Influence on the Physical Properties of Wheat Straw *via* Hydrothermal and Chemical Treatments

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The physical properties of wheat straw treated with hydrothermal and chemical treatments were investigated using an electronic universal testing machine, Fourier transform infrared spectroscopy (FT-IR), and scanning electron microscopy (SEM). The thermal stability of the wheat straw was also investigated using thermogravimetric analysis (TGA). The experimental results showed that the chemical treatment was a main factor governing the enzymatic saccharification of wheat straw. Different treatments of wheat straw had the same mass loss trend. The maximum mass loss occurred in the range between 250 and 400 °C for all straw samples. In this range, the wheat straw treated with NaOH showed an exothermic peak, while samples treated with the other treatments showed an endothermic peak. Chemical treatments disrupted the silicified waxy surface and destroyed the C-O bond. The internal structure of wheat straw treated with NaOH became porous and loose and exposed more accessible surface area of the cellulose to cellulase.

Keywords: Wheat straw; Hydrothermal and chemical treatments; Physical properties; FT-IR

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INTRODUCTION

A large quantity of agricultural (straw) residues available worldwide have been produced after harvesting in recent years (Han *et al*. 2001). In China, tons of unused wheat straw residues are generated every year, and only a very small percentage has been used for applications such as feedstock and energy production. Applications of wheat straw residues in the production of composite materials are considered very helpful for conserving valuable wood resources (Pan *et al*. 2010). However, low interfacial bonding strength between hydrophilic natural fibers and hydrophobic polyolefin limits the reinforcement imparted to the plastic matrix.

Many attempts have been made to improve the bondability between agricultural materials and plastic matrix through raw material pretreatment. A wide range of thermal, mechanical, and chemical pretreatment methods, and combinations thereof, have been reported. Choosing the appropriate pretreatment is frequently a compromise between minimizing the degradation of the hemicellulose and cellulose components while maximizing the ease of hydrolysis of the cellulosic substrate (Saritha *et al*. 2012). The effect of hydrothermal pretreatment on lignocellulosic biomass has been employed for extracting hemicelluloses, cellulose, and lignin. In combination with the partial hemicellulose hydrolysis and solubilization, the solubilized hemicellulose and lignin are present in low concentrations. The lignin is redistributed and, to some extent, removed from the material (Pan *et al*. 2005). Dilute acid pretreatment is probably the most

commonly applied method among the chemical pretreatment methods. It can be used either as a pretreatment of lignocellulose for enzymatic hydrolysis, or as the actual method of hydrolyzing to fermentable sugars (Taherzadeh and Karimi 2008). NaOH causes swelling, increasing the internal surface area of cellulose and decreasing the degree of polymerization and crystallinity, which provokes lignin disruption (Playne 1984). Lignin removal increases enzyme effectiveness by reducing non-productive adsorption sites for enzymes and by increasing cellulose accessibility (Kumar and Wyman 2009). Conversion of hydrothermally pretreated wheat straw into bioethanol has previously been investigated (Kaparaju *et al*. 2009). In the previous investigations, plant tissues were either mixed or not well-defined as a result of mechanical mixing and disruption taking place during pretreatment. Chemical modification of natural fibers has been widely used in the manufacture of wood polymer composites (Hristov *et al*. 2004; Karimi *et al*. 2006). Alkalization can eliminate a large amount of hemicellulose and other impurities of natural fibers, leading to more voids on the fiber surface and rougher surface, and therefore improved adhesion (Cantero *et al*. 2003).

The overall objective of this study was to subject wheat straw to hydrothermal and chemical treatments to improve the adhesion between the wheat straw fibers and hydrophobic thermoplastic polymer. Specifically, the objective of the study was to carefully analyze the treated wheat straw from many directions in order to evaluate their suitability as reinforcement for polymer composites. The effects of these treatments on thermal properties were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The changes of the structural groups of the different wheat straw samples were characterized by Fourier transform infrared spectroscopy (FT-IR), and the effects of the different treatments on the surface microstructure of the wheat straw were observed by stereo microscope.

EXPERIMENTAL

Materials

Wheat straw samples were collected from Wuxi, China. The samples were dried in the sunlight, and the sheath and leaves of the wheat straw were peeled off. The samples were chipped into short pieces with a length of 70 mm by a chipper mill. NaOH and oxalic acid were purchased from Nanjing Jinling Chemical Co., Ltd. (Nanjing, China). Distilled water was produced in-house.

Treatment Methods

Wheat straw is rich in silica and waxes, which makes it unsuitable for some applications (Ndazi *et al*. 2007; Salam *et al*. 2007). To improve the straw properties, different treatments were applied.

Hydrothermal treatment

The wheat straw sample was soaked in distilled water for 24 h at 90 °C, followed by oven drying at 105 °C for about 6 h.

2% NaOH treatment

The sample was soaked in 2% NaOH solution for 2 h at room temperature with occasional shaking, washed with distilled water for 24 h to leach out the absorbed NaOH

until neutral pH (7 ± 0.5) was reached, and subsequently oven-dried at 105 °C for about 6 h (Liu *et al*. 2011).

2% Oxalic acid treatment

The sample was soaked in 2% oxalic acid solution for 2 h at room temperature with occasional shaking. Afterward, the oxalic acid-treated straw was washed with abundant distilled water for 24 h to leach out the absorbed oxalic acid until neutral pH was reached, followed by oven drying at 105 °C for about 6 h (Pan *et al*. 2009).

Analytical Procedures

Tensile strength test

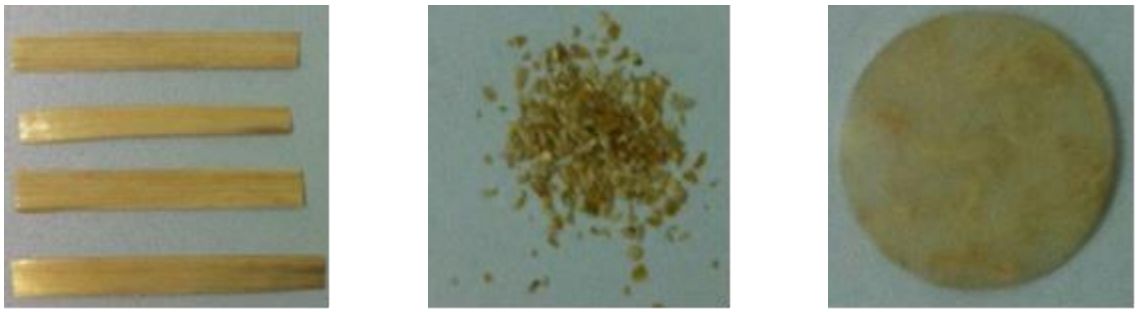
Samples were tested using an electronic universal testing machine (SANS CMT6104, Shanghai, China). Both ends of the straw were held with 600# emery paper, which was secured into the testing machine to reduce skidding. The tensile strength of the wheat straw samples was conducted according to the GB/T 1040.4 (2006), and a tensile speed of 2 mm/min was used. The samples were cut into 70 mm pieces (Fig. 1a), and the gauge was set to 50 mm. The elastic modulus of each sample was tested following the GB/ T9341 (2008), and the loading rate was 2 mm/min. These experiments were performed at room temperature, and the final values were calculated from the average of five measurements.

Thermal stability analysis

The 0.008-g samples were collected from the wheat straw, which was sieved to obtain particles with a mean size of 2 mm (Fig. 1b). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the wheat straw were conducted with a simultaneous thermal analyzer (Nezsch STA 449 F3, Bavaria, Germany) under argon gas at a heating rate of 30 °C/min from 30 °C to 500 °C. The analysis for each sample was repeated to ensure that it followed the same trace for the same conditions.

FT-IR analysis

A Nicolet iS-10 FT-IR (ThermoFisher Scientific, Waltham, USA) was used to obtain spectra for the straw. The 0.002-g samples were mixed with 0.2 g of KBr, and the mixtures were ground and dispersed. The mixtures were dried completely and pressed using the tablet press machine with diameter of 13 mm (Fig. 1c). FT-IR spectra were recorded in a range from 4,000 to 400 cm^{-1}, at a resolution of 4 cm^{-1} with 16 scans.



(a) Tensile strength test **(b)** Thermal stability analysis **(c)** FT-IR analysis

Fig. 1. Images of wheat straw samples before test

Microscopy

The surface of the straw was analyzed by a Nikon SMZ1000 stereo microscope (Tokyo, Japan).

RESULTS AND DISCUSSION

Tensile Properties of Wheat Straw under Different Treatments

The mechanical properties of cellulose depend on the proportion of crystalline and amorphous regions and the spiral angle of microfibrils (Cantero *et al*. 2003). It is well known that lignin and hemicellulose are amorphous polymers. Cellulose is mainly crystalline but does contain amorphous regions within the crystalline lattice (Karimi *et al*. 2006). In view of the above facts, the significant improvement in mechanical properties of the treated wheat straws is probably due to an increase in the extent of crystallinity and a reduction in the extent of amorphous regions (Han *et al*. 2010). Thus it is important to evaluate the mechanical strength of wheat straws treated with different treatments. The tensile properties of wheat straw treated with different treatments were examined (Fig. 2). All treatments greatly influence the tensile strength and elastic modulus. The 2% NaOH treatment resulted in a more noticeable improvement than hydrothermal treatment, while oxalic acid treatment decreased the tensile strength and elastic modulus of the wheat straw. The -OH in the NaOH solution could weaken the hydrogen bonds between cellulose and hemicellulose, and saponify the ester bonds between hemicellulose and lignin molecules during this process. It could also break the chemical bonds between lignin and carbohydrates, which made the lignin structures destroyed and dissolved. This would then lead to more voids on the fiber surface and rougher surface, and therefore improved adhesion (Cantero *et al*. 2003). It also causes the contraction of the tensile section and the cellulose-bearing fiber of the wheat straw, which is why the tensile strength and elastic modulus increased (Li *et al*. 2009).

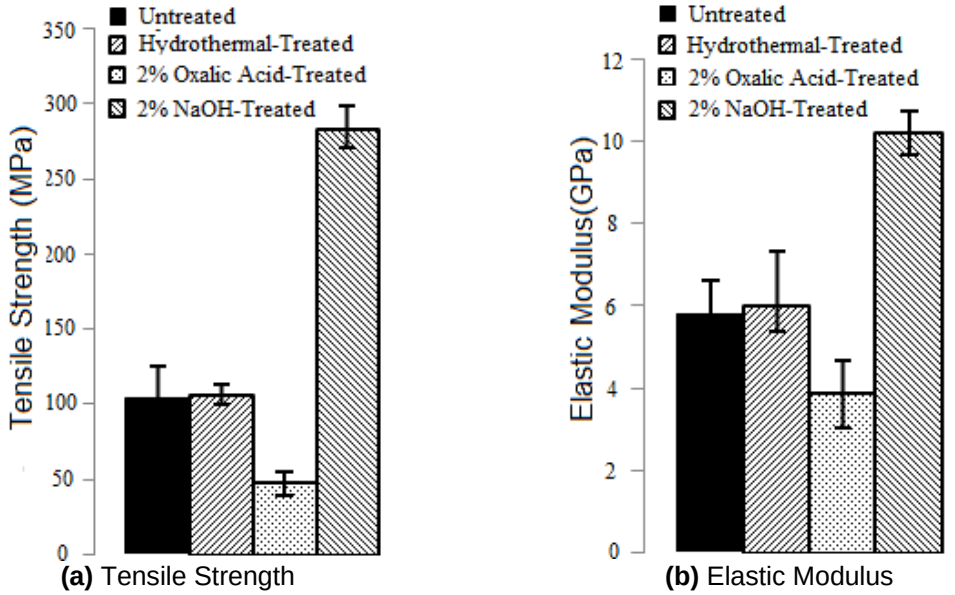


Fig. 2. Tensile properties of wheat straw with different treatments

However, the tensile strength and elastic modulus of samples treated by hydrothermal treatment or 2% oxalic acid were smaller than those of the untreated wheat straw. This was mainly due to the fact that the hydrothermal treatment and the oxalic acid treatment destroyed the structure of the straw, removed the hemicellulose and lignin of the connecting fiber only slightly, and had no effect on the tensile section size of the wheat straw (Jiang *et al*. 2009).

Thermal Stability of Wheat Straw under Different Treatments

Figure 3 shows thermogravimetric (TG) and DSC thermograms for treated samples. The TG results indicate that the mass loss trends among different treatments were basically consistent. Straw pyrolysis was identified as three phases, *i.e*., moisture evaporation (below 250 °C), main devolatilization (250 to 400 °C), and continuous devolatilization (above 400 °C). Biomass material consists mainly of three types of polymers: cellulose, hemicellulose, and lignin. Starting at 250 °C, dehydration and decarboxylation begin, and they increase rapidly around 300 °C. Hemicellulose decomposes first, followed by cellulose, and finally, lignin. The mass loss from large to small was as follows: 2% NaOH-treated (40.19%), untreated (31.62%), hydrothermal-treated (31.34%), and 2% oxalic acid-treated (29.07%).

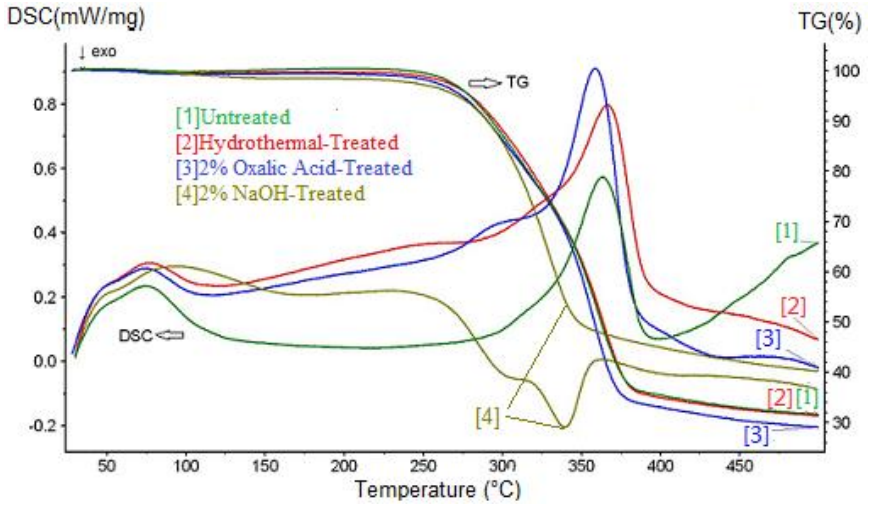


Fig. 3. TG and DSC curves of wheat straw of different treatments

The DSC curves indicate that the thermal decomposition of the wheat straws consisted of four main stages (He *et al*. 2005). In the initial step from 50 °C to 100 °C, all DSC curves showed a smaller endothermic peak. Because only a small amount of molecules and water content escaped from the wheat straw, it had insignificant weight loss and a small endothermic peak in this temperature section (Zeng *et al*. 2011). In the second stage between 100 °C and 250 °C, the DSC curves were smooth, which depended on the moisture and little molecular substance in the wheat straw that had been volatile. The third phase (250 °C to 400 °C) corresponded to the thermal decomposition, as part of the cellulose, hemicellulose, and lignin degraded and evaporated as temperatures continued to rise (Pan *et al*. 2008). Therefore, 2% NaOH-treated wheat straw recorded the highest exothermic peak in the DSC profiles. This result was attributed to the decomposition of hemicelluloses and lignin, which required less calorific value, and the residual material exothermic reaction, which released heat after themolysis. As with untreated wheat straw, hydrothermal-treated and 2% oxalic acid-treated wheat straw had much more cellulose and

lignin, which required a larger calorific value for themolysis and recorded the highest endothermic peak in the DSC profiles. The final stage corresponded to the residual material heating section. Wheat straw decomposition was basically complete when the temperature exceeded 400 °C. Because this stage was mainly residual material carbonization, the DSC curves of the different treated wheat straws recorded an exothermic process, while the untreated wheat straw appeared endothermic. This result indicated that the cellulose, lignin, and residual material continued themolysis (Yang *et al*. 2010).

FT-IR Spectra of Wheat Straw under Different Treatments

The wheat straw samples subjected to different treatments exhibited distinct absorption peaks; part of the absorption was enhanced, diminished, or shifted, and the intensity of the absorption peak changed only slightly compared with the untreated wheat straw FT-IR profiles (Fig. 4). Absorption peaks between 3430 and 3380 cm^{-1} correspond to the stretching vibrations of -OH, which are derived from cellulose, hemicellulose, starch, and other polysaccharides or monosaccharides, *etc*. (Ibrahim *et al*. 2009). The absorption peak here became weak and narrow, especially for the oxalic acid-treated wheat straw. This result indicated that the -OH in the oxalic acid-treated wheat straw had more reduction, which could be due to the fact that oxalic acid treatment greatly destroyed the cellulose and hemicellulose structure.

The absorption peak at 2959 cm^{-1} is the stretching vibration for C-H bonds in the saturated hydrocarbon. The peak at 2918 cm^{-1} is assigned to the C-H antisymmetric stretching vibration absorption peak for CH_2 groups (Moran *et al*. 2008). The different treatments of wheat straw had very different absorption peaks, and the intensity of the peaks decreased from high to low as follows: oxalic acid-treated, hydrothermal-treated, and NaOH-treated. This result indicated that the oxalic acid treatment had a greater influence on the lipophilic material at the surface of wheat straw. The wave numbers between 2130 and 2100 cm^{-1} correspond to the absorption peaks of NH_3^+ from the amino acids. The relative intensity of the peaks from large to small was oxalic acid-treated, hydrothermal-treated, and NaOH-treated. Peaks centered around 1640 cm^{-1} correspond to the characteristic absorption peaks of amide compounds and the stretching vibration of C=O. It is also the characteristic absorption peak of the deformation vibration of water molecules form hydrogen bonds (Chand *et al*. 2009). Differently treated wheat straw samples had complex changes in absorption peaks, with shifts and decreases. This indicated that the different treatments had an influence on the content of lignin and bound water in the wheat straw. The wave numbers between 1160 and 1150 cm^{-1} show the absorption peak of C-O from carbohydrates and the asymmetric stretching vibration of the C-O-C from aliphatic compounds (Jahan *et al*. 2007). The intensity of the peaks from large to small was untreated, hydrothermal-treated, NaOH-treated, and oxalic-acid treated. This indicated that different treatments could effectively reduce the lipotropic substance from the outer surface of the wheat straw. The prominent peaks at 1100 to 970, and 655 to 585 cm^{-1} represent C-O stretching vibrations from carbohydrates and the absorption peak of outer bending vibrations of the hydroxyl outside surface. Peaks from 900 to 890 cm^{-1} are attributed to the absorption peaks of Si-O from silicon compounds (Das *et al*. 2007). Untreated wheat straw had the strongest absorption peak, demonstrating that hydrothermal treatment, oxalic acid treatment, and NaOH treatment could remove cork and silica cells from silica outside the wheat straw surface. Therefore, different treatments removed the lipotropic substance from the outside surface of wheat straw and improved the external surface wettability.

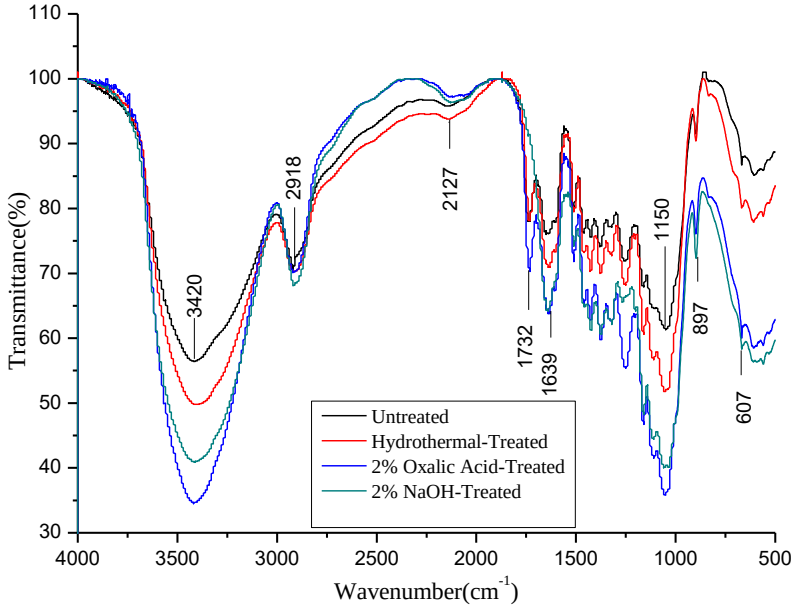
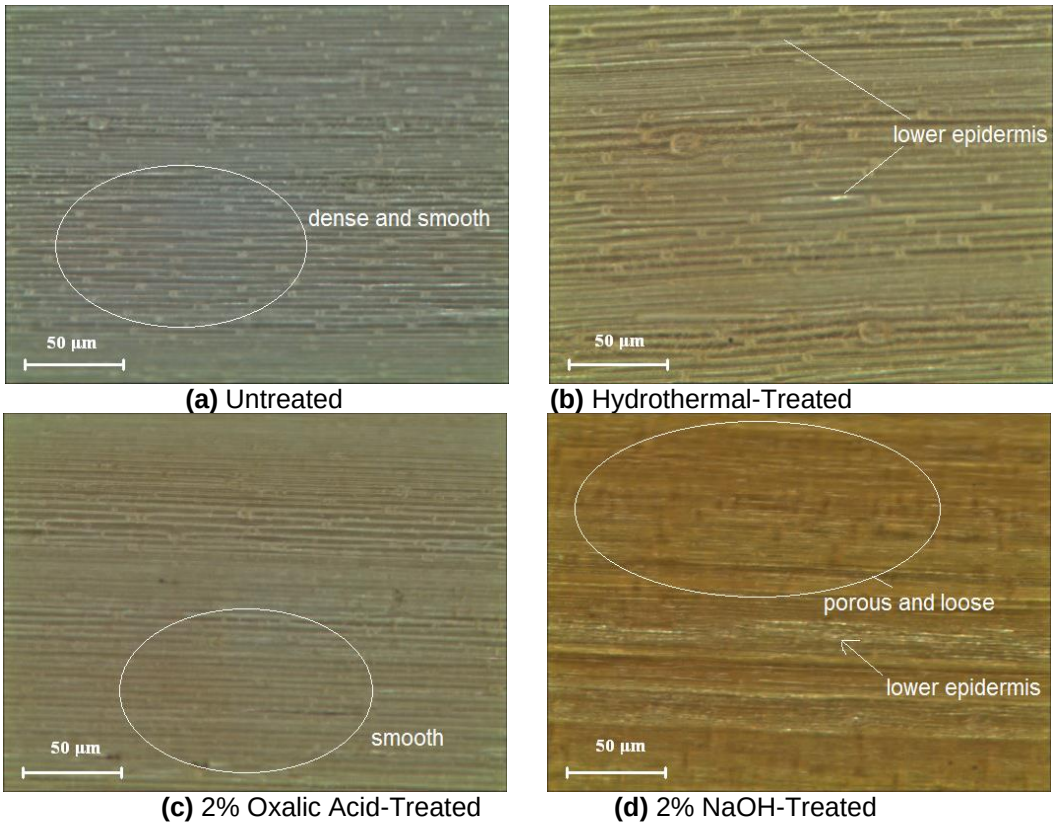


Fig. 4. FT-IR spectra of wheat straw under different treatments

Microstructure of Wheat Straw under Different Treatments

Figures 5(a), (b), and (c) illustrate that the tissue of wheat straw in the outer surface layer was dense and smooth.



(a) Untreated **(b)** Hydrothermal-Treated

(c) 2% Oxalic Acid-Treated **(d)** 2% NaOH-Treated

Fig. 5. Microstructure of the outside surface of differently treated wheat straws

The wax-silicide layer on the surface is rich in SiO_2, silicon, and cork cells (Han *et al*. 2010). Hydrothermal treatment and oxalic acid treatment reduced the external surface gloss of wheat straw, which indicates that the surface wax-silicide layer was partially removed, and the lower epidermis tissue was partially exposed. The samples were still relatively smooth overall and had little difference compared with the untreated samples. Fig. 5(d) illustrates that the external surface of NaOH-treated wheat straw showed evidence of tearing, tension, and produced the fiber development. Most of the wax-silicide layer detached, causing the lower fiber cells to be exposed, and the lignin and hemicelluloses that wrap around the outside of the cellulose were removed (Ma *et al*. 2009). The internal structure became porous and loose, which improved the accessibility of cellulase to cellulose.

CONCLUSIONS

1. Wheat straw could be used as a renewable fuel for heat and power generation, replacing fossil fuels and preventing the pollution from the open burning of wheat straw. All treatments had a great influence on the tensile strength. The 2% NaOH treatment of wheat straw improved the tensile strength and the elastic modulus more noticeably than the other treatments.
2. Different treatments of wheat straw have distinct thermal mass loss, but basically the same trends, with a large mass loss occurring in the range between 250 and 400 °C.
3. Different treatments removed the wheat straw surface wax-silicide layer and reduced the cellulose, hemicellulose, and lignin content, which affected the variation of the peak and the intensity of infrared absorption.

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