Preparation and Performance of Wheat-straw Composite Board with Inorganic Adhesive

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With wheat-straw and inorganic binder as the major raw materials, inorganic wheat-straw composite board was manufactured by mold-pressing. The effect of wheat-straw loading on the physical and mechanical properties of inorganic wheat-straw composite board was studied. X-ray diffraction (XRD), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM) were used to characterize and evaluate the performance of the resulting composite board. Results showed that the optimal glue-straw ratio was 2.1. With the increase in glue-straw ratio during board maintenance, the inhibition effect was weaker during hydration reaction of inorganic materials. This accelerated the process of the hydration reaction in inorganic wheat-straw composite board such that the reaction was carried out more completely and produced more complete crystallization and more inorganic glue. Internal bond strength (IB) and thermal stability of inorganic wheat-straw composite board increased gradually, while TS decreased. Modulus of rupture (MOR) and modulus of elasticity (MOE) firstly increased and then decreased. In summary, the bonding interface between wheat-straw and inorganic adhesive performed well.

Keywords: Inorganic binder; Wheat-straw composite board; Physical and mechanical property; Glue-straw ratio; Thermal stability

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INTRODUCTION

The annual production of crop-straw is approximately 700 million tons in China. However, most of the straw is burned immediately or abandoned, resulting in serious environmental pollution (Yu *et al.* 2005; Wang *et al.* 2010). As a natural biomass, cellulose and hemicellulose contents in crop straw, including rice straw and wheat-straw stalks, are very close to those of wood and are suitable for the preparation of composite board. From an economic perspective, the utilization of such agricultural residuals helps to increase the value of crop straw and benefits local farmers. At present, wood-based panel made from crop-straw commonly uses expensive isocyanate (MDI) and other organic adhesives, limiting its manufacture, development, and application, which greatly restricts value-added utilization and development of crop straw panels (Russell 1996; Bowyer and Stockmann 2001; Okino *et al.* 2005; Olorunnisola and Adefisan 2007).

Inorganic wheat-straw composite board is a biomass-based composite board made by cold mold-pressing using straw residues, inorganic adhesives, and a small amount of additives. Because of its advantages—high strength, flame retardance, insect-resistance, no free formaldehyde release, and energy savings—inorganic wheat-straw composite board has the potential to replace current wood-based panel and can be widely used in furniture manufacturing, indoor and outdoor decoration, and many other fields. Due to a decrease in the availability of wood resources nowadays, developing the crop-straw panel industry can help to convert waste materials to useful resources, create economic and social benefits, and is also in accordance with energy conservation and environmental protection requirements (Rowell 1996; Zhang *et al.* 2000). However, research about inorganic wheat-straw composite board is rarely carried out.

In this paper, inorganic adhesive was prepared with magnesium chloride, oxide magnesium, sodium silicate, sodium phosphate, and ferrous sulfate. After cold-pressing and the mold-pressing process, this inorganic adhesive could be mixed with wheat-straw to form inorganic wheat-straw composite board. The effects of the glue-straw ratio on the physical and mechanical properties of inorganic wheat-straw composite board were studied. X-Ray diffraction (XRD), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM) were used to analyze influencing mechanism of ingredient, providing the theory and technical support for the development of inorganic wheat-straw composite board.

EXPERIMENTAL

Preparation of Inorganic Wheat-straw composite board

The inorganic adhesive used for the composite board was created in the authors' laboratory and is currently patent pending (international and Chinese); for this reason, the specific chemical composition (reagent proportions) are not given here. Briefly, a certain amount of magnesium chloride, magnesium oxide, sodium silicate, sodium phosphate, and ferrous sulfate were mixed with a proportional amount of water and polyvinyl alcohol, and stirred constantly for 20 min. To prepare inorganic wheat-straw particle-board, the inorganic adhesive, and wheat-straw were proportionally mixed in a cycle mixer, stirring fully for 4 min, and then formed into mats manually in molds. These mats were packed and sent to the cold press under a pressure of 5 MPa for 48 h. The packages were then mechanically compacted using several molds for 7 days, followed with oven drying in 80 °C until the moisture content decreases to approximately 10%. The final dimension and density of the obtained board was 300 x 300 x 12 mm^3 and 1.0 g/cm^3, respectively. With an intention to better understand the physical and mechanical performance, proportions of inorganic adhesive to wheat-straw in mass was set to 2.0, 2.1, and 2.2 based on the authors' previous work.

Chemical Composition Measurement

Wheat-straw was collected from Henan Province, China. The moisture content of the straw particle was about 11% after hammer mill processing. Proportion distribution of fiber length for these straw particles was calculated using a vibration sieve, and detailed values are as follows: under 1-mm accounted for 10.7%, approximately 1 to 3-mm for 35.4%, approximately 3 to 5-mm for 43.1%, approximately 5 to 10-mm for 8.3%, over 10-mm for 1.5%. Magnesium chloride, magnesium oxide, sodium silicate, sodium phosphate, ferrous sulfate, and polyvinyl alcohol were chemically pure, and used without any purification. The average molecular weight of polyvinyl alcohol is approximately 16,000 to 20,000.

Characterization

According to the Chinese national GB/T 24312-2009 standard of cement particle board, the modulus of rupture (MOR), modulus of elasticity (MOE), internal bond strength (IB), and 24 h absorbent thickness expansion rate (TS) of wheat-straw particle-board samples were characterized using a DCS-R-100 universal mechanical testing machine (Shimadzu, Japan). X-ray diffraction was carried out on a XD-2 ray diffractometer (Persee, China). The Cu Kα X-ray source (λ=0.154 nm) was set to 40 kV and 35 mA. Samples were examined over the angular range of 50° to 70°, at a scanning rate of 10°/min. The morphologies of fracture section of inorganic wheat-straw particle board and surface analyses were observed using Quanta 450 scanning electron microscope (FEI Company, USA), at a testing voltage of 15 kV. The thermal stability of wheat-straw particle board was investigated using a thermogravimetric analyzer (TGA) and differential scanning calorimeter (DSC) (NETZSCH, Germany) in a nitrogen atmosphere. TGA adopted a continuous heating method in a testing heat of 50 to 600 °C and heating of 10 °C/min. The samples were tested in DSC in a testing heat of 600 °C.

RESULTS AND DISCUSSION

Mechanical Properties Analysis

The physical and mechanical properties of inorganic wheat-straw composite board with different glue-straw ratios are shown in Fig. 1. Figure 1(a) shows that the MOR and MOE of inorganic wheat-straw composite board increased at first and then decreased with the increase in glue-straw ratio. When the glue-straw ratio was 2.1, the MOR and MOE peaked at their maximum value of 15.7 MPa and 4040 MPa, respectively. The results indicated that wheat-straw in the inorganic wheat-straw composite board played a significant reinforcement role for the inorganic adhesive system. When the wheat-straw was at lower loadings, wheat-straw and inorganic adhesive had a good cross-linking enhancement effect and suffered from stress failure effectively, which was helpful to increase the MOR and MOE of the inorganic wheat-straw composite board. However, when the addition of wheat-straw fiber was excessive, the inorganic adhesive was not able to surround wheat-straw fully, and the interfacial adhesion declined remarkably, which subsequently affected the transferring of stress. Meanwhile, when the additive amount was too much, wheat-straw would clot in the board and be unevenly distributed, which would cause localized stress concentrations. The destruction of the small force could cause a lot of cracks and extend broadly to weak boundary layers, which affected the MOR and MOE of the board accordingly.

It is shown in Fig. 1(b) that internal bond strength (IB) of inorganic wheat-straw composite board would increase with the growth of the glue-straw ratio. When the glue-straw ratio increased from 2.0 to 2.2, IB was up to 0.86 MPa from 0.55 MPa, with an increase of 56.4%. However, TS would decrease with the growth of glue-straw ratio. When the glue-straw ratio increased from 2.0 to 2.2, TS decreased from 3.0% to 1.3% with a decrease of 56.7%. This could mean that IB and TS of inorganic wheat-straw composite board depended on the amount of binding material. The more the amount of binding material, the higher IB of composite board would be. As a result, higher IB contributed dramatically to the inhibition of water absorption expansion for these boards. With the increase of glue-straw ratio, inorganic elements in the glue would react more completely, which would increase the reaction velocity of hydration reaction. In this process, binding material would increase greatly with increasing reaction time. Therefore, IB increased and TS decreased gradually, when the glue-straw ratio increased from 2.0 to 2.2.

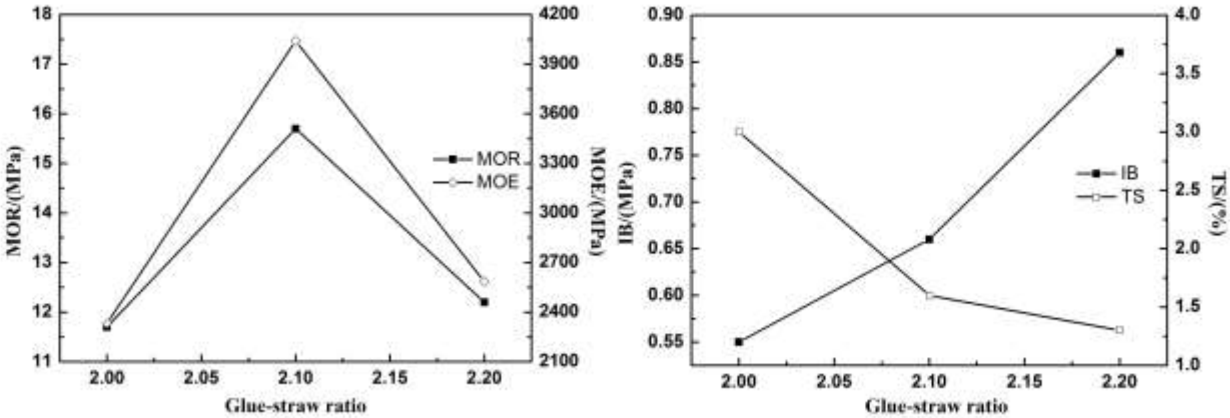

Fig. 1. Physical and mechanical properties of inorganic wheat-straw composite board

Scanning Electron Microscopy (SEM) Analysis

Figure 2(a), 2(b), 2(c) are scanning electron micrographs on the fracture surface for inorganic wheat-straw composite board when adhesives and straw rates are 2.0, 2.1, and 2.2, respectively. Figure 2 shows that when adhesives and straw ratios were over 2.0, straw debris could distribute uniformly in inorganic adhesives and be wrapped by glue. Meanwhile its cross-section was smooth. When straw ratio was 2.0, there were a lot of holes in the cross-section and its surface became uneven. Without sufficient glue material wrapping, the poor bonding conditions existed in the interface between the straw particle and inorganic adhesive (Wang *et al*. 2011). Minor external forces could pull the straw debris from inorganic adhesive, which hampered particles from playing an effective role in enhancing physical and mechanical properties (Wang *et al.* 2009). This result was consistent with the results of mechanical properties of this composite board physical analysis.

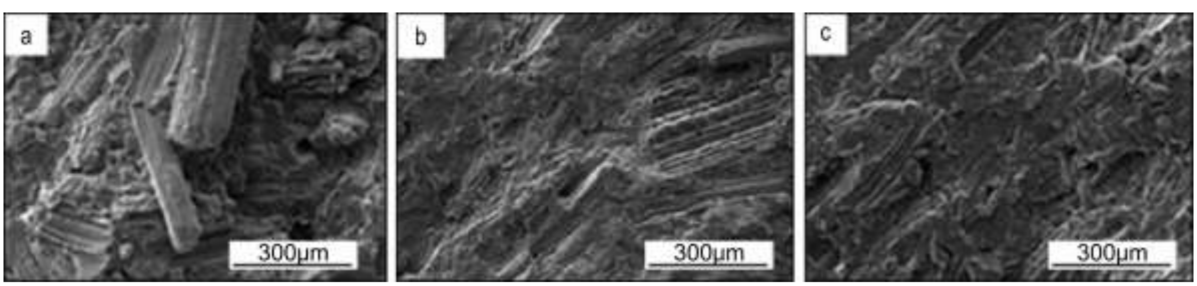

Fig. 2. SEM images of inorganic wheat-straw composite board fracture surface

X-ray Diffraction (XRD) Analysis

Figure 3 shows the XRD patterns of inorganic wheat-straw composite board with different glue-straw ratios. Figure 3 shows that the diffraction peak intensity of inorganic adhesives would increase when the glue-straw ratio in straw adhesives rose from 2.0 to 2.2. When the additive amount of wheat-straw particle was reduced, the degree of hydration reaction became completed gradually in the slab curing process and it would produce more bonding materials and resulted in more completed crystalline grain (Li *et* *al*. 2003; Qing *et al*. 2011; Yu *et al*. 2012). Hence, more network structures of high strength could be formed in this composite board. The IB of inorganic straw particle board increased gradually, and TS decreased correspondingly. These results validated the mechanical properties of inorganic wheat-straw composite board physical analysis further.

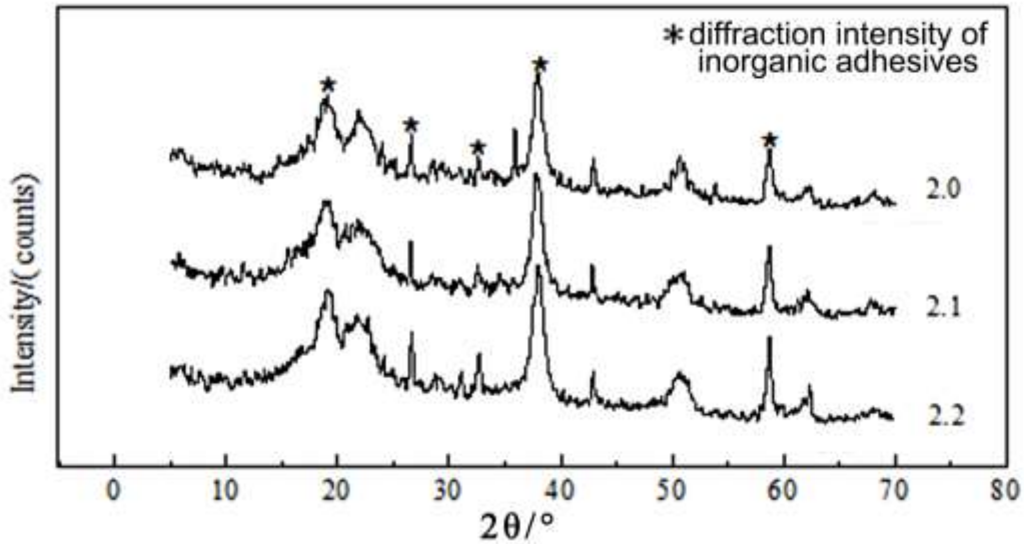

Fig. 3. XRD spectra of inorganic wheat-straw composite board

Thermal Gravimetric (TG) Analysis

Figure 4 shows the TG and DTG curves of inorganic straw particle board of different glue-straw ratios. It is shown in Fig. 4(a) that the weight-loss rate of inorganic wheat-straw particle board grew with the increase of temperature. According to Fig. 4, the weight loss process in inorganic wheat-straw particle board mainly included five stages.

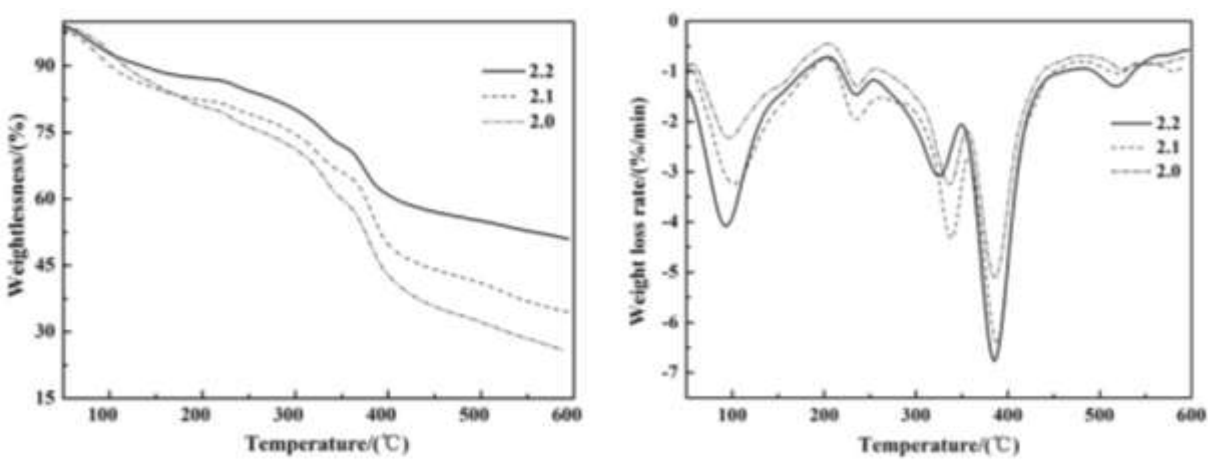

Fig. 4 TG(a) and DTG(b) curves of inorganic wheat-straw composite board

When the temperature was around 100 °C, adsorbed water began to evaporate, and the behavior of weight loss occurred. When the temperature was up to 235 °C, the hemicelluloses and partial cellulose of straw debris in the inorganic particle board started to pyrolyze, and slight weight loss occurred. When the temperature reached 337 °C, most of the cellulose and lignin of straw scrap started to pyrolyze, and crystalline water in inorganic adhesives began to break down. Therefore, the weight loss became obvious. The rest of the cellulose pyrolyzed completely when the temperature was around 387 °C. Meanwhile, the remaining crystal water in the inorganic adhesive would gradually be pyrolyzed. The inorganic adhesive crystalline phase began to change, in which phase weight-loss and weight-loss rate increased significantly. When the temperature was up to 518 °C, all remaining lignin in the straw scrap was beginning the pyrolytic and crystalline phase of inorganic adhesive changes. Comparatively, the weight loss in this stage was less obvious.

Table 1 reports the weight loss of different stages in wheat-straw composite board with various glue-straw ratios. It can be found that the higher the glue-straw ratio, the smaller the weight loss rate of the composite board would be. With more straw fiber in straw composite board, it was easier to pyrolyze the straw composite board than the inorganic adhesive. The increase of glue-straw ratio led to the decrease of the mass loss rate of the inorganic straw particle board. This might be caused by the increase of dispersion uniformity of straw particle in straw composite board, and it resulted in good interfacial bonding performance between the wheat-straw debris and inorganic adhesive. When wheat-straw debris started to pyrolyze, it needed to overcome greater interfacial resistance. Therefore thermal stability of straw particleboard is increased.

Table 1. Weight Loss Rate in Various Stages of Inorganic Wheat-straw composite board

Glue-straw ratio	Weight loss ratio（%）				
	100 (°C)	235 (°C)	337 (°C)	387 (°C)	518 (°C)
2.2	8.0	14.5	25.8	37.2	45.7
2.1	8.0	19.6	32.8	45.9	60.5
2.0	10.0	22.8	36.5	53.1	69.8

Differential Scanning Calorimetry (DSC) Analysis

Figure 5 shows the DSC curves of inorganic straw composite board, of different glue-straw ratios.

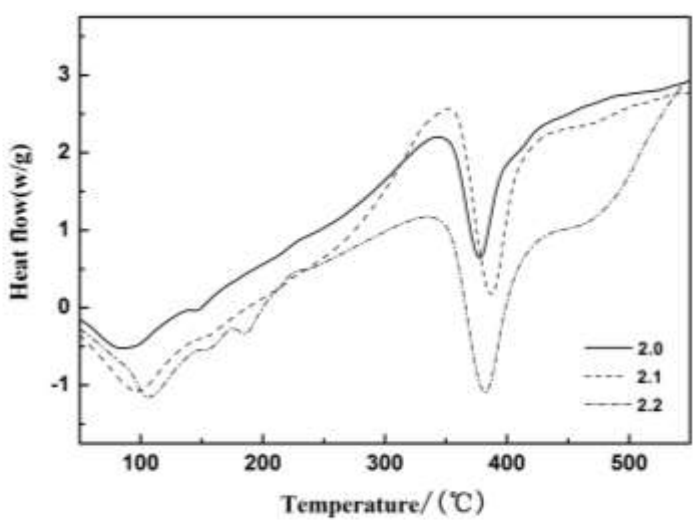

Fig. 5. DSC Curve of inorganic wheat-straw composite board

It is shown in Fig. 5 that the dehydration valley of hydration products of inorganic adhesive (387 °C) gradually increased with the growth of glue-straw ratio. This might mean that the increase of glue-straw ratio accelerated hydration reaction of the slab in the curing process, which brought about more hydration products of adhesive and more complete crystalline solids. As it was mentioned above, due to the growth of glue-straw ratio, inorganic elements in the glue reacted more completely, which increased the reaction velocity of hydration reaction (Lou *et al.* 1999; Qiao *et al.* 2012). In this process, the amount of binding material increased greatly with increasing reaction time. The result was consistent with X-ray diffraction analysis.

CONCLUSIONS

1. With the increase of glue-straw ratio, the inhibition effect weakened in the hydration reaction of inorganic materials. It accelerated the hydration reaction in wheat-straw composite board, resulting in more complete crystallization, and inorganic glue was produced in this reaction.
2. With a greater glue-straw ratio, the properties of the wheat-straw interface performed better. The interface friction also improved, and thermal stability of the plate was strengthened.
3. With a greater of glue-straw ratio, the MOR and MOE of wheat-straw inorganic wheat-straw composite board first increased and then decreased. Meanwhile, IB increased gradually, but TS was always decreasing, considering that the optimization of glue-straw ratio was 2.1.

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