk and rice straw fibers could improve fiber–polymer compatibility.

1. Introduction

Wood-plastic composites (WPCs) have been developed for use in both structural and non-structural applications, although their mechanical performance, wear resistance, and thermal stability are still poorer than those of inorganic fiber-reinforced polymer composites. A considerable number of studies on the mechanical, wear, and thermal properties of WPCs have been published [1, 2]. These published works claim that the incompatibility between hydrophilic fibers and hydrophobic polymers adversely affects the stress transfer, load carrying, and heat diffusion capacity of WPCs, and that it thereby degrades the mechanical performance, wear resistance, and thermal stability of the materials.

Many researchers focused on improving fiber–polymer compatibility by modifying lignocellulosic fibers via chemical and physical field-assisted chemical methods, such as alkalization [3, 4], acetylation [5, 6], steam-assisted alkali modification [7], and ultrasonic-assisted alkali modification [8]. Unfortunately, chemical reagents possess high risk, are dangerous to human health, and can cause environmental pollution. Therefore, researchers have been forced to develop new methods that can substitute chemical modification. Seawater exhibits high economic efficiency and ecological value compared with chemical reagents. However, literature on seawater modification of lignocellulosic fibers is scarce, and most of the available studies have been conducted on sugar palm fibers [9–11]. Rashid et al [12, 13] studied the effect of seawater modification on the physicochemical and thermal properties of sugar palm fibers. The study findings indicated that seawater modification could affect the characterization of sugar palm fibers and thereby improve fiber–polymer compatibility.

In this study, seawater modification of rice husk (RH) and rice straw (RS) fibers was conducted; these fibers are two most abundantly available farm residues in southern China. The effect of seawater modification of RH and RS fibers was determined from their surface, chemical, crystalline, and thermal characterizations. This study will broaden the potential applications of seawater modification in the use of WPCs.
2. Experimental

2.1. Materials

RH and RS fibers were sourced from a farmland in Huainan, China. They were cleaned using tap water and then air-dried until their weights were steady. The SG-5 polyvinyl chloride (PVC) was acquired from Xinjiang Tianye Co., Ltd, China. The silane coupling agent (KH-550) was obtained from Nanjing Chuangshi Chemical Additives Co., Ltd, China. The 603 Ca/Zn composite stabilizer and H-108 polyethylene wax were purchased from Shanghai Wenhua Chemical Pigment Co., Ltd, China. Simulated seawater with a pH 8 was prepared according to ASTM D 1141-98 (2013) [14]. Table 1 shows the components of simulated seawater used and their concentrations.

2.2. Seawater modification

The cleaned and dried fibers were kept immersed in simulated water for 30 d at 30 °C. After modification, the fibers were thoroughly washed with distilled water and then oven-dried for 12 h at 90 °C. Table 2 shows the main components of the RH and RS fibers determined using the Van Soest method.

2.3. Composites preparation

The 3 wt% KH-550 (with respect to the fiber) was prepared by dissolving in absolute ethanol at a volume ratio of 1:5. The diluted solution was dispersed into the powdery fiber (149 μm) by spraying. The silane-treated fiber was air-dried for 12 h and then oven-dried for 12 h at 90 °C.

The homogeneous mixture of silane-treated fiber, PVC, stabilizer, and wax (mass ratio = 100:100:8:5) was melt-blended by a conical twin-screw extruder (Model RM200C, Hapro Electric Technology Co., Ltd, Harbin, China). The screw temperatures were maintained at 150, 155, 160, and 165 °C for zones 1, 2, 3, and 4, respectively, while the screw speed was controlled at 20 rpm. The obtained composites had a width of 10 mm and a thickness of 7 mm.

2.4. Characterization

2.4.1. Surface properties

The topography and elements of the external surfaces of the fibers were analyzed using scanning electron microscopy (SEM; Model FlexSEM 1000, Hitachi Ltd, Tokyo, Japan) equipped with energy-dispersive spectroscopy (EDS; Model 550i, IXRF Ltd, Austin, USA). The samples used had a gold coating to improve image resolution.

2.4.2. Chemical and crystalline properties

The Fourier transform infrared (FTIR) spectra of the fibers were obtained using a FTIR spectrometer (Model Nicolet iS10, Thermo Fisher Scientific Co., Ltd, Shanghai, China). Data were recorded in the 500–4000 cm\(^{-1}\) wavenumber range at a resolution of 4 cm\(^{-1}\).

The x-ray diffraction (XRD) spectra of the fibers were obtained using an x-ray diffractometer (Model X’Pert PRO, PANalytical B.V., Almelo, Netherlands). Data were recorded in the 2θ range of 10° to 90° at a scan speed of 0.33° min\(^{-1}\). The crystallinity index (CrI) was calculated using equation (1):

\[
CrI = \left[1 - \frac{I_{am}}{I_{002}}\right] \times 100
\]

where \(I_{am}\) (at an approximate 2θ angle of 18°) and \(I_{002}\) (at an approximate 2θ angle of 22.5°) represent the relative amounts of amorphous and crystalline constituents, respectively.

| Component | NaCl | MgCl\(_2\) | Na\(_2\)SO\(_4\) | CaCl\(_2\) | KCl | NaHCO\(_3\) | KBr | H\(_3\)BO\(_3\) | SrCl\(_2\) | NaF |
|-----------|------|-----------|----------------|----------|-----|-------------|-----|-------------|--------|-----|
| Concentration (g · l\(^{-1}\)) | 24.53 | 5.20 | 4.09 | 1.16 | 0.695 | 0.201 | 0.101 | 0.027 | 0.025 | 0.003 |

| Fiber ID | Cellulose (%) | Hemicellulose (%) | Lignin (%) | Ash (%) |
|-----------|----------------|-------------------|------------|--------|
| Unmodified RH | 45.8 | 16.9 | 17.2 | 6.9 |
| Unmodified RS | 42.2 | 23.7 | 13.1 | 4.5 |
| Modified RH | 47.3 | 14.8 | 15.6 | 5.0 |
| Modified RS | 44.9 | 19.2 | 12.3 | 3.4 |

Table 1. Detailed components of simulated seawater.

Table 2. Main components of RH and RS fibers.
2.4.3. Thermal properties
The thermogravimetry analysis (TGA) measurements of the fibers were performed using a synchronized thermal analyzer (Model STA 449 F3, NETZSCH Scientific Instrument Trading Co., Ltd, Selb, Germany). A sample (approximately 8 mg) was placed in an Al₂O₃ crucible and tested in an argon atmosphere from 30 to 800 °C at a heating rate of 20 °C·min⁻¹.

2.4.4. Mechanical properties
The tensile and flexural tests of the composites were performed using an electronic universal testing machine (Model CMT6104, MTS Industrial Systems Co., Ltd, Shanghai, China) at a loading speed of 2 mm·min⁻¹, according to ASTM D 638-14 [15] and ASTM D 790-10 [16], respectively.

3. Results and discussion

3.1. Surface analysis
The SEM images of the external surfaces of the RH and RS fibers are shown in figure 1. Figures 1(a)–(b) show that the external surfaces of the unmodified fibers contain undesirable impurities, such as waxy and oily materials. However, as figures 1(c)–(d) indicate, in the modified fibers, most of the waxy and oily materials have been removed. Thus, seawater modification helps to dissolve waxy and oily materials owing to the weak alkalinity and high salinity of simulated seawater. The removal of waxy and oily materials increases the external surface roughness of the fibers. This increase in the external surface roughness enhances the surface frictional forces of lignocellulosic fibers, improving the mechanical interlocking between the fiber surfaces and polymer matrices [8].

The analysis of silicon (Si) elements with high heat resistance that are present in the lignocellulosic fibers can provide information about the thermal stability of the fibers. The EDS profiles of the external surfaces of the RH and RS fibers shown in figure 2 indicate that compared with RS fiber surfaces, RH fiber surfaces exhibit a high Si content before seawater modification, which agrees with the ash contents of the RH and RS fibers listed in table 2. (Ash is the major product of SiO₂.) Moreover, the EDS profiles also reveal that after seawater modification, the Si content in the fibers tends to dwindle as waxy and oily materials (largely SiO₂) are removed; the weight percentage of Si in the RH and RS fibers decreased from 58.1 to 45.2 wt% and from 37.5 to 21.6 wt%,
respectively. This observation indicates that seawater modification may reduce the thermal stability of RH and RS fibers, discussed in-depth in the subsection on thermal analysis.

3.2. Chemical and crystalline analysis
Lignocellulosic fibers with a small amount of amorphous materials, such as hemicellulose and lignin, are required in WPCs, because amorphous materials affect fiber hydrophilicity and crystallinity. Seawater modification removes amorphous materials from lignocellulosic fibers and improves their crystallinity, enhancing their strength and stiffness [17, 18]. Figures 3 and 4 show the FTIR and XRD spectra of the RH and RS fibers, respectively. In general, the higher the content of cellulose and hemicellulose, the higher the peak intensity at 3500–3300 cm$^{-1}$; the higher the content of hemicellulose and lignin, the higher the peak intensity at 1735–1700 cm$^{-1}$ and lower the crystallinity. This conclusion is validated by the close relationship between the peak intensity or crystallinity and the main components of the RH and RS fibers (table 2).

The peak appearing at 3500–3300 cm$^{-1}$ in the FTIR spectra of unmodified fibers indicates the O–H stretching of cellulose and hemicellulose hydroxyl groups, which have been weakened with seawater modification, indicating the removal of hemicellulose [19]. Similarly, the characteristic peak at 1735–1700 cm$^{-1}$ in these unmodified fibers represents the C = O stretching of hemicellulose and lignin, which decreases in intensity as hemicellulose and lignin are removed by seawater modification [20]. The modified fibers possessed higher crystallinity than unmodified fibers, revealing that amorphous materials had been removed from the
fiber bundles, allowing the cellulose fibers to have an improved crystalline structure. Specifically, the crystallinity of RH and RS fibers increased from 53.9% and 47.7% to 59.4% and 56.5%, respectively.

3.3. Thermal analysis

Figure 5 and table 3 show the TGA curves and pyrolysis characteristic data of the RH and RS fibers, respectively. The weight loss of unmodified or modified fibers occurred in two stages. The primary weight loss occurred between 30 and 150 °C, caused by the evaporation of free and bound water. Thereafter, a noticeable weight loss occurred between 300 and 500 °C, due to the degradation of the cellulose structure.
occurred at a temperature between 150 and 800 °C, primarily because of the degradation of hemicellulose (150 °C–350 °C), cellulose (275 °C–350 °C), and lignin (250 °C–500 °C) \[21–23\]. Compared with unmodified RH fibers, modified RH fibers had a lower onset and termination pyrolysis temperature in the second stage. A similar trend was observed in the RS fibers. This result can be attributed to the removal of Si with high heat resistance, as reported previously.

The pyrolysis temperature of lignocellulosic fibers at 5% weight loss \(T_{5\%}\) is typically used to assess their thermal stability \[24\]. The rankings of the thermal stabilities of the fibers were: modified RH \(T_{5\%} = 279.0^\circ C\) > unmodified RH \(T_{5\%} = 270.0^\circ C\) > modified RS \(T_{5\%} = 269.0^\circ C\) > unmodified RS \(T_{5\%} = 238.0^\circ C\). The modified fibers showed an increased thermal stability compared with unmodified fibers, which can be attributed to the removal of hemicellulose with low heat resistance, as reported previously.

3.4. Fiber–polymer compatibility analysis

The surface, chemical, crystalline, and thermal properties of lignocellulosic fibers control the mechanical performance, wear resistance, and thermal stability of WPCs. Unlike their wear resistance and thermal stability, the mechanical performance of WPCs are generally used as quantitative criteria to assess fiber–polymer compatibility. These mechanical performance of WPCs depend on their ability to transfer stress from matrices to fibers (the better the fiber–polymer compatibility is, the more efficient the stress transfer will be). Figure 6 shows the mechanical performance of RH/PVC and RS/PVC composites; seawater modification has improved the tensile and flexural properties of the composites. The tensile strength of RH/PVC and RS/PVC composites increased from 16.1 to 21.4 MPa and from 14.2 to 18.9 MPa, respectively. The flexural strength of RH/PVC and RS/PVC composites increased from 35.2 to 42.0 MPa and from 31.4 to 38.7 MPa, respectively. These values indicate that seawater modification has the potential for improving fiber–polymer compatibility.

4. Conclusions

In the present study, the physicochemical and thermal properties of modified and unmodified RH and RS fibers were compared and the main conclusions can be drawn as follow:

(1) SEM and EDS analysis revealed that the removal of waxy and oily materials using seawater modification causes the external surfaces of the fibers to become rougher and reduces the Si content of the fibers. The loss ratio of Si of the RH and RS fibers was 22.2% and 42.4%, respectively.

(2) FTIR and XRD analysis confirmed that seawater modification removes hemicellulose and lignin from the fibers, increasing fiber crystallinity. The growth ratio of RH and RS fiber crystallinity was 10.2% and 18.4%, respectively.

(3) TGA analysis indicated that the removal of hemicellulose with low heat resistance, making the fibers more stable thermally. The growth ratio of \(T_{5\%}\) of the RH and RS fibers was 3.3% and 13.0%, respectively.
(4) Mechanical analysis verified that seawater modified the RH and RS fibers, which helped to improve fiber–polymer compatibility.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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