Preparation of Glue-free Wheat Straw-based Fiberboard with Zero Formaldehyde

Qiong Su[1*], *Shuangyan* Li[1]

[1]Key Laboratory of Environment-Friendly Composite Materials of the State Ethnic Affairs Commission, Gansu Provincial Biomass Function Composites Engineering Research Center, Key Laboratory for Utility of Environment-Friendly Composite Materials and Biomass in University of Gansu Province, Gansu Province Research Center for Basic Sciences of Surface and Interface Chemistry, College of Chemical Engineering, Northwest Minzu University, Lanzhou 730124, China

Abstracts. Glue-free wheat straw-based fiberboard has the advantages of excellent performance, such as no formaldehyde release, being renewable, and being degradable, which presents a novel approach to enhance the utilization value of straw and protect the environment.. In this study, wheat straw was first pre-treated to remove impurities such as wax and silica contained in wheat straw by a 2% sodium hydroxide solution, and further modified by carboxymethylation and acylation to obtain wheat straw fiberboard raw materials with different functional properties. Then, H_2O_2 was used as the initiator, and the wheat straw fiberboard raw materials were hot-pressed at 100 °C and 140 kg/cm^2 to prepare glue-free wheat straw-based fiberboard with the bending strength of 95.43 MPa, the impact toughness of 2.68 kJ/m^2, the tensile strength of 9.2 MPa, the elastic modulus of 1773.03 MPa, and the hardness of 81D. The performances of the prepared glue-free wheat straw-based fiberboard with zero formaldehyde have surpassed that of the general glue-free board and have the potential to replace wood board.

1. Introduction

Fiberboard is made of wood fiber or other plant fibers intertwined and glued together, while straw-based fiberboard comes from straw through the processes of chopping, softening, pulping, molding, and hot pressing. Straw-based fiberboard can be divided into adhesive straw-based fiberboard and non-adhesive straw-based fiberboard according to whether adhesives are used in the preparation process. During the preparation process of adhesive straw-based fiberboard, the straw particles are bonded by adhesive to improve the mechanical and hydrophobic properties[1–2]. Dorota Dukarska[3] et al prepared panels with good mechanical properties using rape straw as raw material, polymerized 4,4′-methylene diphenyl isocyanate, and phenolic resin as a binder. Traditional adhesives can effectively improve the mechanical properties of fiberboards, but the fiberboard has formaldehyde release, poor water resistance et al. The glue-free straw-based fiberboard is prepared by a hot pressing process, which does not use adhesives at all, and self-bonding occurs between plant fibers.

---

[*] Corresponding author: hgsq@xbmu.edu.cn

Ramunas Tupciauskas[4] et al. applied a hot pressing method to produce straw fiberboard from wheat straw with the modulus of rupture of 21 MPa, the absorbent thickness expansion rate of 10%, and water absorption of 41%. Therefore, glue-free wheat straw-based fiberboard has the advantages of excellent performance, such as no formaldehyde release and being renewable and degradable, which can not only reduce and eliminate the use of synthetic resin but also provide a new way to alleviate the oil crisis, protect the environment, and improve the utilization value of straws.

In this study, wheat straws were selected as the raw material, the waxes and silica in wheat straws were removed by sodium hydroxide solution, and active groups were introduced by carboxymethylation reactions and acylation reactions to produce wheat straw sheets with different functional properties. Then, H_2O_2 was used as the initiator, and glue-free wheat straw-based fiberboard with zero formaldehyde was prepared by hot pressing.

2. Experimental section

2.1. Materials

The wheat straws were sourced from Yuzhong County, Lanzhou (Gansu, China) while the sodium hydroxide, hydrochloric acid, N,N-dimethylformamide, acryloyl chloride, nitrogen, chloroacetic acid, triethylamine and sodium bicarbonate were purchased from various suppliers including Wokai Biotechnology Co., Ltd (Shanghai, China), Leyline Bohua Pharmaceutical Chemical Co., Ltd (Tianjin, China), McLean Biochemical Technology Co., Ltd (Shanghai, China), Guanggang Gas Co., Ltd (Guangzhou, China), and Sarn Chemical Technology Co., Ltd (Shanghai, China) respectively.

2.2. Preparation of Glue-free Wheat Straw-based Fiberboard

2.2.1. Pretreatment of wheat straws.

Wheat straw powders were combined with sodium hydroxide solution and stirred at room temperature for 2 hours. The pH value was then adjusted to 6.0 using a HCl aqueous solution. After centrifugation, washing to neutral, filtration, drying and finely ground, alkali-treated straw powders were prepared.

2.2.2. Preparation of modified wheat straws.

N, N-dimethylformamide, triethylamine, and acryloyl chloride were mixed with alkali-treated wheat straws. Then, the reaction was carried out in a nitrogen-protected and ice-water bath for 1 h, followed by water-bath heating for 5 h. After cooling, filtering, drying, and washing with sodium bicarbonate, modified wheat straws A were produced. Powder A, deionized water, sodium hydroxide, and chloroacetic acid were mixed and reacted in a thermostatic water bath at 80 °C for 10 h, keeping the solution pH between 9 and 10, modified wheat straws B were obtained by cooling, acidifying with a hydrochloric acid solution, filtering, and then drying.

2.3. Preparation of straw glue-free sheets

Alkali-treated wheat stalks, modified wheat stalks B, A mixed B were respectively selected as the three pressing raw materials, which were pressed at 100 °C and 140 kg/cm^2 for 24 h using 2 mL of H_2O_2 as the initiator to obtain 30 mm-diameter sheets[5].

2.4 Structural characterization of the materials

2.4.1. Fourier transform-infrared spectroscopy (FT-IR) characterization.

Potassium bromide and wheat straw powder samples were thoroughly ground and compressed into tablets. The spectra were obtained using a Nicolet 380 spectrometer (Thermo Electron, America) with wavenumber ranging from 4000 to 400 cm-1.

2.4.2 X-ray diffraction (XRD) characterization.

The crystalline structure of the wheat straw powder samples was analyzed using an XRD diffractometer from Panalytical X′Pert PRO (PANalytical B.V., Holland, 40 kV, 40 mA, CuK α) in the diffraction angle (2θ) range of 7.0° to 55.0°, with a scanning rate of 0.5°/min and sampling interval of 0.02°.

2.4.3 Thermogravimetric Analysis (TGA).

The thermal properties of the wheat straw powder samples were analyzed using TGA (TG209 F3 or STA 449F3, NETZSCH, Germany). Measurements were taken under a nitrogen atmosphere, with a heating rate of 10 ℃/min from 40 ℃ to 800 ℃.

2.4.4 Scanning Electron Microscopy (SEM).

The samples were characterized using SEM (JSM 6330 F, Shimadzu, Japan) or (Sirion 200, FEI, America).

2.5. physical and mechanical properties of the straw glue-free sheets

2.5.1 The measurement of the bending strength.

The bending strength of 30mm×10mm slats made from hot compression-molded wheat straw non-wooden panels was assessed using DY35 universal material testing equipment[6]. The plates with the highest flexural strength were chosen for further mechanical research. The bending strength is calculated according to formula (1).

$$P = \frac{3FL}{2bh^2} \tag{1}$$

P is the bending strength, MPa; F is the applied pressure, N; L is across distances, mm; b is the width of the plate, mm; h is the thickness of the plate, mm.

2.5.2 The measurement of the tensile strength.

The composite panels were formed into dumbbell-shaped specimens at 23 °C for 4 hours. The specimens were preheated for 15 minutes to rectify the condition before being assessed with the DY35 Universal Material Tester. The thickness was measured at the original specimen marks at both ends and three locations in the middle to calculate the tensile strength[7]. The *tensile strength* is calculated according to formula (2). The elastic modulus was also obtained[8].

$$P = \frac{F}{bh} \tag{2}$$

P is the tensile strength, MPa; F is the applied pressure, N; b is the width of the plate, mm; h is the thickness of the plate, mm.

2.5.3 The measurement of the hardness.

A D-type Shore hardness tester was used to measure the composite plates' hardness. Seven equal points were chosen for testing, the greatest and lowest results were removed, and the sample's microhardness was determined by averaging the remaining five points[9]. The D-type Shore hardness is calculated according to formula (3).

$$HD = 100 - \frac{L}{0.025} \tag{3}$$

HD is the Shore D hardness symbol; L is the length of the press pin extension, mm.

2.5.4 The measurement of the impact toughness.

The test machine pendulum fractures the specimen in one go after it was positioned symmetrically on the support of the apparatus[10]. Impact toughness is calculated according to formula (4).

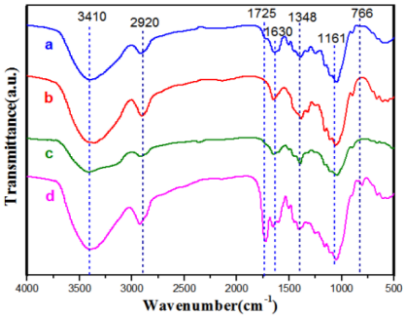
$$A = \frac{1000Q}{bh} \tag{4}$$

A is impact toughness, kJ/m^2; Q is the energy absorbed, J; b is the width of the sample, mm; h is the height of the sample, mm.

3. Results and discussion

3.1. Fourier transform-infrared spectroscopy (FT-IR) characterization

The FT-IR spectra of Straw feedstock(a), alkali-treated straws(b), acrylated modified wheat straws A(c) and acylated-carboxymethylated bimodified wheat straws B(d) were utilized to examine the molecular structure of wheat straw powders, as depicted in Figure 1. The spectrum showed several characteristic peaks: 3400 cm-1 corresponded to the O-H stretching vibration, 1600-1450 cm-1 represented the vibrations of the aromatic backbone and distinctive peak of lignin, 1630 cm-1 was associated with cellulose absorption bands, and 1350 cm-1 corresponded to the cellulose C-OH ethanol group[11-14]. Alkali treatment had no effect on the basic chemical structures of celluloses, hemicellulose, lignin in the composition of straws, but the vibration peaks of -OH were strengthened, which indicated that alkali exposed the celluloses. As can be seen from Figure 1(c), the vibration of -OH at 3400 cm^{-1} was weakened, indicating that acryloyl chloride may react with phenolic hydroxyl and some primary hydroxyl groups on straws to introduce the reactive group acryloyl groups. The absorption peak at 3400 cm^{-1} in Figure 1(d) regained strength compared to Figure 1(c), indicating that chloroacetic acid reacted with the primary and secondary hydroxyl groups on the acylated-modified wheat straws A to introduce a reactive group during esterification.



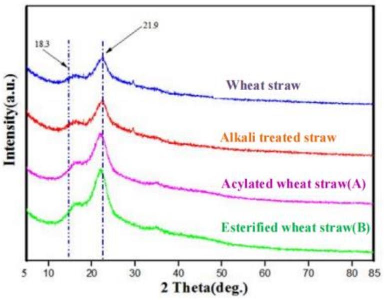


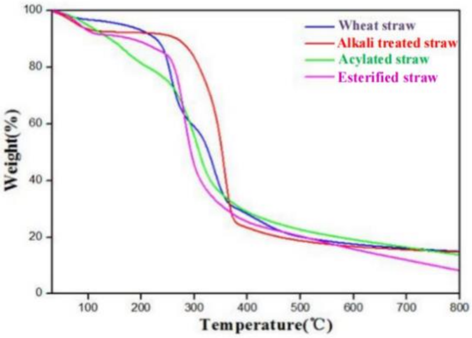
Fig. 1 Infrared spectrogram of wheat straws **Fig. 2** XRD spectra of wheat straws

3.2. X-ray diffraction (XRD) characterization

The X-ray diffraction patterns of various wheat straw powders were depicted in Figure 2. Before and after modification, the diffraction peaks were seen at 2θ=18.3° and 21.9°, respectively. Compared to untreated wheat straws, the diffraction peak at 2θ=18.3° of the alkali-treated straws showed a little enhancement, but the diffraction peak at 2θ=18.3° of acylated and esterified wheat straws became weaker, the diffraction peak at 2θ=21.9° was obviously strengthened. This showed that the celluloses in the wheat straws were liberated and their relative content in the crystalline region increased as a result of the alkali treatment, which also eliminated impurities like wax and silica, while acylation and esterification altered the crystal structure of the wheat straws.

3.3. Thermogravimetric analysis (TGA) characterization

Figure 3 displays the results of analyzing the TGA traces of several wheat straw powders to see how modifications affected their thermal conversion characteristics. About 240 ℃ was the point at which the rate of mass loss of straws began to grow dramatically. The mass loss of alkali-treated straws began to occur at a faster pace than that of unmodified straws at approximately 300 ℃. As temperature increased, acylated straws lost weight slowly and at a negligible rate of mass loss. After the esterification modification, the initial decomposition temperature was slightly raised, but the esterified straws lost the most mass in the end. This was likely due to the rise in temperature, which caused the intermolecular chemical bonds in the esterified straws to break. As a result, the molecular mass increased and the molecules were able to escape, leading to a further decrease in mass from the esterified straws.



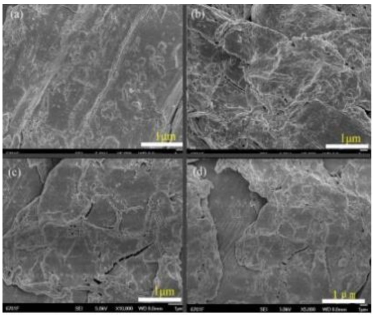


Fig. 3 TG spectrum of wheat straws **Fig. 4** SEM spectra of modified wheat straws

3.4. Scanning electron microscopy (SEM) characterization

The morphologies of different wheat straw powders of straw feedstock(a), alkali-treated straws(b), acrylated modified wheat straws A(c) and acylated-carboxymethylated bimodified wheat straws B(d) were shown in Figure 4. As illustrated in Figure 4,, the surface of wheat straw raw material had a waxy layer and was overall smooth. After alkali treatment, the waxy covering nearly totally separated, revealing the fibers, and the outer surface displayed ripping and peeling off phenomena. Wheat straws were demonstrated to have surface tissue after acylation and esterification.

Figure 5 displayed the morphology of the six different types of straw plates made with various raw materials and initiator. (1), (2) of straw plates used alkali-treated straw as the raw material, (3), (4) employed B as the raw material, and (5), (6) occupied equal masses of A and B. (1), (3), (5) were added hydrogen peroxide as the initiator, while (2), (4), (6) were thermo-pressed and molded in direct without initiator. It is apparent in plate (5) that smooth tree grain stripe is similar to in wood panels, which often have the maximum bending strength, upon reviewing a plethora of research.

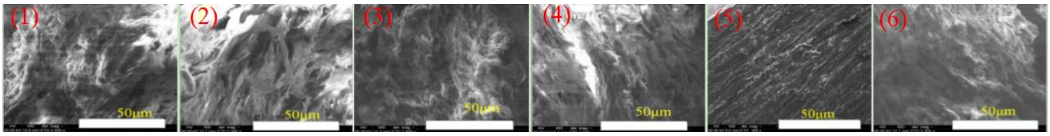


Fig. 5 SEM images of sheets, (1,2) Alkali-treated wheat stalks, (3,4) B, (5,6) A mixed B

3.5. Study on physical and mechanical properties of wheat straw glue-free sheets

The Bending strength of straw-based glue-free sheets was tested according to GB/T 9341-2008 “Measurement of Bending properties of plastics”[6], the tensile strength was tested according to GB/T 1040.2-2006 “Measurement of tensile properties of plastics”[7], the compressive strength was tested according to GB/T 1041-2008 “Measurement of compression properties of plastics”[8], the hardness was tested according to JJG1039-2008“ D-type Shore Hardness Tester”[9], and the impact toughness was tested according to GB/T 1940-2009 “Test Method for Impact Toughness of Wood”[10].

3.5.1. Bending strength.

In the order of Figure 5 above, flexural strength tests were conducted on sheets (1) to (6). As can be seen from table 1, the maximum bending strength was 95.43 MPa of sheet (5).

Table 1. Bending strength of glue-free sheets with different wheat straw sheets

samples	Apply maximum pressure /N	Plate thickness /mm	Bending strength /MPa
(1)	40.52	4.1	10.85
(2)	72.61	4.1	19.47
(3)	37.08	3.1	17.82
(4)	42.81	3.1	20.05
(5)	203.80	3.1	95.43
(6)	66.46	3.2	29.21

3.5.2. Impact toughness and Tensile strength.

Table 1 shows that sheet (5) has the best flexural strength. Three more sheets were manufactured in the same way and put through tests for tensile strength and impact toughness. Table 2 shows that maximum impact the toughness and the maximum tensile strength can attain 2.68 kJ/m^2 and 9.2 MPa, respectively.

Table 2. Sheet Impact Toughness and Tensile Strength

sample	Impact toughness /(kJ/m^2)	tensile strength /MPa
1	2.41	8.3
2	2.65	8.9
3	2.68	9.2

3.5.3. Elastic modulus and hardness.

The modulus of elasticity and hardness were measured using the sheets listed in Table 2. As can be seen in Figure 6, maximum elastic modulus can attain 1773.03 MPa and maximum hardness is 81D.

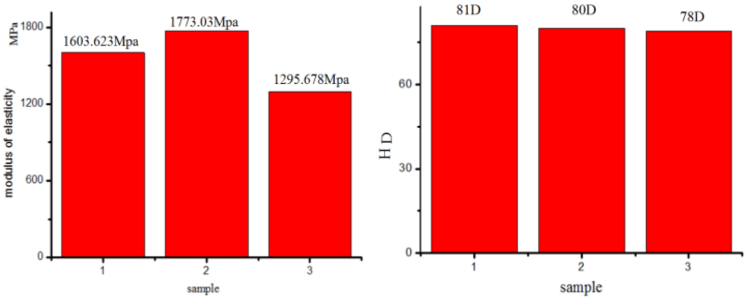


Fig. 6 Elastic modulus and hardness of wheat straw sheets

The three wheat straw raw material formulations (alkali-treated wheat stalks, modified wheat stalks B, A mixed B) were chosen, and the free radical initiation method was applied to produce glue-free wheat straw panels by hot pressing. The optimal hot pressing process parameters were as follows: hydrogen peroxide was used as the initiator, equal mass ratios of A and B were combined and hot pressed at 100 °C and 140 kg/cm^2 for 24 h. The performance of wheat straw sheets pressed with a combination of A and B was superior to that of those pressed with alkali-treated wheat straw or B straw alone. This was likely due to the chemical bond formed by the combination of A and B, ether and carbonyl groups, which created intermolecular hydrogen bonding; additionally, the cross-linking polymerization reaction resulted in a linear reticulation polymer inner chain; and finally, a distinct smooth-type tree-grain stripe which was similar to that of timber and had the highest smooth-grain strength was formed and consequently, had good physical-mechanical properties.

4. Conclusions

Wheat straws were employed to prepare glue-free wheat straw-based fiberboards with zero formaldehyde in this work, which provides a new technical approach for the economical and efficient utilization of wheat straw. Board raw materials with various functional activities were created by acylation and carboxymethylation of wheat straw and then self-bonded to produce glue-free fiberboard by hot-pressing. This glue-free wheat straw fiberboard had unique characteristics, including maximum tensile strength of 9.2 MPa, elasticity modulus of 1773.03 MPa, bending strength of 95.43 MPa, impact toughness of 2.68 kJ/m^2, and hardness of 81D, and its strength was comparable to that of conventional man-made and wood sheets, and even greater than that of the typical glueless sheets. Furthermore, glue-free straw fiberboard was environmentally benign and green because no resin adhesive is required during the hot pressing process, which can effectively reduce greenhouse gas emissions, stabilize the ecological balance, promote the sustainable development of agriculture, achieve the carbon peak of the board industry, in line with the sustainable development of ecological environmental protection, which was highly significant and had a wide market outlook.

Acknowledgments

The authors would like to thank the financial supports of fund of the National Natural Science Foundation of China (21968032, 22165025), Gansu Provincial Department of Education: Industrial Support Plan Project (2024CYZC-04), Basic scientific research expenses for central universities (31920220044, 31920230003, 31920230022, 31920230023), Provincial first-class professional construction project (2019SJYLZY-08), Innovation and Entrepreneurship Education Reform Project of Provincial School of Higher Education (2021SJCXCYXM-01, 2021SJCXCYTD-01), National College Student Innovation Entrepreneurship Training Program (202310742011). We extend our gratitude to Xinyu Lu and Fang Ren for their assistance with the experimental work, and to Ke Sun and Prof. Yanbin Wang for their invaluable discussions.

References

1. Ferrández-García A, Ferrández-Villena M, Ferrández-García C E, García-Ortuño T and Ferrández-García M T 2017 *BioResources,* Potential use of Phoenix canariensis biomass in binderless particleboards at low temperature and pressure **12** 6698-712
2. Domínguez-Robles J, Tarres Q, Alcala M, El Mansouri N E, Rodríguez A, Mutje P and Delgado-Aguilar M 2020 *Construction and Building Materials,* Development of high-performance binderless fiberboards from wheat straw residue **232** 117247
3. Dukarska D, Czarnecki R, Dziurka D and Mirski R 2017 *European Journal of Wood and Wood Products,* Construction particleboards made from rapeseed straw glued with hybrid pMDI/PF resin **75** 175-84
4. Tupciauskas R, Rizhikovs J, Brazdausks P, Fridrihsone V and Andzs M 2021 *Industrial Crops and Products,* Influence of steam explosion pre-treatment conditions on binder-less boards from hemp shives and wheat straw **170** 113717
5. Song J W et al. 2018 *Nature,* Processing bulk natural wood into a high-performance structural Material **554** 224.
6. National Plastics Standardization Technical Committee 2008 *GB/T 9341-2008Determination of flexural properties of plastics* (Beijing: China Standard Publishing House)
7. National Plastics Standardization Technical Committee 2006 *GB/T 1040.2-2006Determination of Tensile Properties of Plastics* (Beijing: China Standard Publishing House)
8. National Plastics Standardization Technical Committee 2008 *GB/T 1041-2008Determination of the compressive properties of plastics* (Beijing: China Standard Publishing House)
9. Standardization Administration of the People's Republic of China 2008 *JJG1039-2008DShore hardness tester* (Beijing: China Metrology Press)

10. Standardization Administration of China (SAC) 2009 *GB/T 1940-2009 Test Method for Impact Toughness of Wood* (Beijing: China Standard Publishing House)
11. Yang H, Yan R, Chen H, Lee D H and Zheng C 2007 *Fuel,* Characteristics of hemicellulose, cellulose and lignin pyrolysis **86** 1781-88
12. Peng X, Ye L L, Wang C H, Zhou H and Sun B. 2011 *Soil and Tillage Research,* Temperature-and duration-dependent rice straw-derived biochar: Characteristics and its effects on soil properties of an Ultisol in southern China.**112** 159-66
13. Xiao X, Chen B and Zhu L 2014 *Environmental Science & Technology,* Transformation, morphology, and dissolution of silicon and carbon in rice straw-derived biochars under different pyrolytic temperatures **48** 3411-19
14. Chen Z, Chen B and Chiou C T 2012 *Environmental Science & Technology,* Fast and slow rates of naphthalene sorption to biochars produced at different temperatures **46** 11104-111