Physicochemical and thermal properties of lignocellulosic fibers from wheat straw: Effect of seawater modification

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Abstract
Lignocellulosic fibers have been widely used to reinforce polymer composites. Chemical modification of the fibers can improve the fiber properties and fiber-polymer interfacial compatibility. This study considered an eco-friendly process that can reduce environmental pollution by modifying lignocellulosic fibers using seawater rather than chemical reagents. The effects of seawater modification on the physical, chemical, and thermal properties of lignocellulosic fibers obtained from wheat straw were investigated. After seawater modification, the modified fibers had a lower number of hydrogen bonds, hemicellulose, lignin, and silicon content, and higher water absorption, crystallinity, surface roughness, and thermal stability. Considering the essential components of seawater, the contribution of NaCl during the modification process was the most significant, followed by that of the bivalent salts (MgCl₂ + CaCl₂ + SrCl₂), Na₂SO₄, and trace-component (KCl + NaHCO₃ + KBr + H₃BO₃ + NaF).

1. Introduction
Polymer composites reinforced with lignocellulosic fibers are widely used in automobiles, construction, and other industrial industries due to their low cost, high rigidity, and good mechanical properties [1–3]. The functional performance of fiber-polymer composites depends on the properties of the individual components and the fiber-polymer interfacial compatibility. Physical or chemical modifications of lignocellulosic fibers are the most common methods used to improve fiber properties and fiber-polymer interfacial compatibility. These methods include steam explosion [4, 5], hydrothermal treatment [6, 7], acetylation [8, 9], and alkalization [10, 11]. Among these modification methods, the chemical modification method is considered the most effective. However, chemical modification methods possess high risk, are dangerous to human health, and can cause environmental pollution. Therefore, researchers have been motivated to develop new methods that can substitute chemical modification.

Seawater modification is a biological method that can replace chemical modification methods. However, studies on seawater modification are scarce. Most of the available studies have been conducted on lignocellulosic fibers obtained from sugar palm fibers (SPFs), and no study was found on other sources of lignocellulosic fibers [12–14]. Rashid et al [15, 16] determined the physical, chemical, and thermal properties of SPFs after the fibers underwent seawater modification. The authors concluded that seawater modification significantly alters the fiber properties and improves the fiber-polymer interfacial compatibility. Hence, investigating seawater modification of other lignocellulosic fibers is of great significance.

The effects of seawater modification were determined relative to physicochemical and thermal properties of lignocellulosic fibers obtained from wheat straw (WSFs). The weight retention/water absorption, Fourier transform infrared (FTIR)/x-ray diffraction (XRD) spectra, thermogravimetry (TG)/derivative thermal gravity (DTG), and surface morphology and elemental components (scanning electron microscopy (SEM)/energy dispersive spectroscopy (EDS)) of the WSFs were analyzed. The findings of this study will broaden the applications of lignocellulosic fiber in an environmentally safe way.
2. Experimental

2.1. Materials
WSFs (cellulose 42.8%, hemicellulose 21.5%, and lignin 15.7%) were locally obtained from Huainan, China. The fibers were washed with tap water to remove impurities, and thereafter the fibers were air-dried at an ambient temperature of 25 °C for 7 d. NaCl, MgCl₂, Na₂SO₄, CaCl₂, KCl, NaHCO₃, KBr, H₃BO₃, SrCl₂, NaF, and NaOH were purchased from Sinopharm Chemical Reagent Co., Ltd, Beijing, China.

2.2. Seawater modification
To prevent error and alterations that may result from the constituents of actual seawater, standard seawater was prepared according to the ASTM D 1141–98 (2013) [17]. The standard seawater was prepared with 10 chemical reagents of different concentrations (table 1), which was then adjusted with NaOH to a pH of 8.0. To determine the modification mechanism of seawater on WSFs, the standard seawater was further divided into four independent component solutions, i.e., main-component solution (NaCl), sulfate solution (Na₂SO₄), bivalent-salt solution (MgCl₂ + CaCl₂ + SrCl₂), and trace-component solution (KCl + NaHCO₃ + KBr + H₃BO₃ + NaF).

The WSFs were immersed in standard seawater and independent component solutions at a water temperature of 20 °C (See figure 1). After modifying WSFs for 30 d, WSFs were rinsed with distilled water and oven-dried at 90 °C for 12 h.

2.3. Characterization
2.3.1. Analyses of weight retention and water absorption
The weight retention (WR) and water absorption (WA) capacities of the WSFs were calculated using equations (1) and (2), respectively,

\[
WR = \frac{WR_2}{WR_1} \quad (1)
\]

\[
WA = \frac{(WA_2 - WA_1)}{WA_1} \quad (2)
\]

where \(WR_1\) (mg) is the dry weight of WSFs before modification, \(WR_2\) (mg) is the dry weight of WSFs after modification, \(WA_1\) (mg) is the dry weight of WSFs before immersion, and \(WA_2\) (mg) is the wet weight of WSFs after immersion. Each test was replicated five times with an accuracy of 0.1 mg.

The dry weight is the weight of the WSFs after drying of the WSFs at an oven temperature of 90 °C for 12 h, whereas the wet weight is the weight of the WSFs after immersion of the WSFs in distilled water at a water temperature of 20 °C for 24 h, after removal of surface water.

Table 1. Chemical components of standard seawater.

| Component     | NaCl | MgCl₂ | Na₂SO₄ | CaCl₂ | KCl |
|---------------|------|-------|--------|-------|-----|
| Concentration (g·L⁻¹) | 24.53 | 5.20  | 4.09   | 1.16  | 0.695 |
| Component     | NaHCO₃ | KBr | H₃BO₃ | SrCl₂ | NaF |
| Concentration (g·L⁻¹) | 0.201 | 0.101 | 0.027  | 0.025 | 0.003 |

Figure 1. Schematic diagram of seawater modification of the WSFs.
2.3.2. FTIR and XRD analyses
FTIR analysis was conducted using a Nicolet iS10 FTIR spectrometer (Thermo Fisher Scientific Co., Ltd, Shanghai, China). The spectra were collected at a resolution of 4 cm\(^{-1}\) in the range of 1000 to 4000 cm\(^{-1}\).

XRD analysis was conducted using a X’Pert PRO x-ray diffractometer (PANalytical B.versus, Almelo, Netherlands) with a Cu–K\(\alpha\) radiation source (\(\lambda = 0.15406\) Å). The spectra were collected at a speed of 0.33°·min\(^{-1}\) in the range of 10° to 90°. The crystallinity index (CrI) was calculated as shown in equation 3,

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

where \(I_{am}\) is the intensity of the amorphous phase at 18°, and \(I_{002}\) is the intensity of the crystalline phase at 22.5°.

2.3.3. Analyses of surface morphology and elemental composition
The surface morphological and elemental analyses were conducted using a FlexSEM 1000 SEM (Hitachi Ltd, Tokyo, Japan) equipped with a 550i EDS (IXRF Ltd, Austin, USA). The characterized surfaces were prepared by sputtering them with gold.

2.3.4. TG and DTG analyses
Both TG and DTG analyses were conducted using an STA 449 F3 synchronized thermal analyzer (NETZSCH Scientific Instrument Trading Co., Ltd, Selb, Germany). The spectra were collected in an argon atmosphere at a heating rate of 20 °C·min\(^{-1}\) from 30 to 800 °C.

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**Figure 2.** Weight retention of the WSFs: 1, 2, 3, 4, 5, and 6 represent the unmodified, seawater, NaCl, Na\(_2\)SO\(_4\), bivalent-salt, and trace-component modified WSFs, respectively.

**Figure 3.** Water absorption capacities of the WSFs: 1, 2, 3, 4, 5, and 6 represent the unmodified, seawater, NaCl, Na\(_2\)SO\(_4\), bivalent-salt, and trace-component modified WSFs, respectively.
3. Results and discussion

3.1. Weight retention and water absorption analyses
The WR and WA capacities of the WSFs are shown in figures 2 and 3, respectively. The variations in WR and WA capacities of seawater modified WSFs were −12.3% and +40.9%, respectively. For NaCl modified WSFs, the variations were −10.5% and +33.8%, respectively; for Na2SO4 modified WSFs, the variations were −8.9% and +22.3%, respectively; for bivalent-salt modified WSFs, the variations were −9.2% and +25.4%, respectively; and for trace-component modified WSFs, the variations were −5.6% and +13.0%, respectively. The dry weight of lignocellulosic fibers is mainly attributable to their cellulose, hemicellulose, and lignin contents. Seawater modification can remove non-cellulosic material from lignocellulosic fibers [15, 18]. Hence, the reduction in WR can be attributed to the removal of hemicellulose and lignin. However, hemicellulose plays a decisive role in defining WA capacity of WSFs. Therefore, a higher amount of hemicellulose removal results in a lower WA capacity of lignocellulosic fibers. The contradiction between WA and hemicellulose content can be attributed to the increase in the water permeability of the lignocellulosic fiber. This behavior was due to the removal of non-cellulosic material. The increase in water permeability enables improved penetration of polymer inside the fibers. Based on the results obtained from WR and WA analyses, the modification by seawater had the greatest effect on the physical properties of WSFs, followed by that of NaCl, bivalent-salt, Na2SO4, and trace-component modification.
3.2. FTIR and XRD analyses

The FTIR spectra and XRD pattern of the WSFs are shown in figures 4 and 5, respectively. As shown in figure 4, absorption peaks attributed to the O–H stretching vibration in hydroxyl groups (3500 to 3300 cm\(^{-1}\)) and C=O stretching vibration in hemicellulose and lignin (1735 to 1700 cm\(^{-1}\))\(^{[19]}\) were observed. The O–H stretching peak at 3448.4 cm\(^{-1}\) in unmodified the WSFs shifted to 3445.2, 3447.6, 3441.9, 3447.4, and 3447.5 cm\(^{-1}\) for the seawater, NaCl, Na\(_2\)SO\(_4\), bivalent-salt, and trace-component modified WSFs, respectively. The reason for this observation may be because the –OH was attracted by Na\(^+\) and Cl\(^-\), where the dissimilarity in their polarity tends to bind one to another to form ionic bonds, which resulted in the reduction of hydrogen bonds between molecules\(^{[20, 21]}\). A similar trend can be observed in the C=O stretching vibration, the C=O stretching peak of the modified WSFs were observed at lower wavenumber compared with the unmodified WSFs, indicating a reduction in hemicellulose and lignin content. The reduced number of hydrogen bonds and non-cellulosic material provides more contact sites between fibers and polymer and enable better penetration of polymer inside the fibers.

From figure 5, the crystallinity of the WSFs varied significantly when compared with the unmodified WSFs. Specifically, the crystallinity of unmodified, seawater, NaCl, Na\(_2\)SO\(_4\), bivalent-salt, and trace-component modified WSFs were 48.5%, 53.1%, 52.3%, 49.4%, 50.4%, and 48.8%, respectively. The increase in crystallinity of the modified WSFs can be attributed to the removal of hemicellulose and lignin (non-crystalline material). Therefore, the higher the removal of non-crystalline material, the higher the crystallinity of the WSFs. Based on
the crystallinity, the chemical properties of WSFs are best modified by seawater, followed by NaCl, bivalent-salt, Na$_2$SO$_4$, and trace-component modification.

### 3.3. Surface morphology and element analyses

The SEM images and EDS spectra of the external surface of WSFs are shown in figures 6 and 7, respectively. Figure 6(a) shows that the external surface of the unmodified WSFs is covered with a smooth layer that contains wax, SiO$_2$, and some undesirable constituents. In contrast, figures 6(b) through 6(f) shows that seawater and its independent component modifications caused increased roughness on the external surface of the WSFs by removing the wax and other impurities, and it also led to fibrillation (i.e., splitting of the fiber bundles into fibers), which can increase the contact surface and the degree of mechanical interlocking with the polymer in a biphasic system.

Oxygen (O) is the main component of lignocellulosic fiber structures, and the smooth layer on the external surface of the WSFs mainly consists of silicon (Si). Figure 7 shows that the content of Si in the modified WSFs was lower than that in the unmodified WSFs. Specifically, the weight percentage of Si was lowered by 89.6%, 84.9%,

| Sample ID | $T_{5\%}(^\circ\text{C})$ | Peak I | Peak II | Peak III |
|-----------|--------------------------|--------|---------|----------|
|           | $T(^\circ\text{C})$ | $T(^\circ\text{C})$ | $T(^\circ\text{C})$ |
| 1         | 96.0                     | 93.8   | 293.1   | 365.0    |
| 2         | 276.0                    | 97.5   | 281.0   | 353.8    |
| 3         | 251.0                    | 84.3   | 285.6   | 346.2    |
| 4         | 105.0                    | 85.9   | 279.3   | 351.8    |
| 5         | 107.0                    | 95.9   | 291.6   | 350.0    |
| 6         | 97.0                     | 81.2   | 284.9   | 364.2    |

*Figure 8. TG curves of the WSFs.*

*Figure 9. DTG curves of the WSFs.*
59.9%, 78.6%, and 22.7% after modification with seawater, NaCl, Na2SO4, bivalent-salt, and trace-component, respectively. The reduction in Si content can be attributed to the removal of the smooth layer. Based on the Si contents in the modified samples, seawater had the greatest effect on the surface properties of the modified sample, followed by NaCl, bivalent-salt, Na2SO4, and trace-component modification.

3.4. TG and DTG analyses
The TG and DTG curves of the WSFs are shown in figures 8 and 9, respectively. Table 2 contains a summary of the characteristic data of the pyrolysis process. The weight loss in WSFs can be divided into two stages. The first stage occurred between 30 and 150 °C, with an endothermic peak (designated as peak I) owing to dehydration of the WSFs. The second stage occurred between 150 and 800 °C, which corresponds to the degradation of hemicellulose (150 to 350 °C), cellulose (275 to 350 °C), and lignin (250 to 500 °C) in the WSFs [22].

The degradation of hemicellulose occurred at endothermic peaks (designated as peak II) of 293.1, 281.0, 285.6, 279.3, 291.6, and 284.9 °C in the unmodified, seawater, NaCl, Na2SO4, bivalent-salt, and trace-component modified WSFs, respectively. A similar trend was observed in the degradation of cellulose; the endothermic peak (designated as peak III) of the modified WSFs was observed at a lower temperature than that of the unmodified WSFs. These observations agree with those by Rashid et al [15], and which can be attributed to the reduction in Si (with high heat resistance) content. The degradation of lignin occurred within a wide temperature range with a low weight loss rate, and this led to the flattening of the endothermic peak in the DTG curve.

The thermal stability of lignocellulosic fiber was investigated at 5% weight loss (designated as T5%), which is the initial degradation of lignocellulosic fiber [23]. The thermal stability of WSFs can be ranked as follows (table 2): Seawater modified > NaCl modified > bivalent-salt modified > Na2SO4 modified > trace-component modified > unmodified. The higher thermal stability of modified WSFs can be attributed to the lower content of hemicellulose (with low heat resistance) in the modified WSFs than that of the unmodified WSFs.

4. Conclusions
Herein, the effects of seawater modification were investigated relative to the physicochemical and thermal properties of wheat straw fibers (WSFs). The main conclusions are summarized as follows:

(1) Seawater modification can reduce the number of hydrogen bonds as well as the hemicellulose, lignin, and silicon contents. It can also improve the water absorption (WA) capacity, crystallinity, surface roughness, and thermal stability of the WSFs.

(2) NaCl, bivalent-salt, Na2SO4, and trace-component significantly contributed to the seawater modification process; the degree rankings of contribution were: NaCl > bivalent-salt, Na2SO4 > trace-component.

(3) Seawater modification enhanced the properties of the WSFs; therefore, it was concluded that seawater modification can help to improve fiber-polymer interfacial compatibility.

(4) Seawater exhibits high economic efficiency and ecological value compared with chemical reagents. Therefore, seawater can be considered as a modification method worth promoting.

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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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