Thermal Stability and Bonding Mechanisms of Corn Stalk Rind

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Removing the epidermis of corn stalk rind can remarkably improve its bonding properties. This study aimed to determine the plate-making process by using intact corn stalk rind and thus utilize the crushed, removed epidermis. The thermal stability of corn stalk rind was investigated before and after removing the epidermis and gluing of the material using the hyphenated technique by simultaneous thermal analysis (STA), Fourier transform infrared spectroscopy (FT-IR), and gas chromatography-mass spectrometry (GC-MS). The results showed that the epidermis of corn stalk rind, from 90 °C to 200 °C, was conducive to softening the lignin in corn stalk rind and solidifying it as an adhesive. When the temperature was higher than 220 °C, the rate of weight loss rapidly increased and the thermal decomposition of hemicelluloses and cellulose in corn stalk rind after gluing was accelerated. The bonding process of corn stalk rind and adhesives is extremely complex, and intricate physical and chemical changes occur. Adhesive filled the surface cracks and depressions on the corn stalk rind, which not only improved its thermal stability, but also fixed corn stalk rind by forming connections.

Keywords: Corn stalk rind; Epidermis; Thermal stability; Bonding mechanism

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INTRODUCTION

Corn straw is abundant in China, but its value in use is low (Wang *et al*. 2014). Separating components of corn stalk rind, stalk, and leaves, and using them for different purposes are effective ways to improve the added value of resource utilisation (Zeng *et al*. 2012a, 2012b). Corn stalk rind, as the main component of corn stalk, and showing similar fibre morphologies as wood, has high mechanical strength and is used as a substitute raw material for timber in producing nonstructural plates (He *et al.* 2016a). The SiO_2 compound material in the epidermis of corn straw rind is not conducive to good bonding (Akgul *et al.* 2010). In general, corn straw rind is pulverised to produce chip or particle board, but the complex processes required for treating such raw materials, and the associated high energy consumption, hamper production (Zhang *et al.* 2012). Due to SiO_2 compound material's presence in the epidermis of corn stalk rind, the flexural strength, thermal stability, and hydrophobicity are improved, and thus the epidermis needs to be removed in plate-making when using intact corn stalk rind (Ashori and Nourbakhsh 2008), thus justifying this research.

Since the 1940s, research relating to bonding mechanisms has covered adsorption theory, electrostatics, diffusion theory, chemical bonding theory, mechanical bonding theory, weak interface layer theory, and rheology of such adhesives (Banik *et al.* 2003). Bonding is a process connecting an adhesive and the surfaces of bonded objects to form stable mechanical strength and adhesive forces (Song *et al.* 2014). The formation of a bonding force is distinct for different kinds of adhesive and bonding materials, as well as bonding processes. The bonding process, as a complex physico-chemical process, includes many other processes, such as liquefaction, sliding, wetting, solidification, deformation, and failure of different kinds of adhesives. Therefore, no bonding theory can directly explain all bonding phenomena until now (Zhao *et al.* 2012). As for crop stalk, it is obvious that bonding processes are complex because of the variety of crop straws and its complex varieties, along with cropping system effects. The changes in corn stalk rind and its thermal stability after bonding reflects one of the main characteristics of hot-press moulding, such as the range of hot-pressing temperatures, time, and the selection of adhesive type (Li *et al.* 2009; Xu *et al.* 2009; He *et al.* 2016b).

Therefore, this study investigated the changes of thermal stability of corn stalk rind before and after removing the epidermis. An assay of the components of thermal decomposition of corn stalk rind after gluing was undertaken using the hyphenated technique by simultaneous thermal analysis (STA), Fourier transform infrared spectroscopy (FT-IR), and gas chromatography-mass spectrometry (GC-MS). Furthermore, through scanning electron microscopy (SEM) observation, the bonding mechanisms of corn stalk rind, after removing the epidermis, were studied, and the physico-chemical changes in corn stalk rind and adhesives in hot-press moulding were analyzed. This provides both theoretical and technical bases for selecting methods for removing the epidermis from corn stalk rind and the optimal ranges of hot-press temperature and other process conditions for plate-making.

EXPERIMENTAL

Materials

The corn stalk rind of the Xianyu 335 variety planted in Maozhuang Farm, Henan Agricultural University, Zhengzhou, China was used in this experiment. Disease-free corn stalks with a root diameter of 25 mm to 30 mm and 2,000 mm-long stems were selected. The experimental materials were divided into three groups and treated as corn stalk rind with the epidermis removed, epidermis of corn stalk rind, and corn stalk rind with 5% gluing. Polymeric diphenylmethane isocyanate (pMDI) was used as the adhesive with a solid mass fraction of 60% ± 1%, Brookfield viscosity of 10,000 MPa·s to 13,000 MPa·s (25 °C), and a pH of 6.6 to 7.5.

Methods

Thermogravimetric experiment

The three samples, *i.e.* the epidermis of corn stalk rind, corn stalk rind without epidermis, and corn stalk rind after gluing were ground, screened, and then adjusted to the same gravimetric water content. Then, 10 mg of each sample were weighed at 30 °C. The experiment was conducted in N_2 and the temperature was raised to 900 °C at a rate of 20 °C/min. The temperature of the gas cell and transmission pipeline was 290 °C, and the gas flow rate was 70 mL/min.

Measuring the products of thermal decomposition

Both STA-IR-MS on-line and STA-IR-GCMS off-line analyses were conducted on 10 mg samples of corn stalk rind after gluing (Clarus; 600/600T, Perkin-Elmer, Waltham, USA). The STA-IR-MS on-line analysis was performed in N_2 and the temperature was raised to 900 °C at 20 °C/min. The temperature of the gas cell and transmission pipeline was 290 °C, and the ionization mode was 70 eV electron bombardment. Furthermore, the gas flow rate, scanning range, and temperature of the ion source were 70 mL/min, 30 amu to 450 amu, and 230 °C, respectively. The conditions for STA-IR-GCMS off-line analysis were as follows: N_2 was used as the atmosphere, and the temperature was raised to that used for sampling (maintained for 2 min to 4 min) at 20 °C/min and then to 900 °C at 40 °C/min. The temperature of the gas cell and transmission pipeline was 290 °C and the gas flow rate was 70 mL/min. In addition, as under GC-MS conditions, the Elite-5MS chromatographic column (30 m × 0.25 mm × 0.25 μm) (Clarus; 600/600T, Perkin-Elmer, Waltham, USA) was used with the temperature programming set to preserve the sample at 40 °C for 1 min, before increasing the temperature to 290 °C at 10 °C/min. The scanning range and temperature of the ion sources were 30 amu to 450 amu, and 230 °C, respectively, and 70 eV electron bombardment was used as the ionization mode.

SEM observation

The epidermis of corn stalk rind was removed and then uniformly sized with 5% adhesive (wt. %). The hot-press table was subjected to a force of 100 kN, the adhesive was completely solidified, and the laminated veneer lumber samples of corn stalk rind were made when the heating temperature of the mold, the loading velocity, and target density of the plates were 170 °C, 2 mm/min, and 0.610 g/cm^3, respectively.

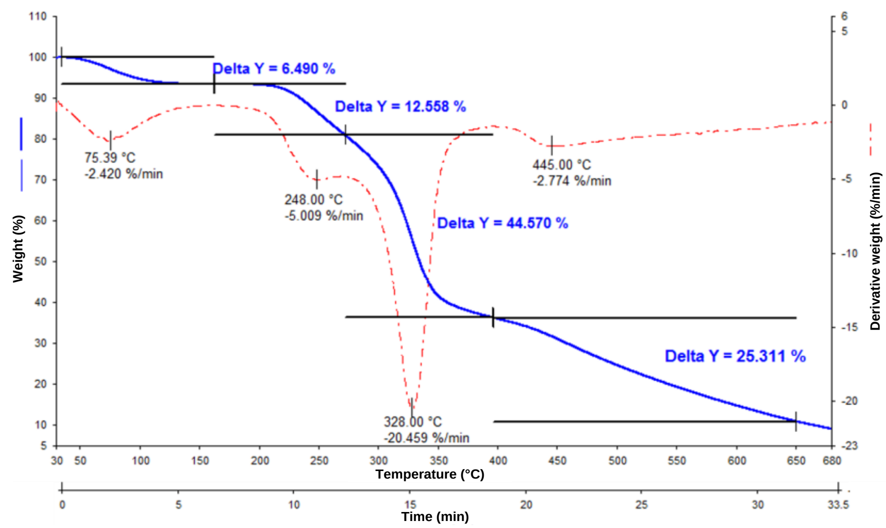
The samples were fixed on a sample table using double-sided adhesive tape, marked, and then gold-sprayed in a vacuum-sputtering process. The samples were then examined under the microscope (-3400N, Hitachi, Tokyo, Japan).

RESULTS AND DISCUSSION

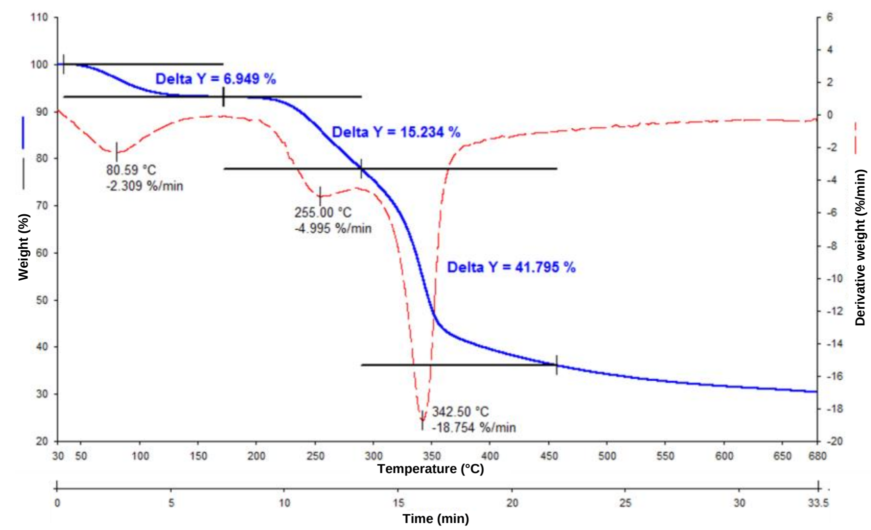
Pyrolysis characteristics of Corn Stalk Rind Before and After Removing the Epidermis and Gluing

Figure 1 shows the pyrolysis characteristics of corn stalk rind, the epidermis of corn stalk rind, and corn stalk rind after gluing. The combustion of crop stalks can be divided into four stages, including desiccation, thermal decomposition of hemicelluloses and cellulose, and carbonisation (Faborode and O'Callaghan 1986). The thermal gravity (TG) curve decreased slowly during the desiccation process, while the differential thermal gravity (DTG) curve reached its first peak during the thermal decomposition of hemicelluloses. In the thermal decomposition of the cellulose, the TG curve was extremely steep, while the global maximum appeared on the DTG curve. Furthermore, carbonisation, when the lignin is burnt to form coal and ash, caused the TG and DTG curves to return to their previous smooth form.

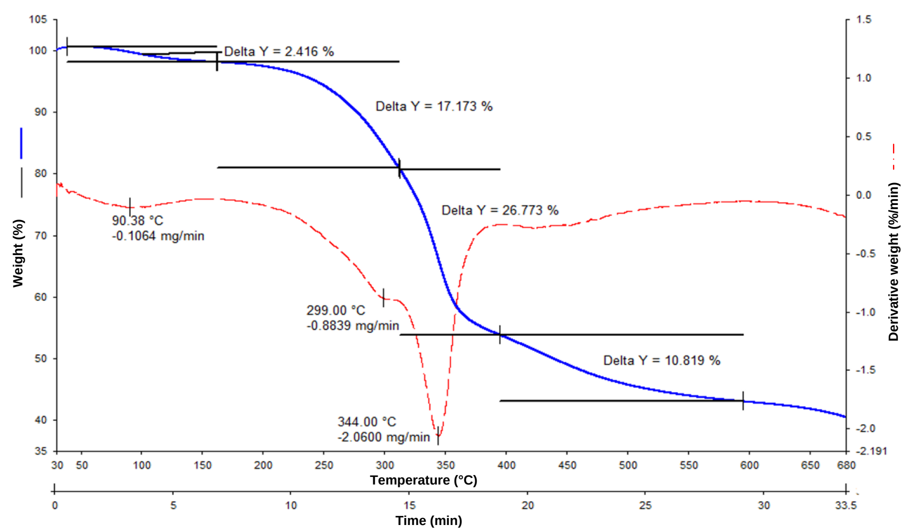
According to the TG-DTG pyrolysis characteristic curve, the three samples underwent similar pyrolysis processes and showed four weight loss steps and two large weight loss points. Two large weight loss points of corn stalk rind with the epidermis removed appeared at 248 °C and 328 °C, while those of the epidermis alone occurred at 255 °C and 342.5 °C, respectively. Moreover, corn stalk rind after gluing showed two large weight loss points at 299 °C and 344 °C, separately.



a) After removal of the epidermis



b) Epidermis of corn stalk rind



c) After gluing

Fig. 1. Pyrolysis characteristics of corn stalk rind

In the first weight loss step, the weight losses of corn stalk rind with epidermis removed, epidermis of corn stalk rind, and corn stalk rind after gluing were 6.49%, 6.95%, and 2.42%, respectively, with mostly water being lost. While the weight losses in the second step were 12.6%, 15.2%, and 17.2%, respectively, which mainly represented the thermal decomposition of some hemicelluloses. In the third weight loss step, each DTG curve of the three samples demonstrated a shoulder peak that denoted the main pyrolysis characteristics of woody biomass, as opposed to that seen with herbaceous biomass specimens (Magdziarz and Wilk 2013). Then, thermal decomposition and combustion of hemicelluloses and cellulose were superimposed and the largest peak appeared at temperatures of greater than 300 °C on the DTG curve. In the weight loss interval from 220 °C to 290 °C, the weight losses of corn stalk rind with the epidermis removed, epidermis, and corn stalk rind after gluing were 44.6%, 41.8%, and 26.8%, respectively.

Based on the above analysis, by comparing the three samples, the peak for the corn stalk rind after gluing appeared at the highest temperature and the rate of weight loss was at a minimum during heating combustion. However, the rate of weight loss of the epidermis of corn stalk rind was smaller than that of corn stalk rind with the epidermis removed. The bonding of adhesive and corn stalk rind increased the ignition temperature and thermal stability of corn stalk rind, and reduced the amount of thermal decomposition of the hemicelluloses and cellulose. The range of hot-pressing temperatures was determined to be less than 200 °C. This was not only conducive to decreasing the thermal decomposition of the hemicelluloses and cellulose in the bonding and solidifying of corn stalk rind, but also could reduce the separation of organic components in the adhesive. In addition, the epidermis of corn stalk rind could be used as a material for improving the fire-resistance, to reduce production costs, and improve the usability of such plates.

Components of Thermal Decomposition of Corn Stalk Rind after Gluing

In the hot-press bonding process, temperature-related factors significantly affect the properties of the adhesive (Sernek and Kamke 2007). In this study, the physical and chemical changes in the corn stalk rind and adhesive during hot-press bonding need to be analyzed, as well as determine the corn stalk rind properties, and select the control ranges for process factors such as the hot-pressing temperature. For this purpose, according to the results in Fig. 4, the products at four weight loss points (30 °C, 90 °C, 299 °C, and 344 °C) of corn stalk rind after gluing were fed into a GC-MS system to capture pyrolysis products at weight loss points for GC-MS analysis and the detected material components were analyzed.

Figure 2 shows the infrared spectra of gases produced by corn stalk rind after gluing, as collected at 30 °C and 90 °C. After analysis, the first wave peak appeared at approximately 90 °C, mainly describing the dissipation of H_2O and the separation of some of the CO_2.

Figures 3 and 4 show the FT-IR spectra and GC-MS chromatogram of corn stalk rind after gluing at 299 °C and 344 °C. By conducting a FT-IR analysis of the gases produced by corn stalk rind after gluing at two weight loss points (299 °C and 344 °C), the corn stalk rind is seen to have been combusted more violently at 344 °C. Moreover, acid-, or ester-stretching vibration appeared at between 1100 cm^{-1} to 1200 cm^{-1}, while the stretching vibration of the C=C functional group was seen at around 1600 cm^{-1}. Moreover, the stretching vibration of ketones, esters, or acids is seen at around 1700 cm^{-1} and that of C≡O or C≡N functional groups appears at around 2200 cm^{-1}.

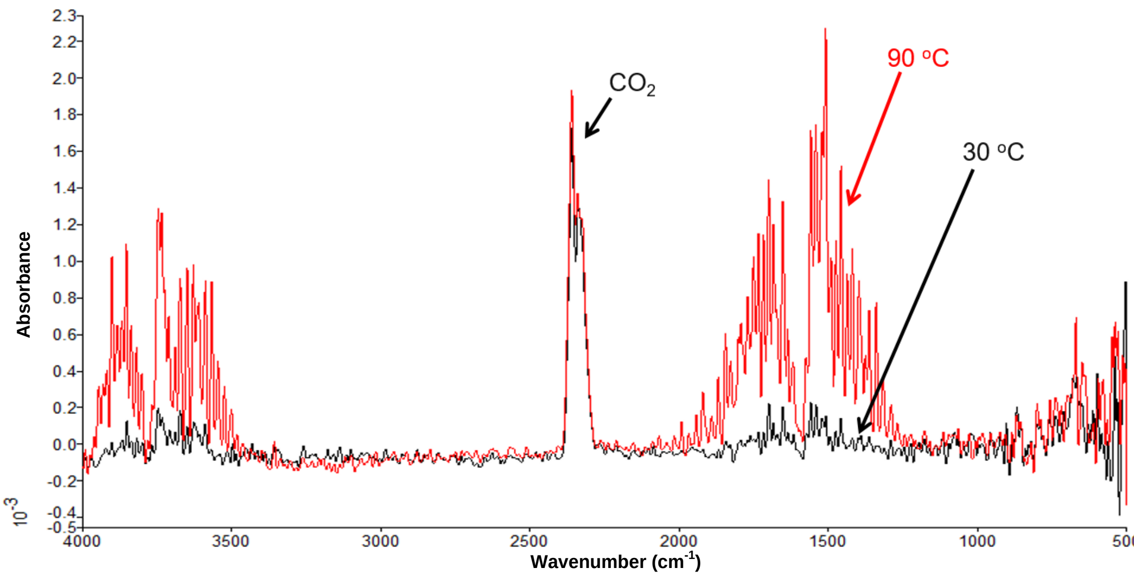


Fig. 2. The FT-IR spectra of corn stalk rind after gluing at 30 °C and 90 °C

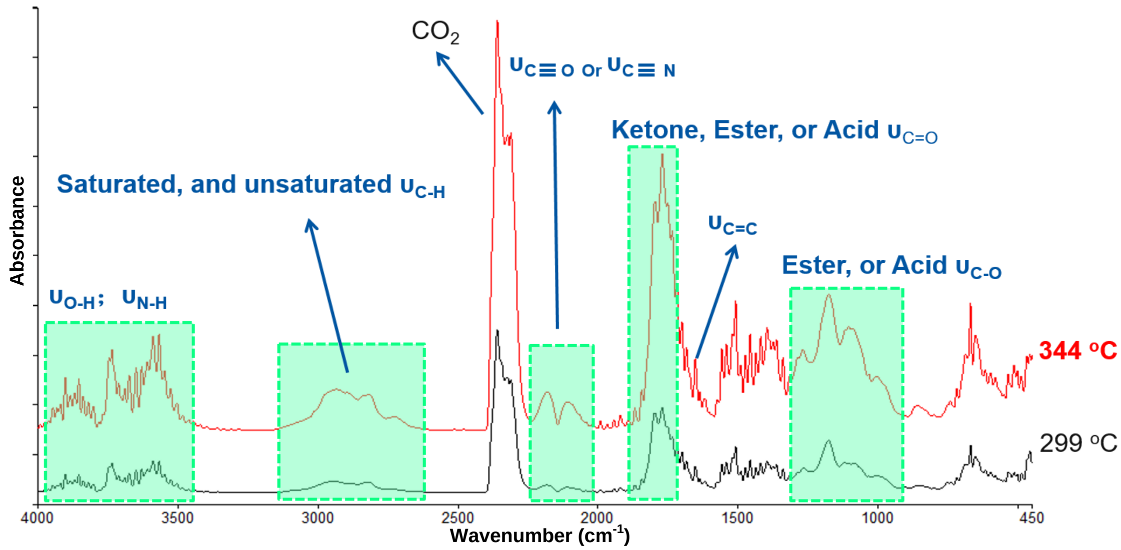


Fig. 3. The FT-IR spectra of corn stalk rind after gluing at 299 °C and 344 °C

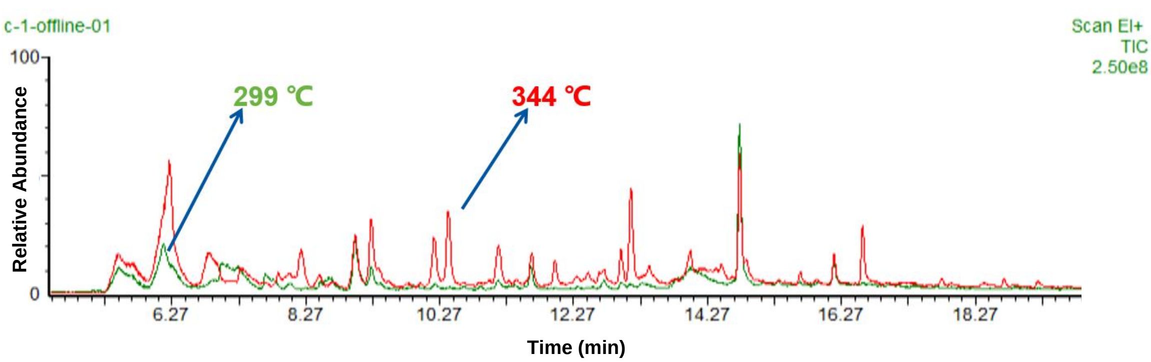


Fig. 4. GC-MS chromatogram of corn stalk rind after gluing at 299 °C and 344 °C

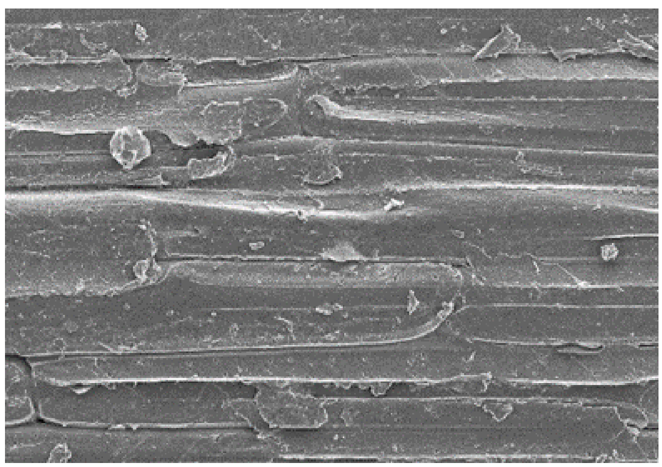
The stretching vibration of saturated and unsaturated C-H functional groups is observed in the vicinity of 2800 cm^{-1}, and O-H and N-H functional groups exhibited stretching vibrations between 3500 cm^{-1} and 4000 cm^{-1}.

The main components produced in this process were passed to the National Institute of Standards and Technology (NIST) library for qualitative analysis, and the main components produced in the thermal decomposition of corn stalk rind after gluing were obtained. Through analysis, the weight loss of corn stalk rind after gluing occurred at around 299 °C and 344 °C, mainly releasing micro-molecules, such as: CO_2, CO, and H_2O, as well as organic substances such as squalene, acetic acid, furfural, furfuryl ester, and phenol.

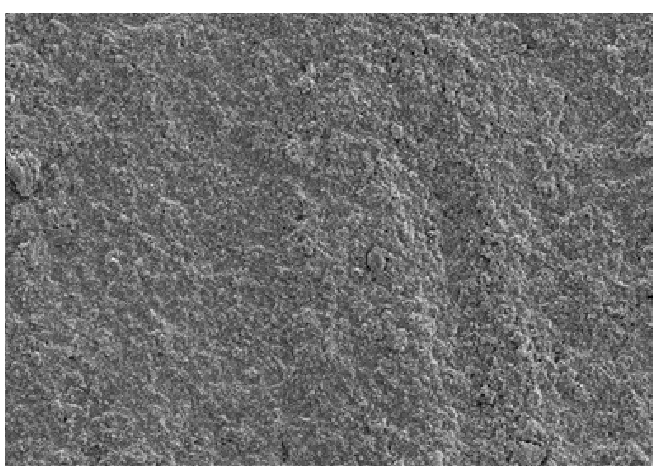
Based on the above analysis, in the hot-pressing of corn stalk rind after gluing, a temperature between 90 °C and 200 °C was favourable to the softening of lignin and solidifying of the adhesive in corn stalk rind. When the temperature was higher than 220 °C, the rate of weight loss increased rapidly, accelerating the thermal decomposition of the hemicelluloses and cellulose in the corn stalk rind after gluing.

Bonding Performances of Corn Stalk Rind with the Epidermis Removed

Figure 5 shows the micro-morphologies of corn stalk rind before and after gluing.



(a) Before gluing (×500, 100 μm)



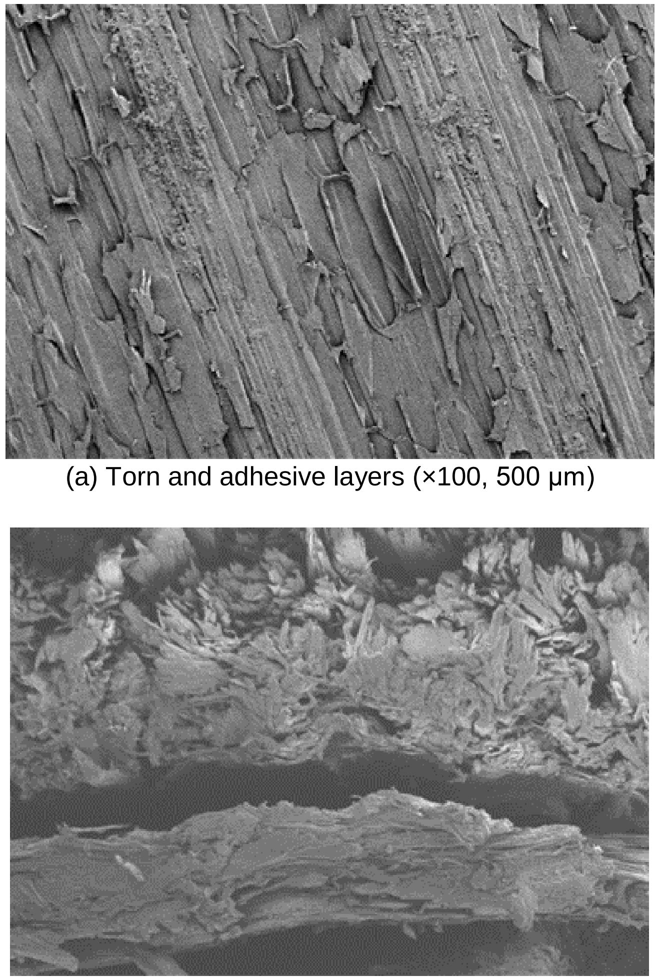
(b) After gluing (×200, 200 μm)

Fig. 5. Microscopic observation of the surface of corn stalk rind

Parts (a) and (b) of the figure show that corn stalk rind with its epidermis removed had a rough surface and adhesive filled the grooves and gaps in the surface of the corn stalk rind after gluing. Based on adsorption theory, the bonding effects of corn stalk rind and adhesive were caused by mutual adsorption of polar molecules of adhesive and corn stalk rind on interfaces and were the results of the joint effects of physical and chemical adsorption (Li *et al.* 2009). In the first stage, adhesive was moved and diffused to the surface of corn stalk rind through Brownian motion, drawing their polar groups or molecular chains closer to each other. In this process, increasing temperature, decreasing adhesive viscosity, or rising contact pressures were conducive to Brownian motion (He *et al.* 2016a). In the second stage, under the effects of pressure and temperature, intermolecular force, namely Van der Waals' force, was produced when the distance between molecules of adhesive and corn stalk rind was less than 10 Å. Based on the relationships between bonding energy and molecular dipole moment, polarisability, molecular ionisation energy, intermolecular distance, and thermodynamic temperature, the larger the polarity of the adhesive and corn stalk rind, the closer their mutual contact, and the greater the adsorption, thus physical adsorption exerted a greater effect on the bonding strength.

The microstructure of the torn and damaged adhesive layers of laminated veneer lumber made from corn stalk rind is shown in Fig. 6(a): adhesive filled the cracks and depressions in the corn stalk rind and bonding in the form of glue nails was produced on the surface of corn stalk rind to play the role of an anchoring or fastening effect. However, the bonding force was smaller than the binding force between fibrous tissues in the corn stalk rind, and thus bonding interfaces in the laminated veneer lumber made of corn stalk rind were damaged, but the fibrous layers in the corn stalk rind were not torn in otherwise damaged areas. According to mechanical bonding theory, it is considered that meshing connections or casting anchor effects caused by solidification of adhesive appear in interface areas. The adhesive force is related to pressure, the concave-convex height of the material surface, and frictional forces. The theory attributes the bonding effects to the mechanical adhesion that is irrelevant to the infiltration and intermolecular forces. With regard to wooden materials, this theory can reveal the basic bonding phenomenon of porous materials with adhesives, while failing to explain the behaviour of non-porous materials. In addition, from the perspectives of the chemical bonding theory, bonding results from high-intensity ionic bonds or covalent bonds formed in the chemical reaction of molecules between adhesive and adhesively bonded objects. The -NH_2 polar molecule in the adhesive and the -OH polar molecule in the corn stalk rind share hydrogen atoms to form hydrogen bonds, as well as connect materials in a manner analogous to pastern nails on the surface of the corn stalk rind, thus closely binding fibres of corn stalk rind by using the adhesive (Li *et al.* 2009b; He *et al.* 2016b).

Figure 6(b) shows the cross-sectional morphology of damaged laminated veneer lumber produced with corn stalk rind. As shown, stratification appears in the damaged area showing the poor wetting effects of the adhesive and corn stalk rind that were mainly concentrated in the central layers of the plates. This was mainly because the effects of water and air inhibited bonding, which led to the formation of weak interface layers on uneven surfaces of the corn stalk rind. Moreover, as pressure and temperature, effects were transferred from both sides of the plate blank to the center, the plate blanks were heated nonuniformly. Moreover, air and water were mainly accumulated in these central layers. Therefore, to reduce stratification therein, the water contents of raw materials in plate blanks should be controlled and the plate blanks need to be uniformly heated in the hot-pressing process, in addition to the need to improve overall bonding performances.



(a) Torn and adhesive layers (×100, 500 μm)

(b) Cross-section of the damaged laminated veneer lumber (×70, 500 μm)

Fig. 6. Microscopic observation of damaged laminated veneer lumber from corn stalk rind

Analysis of the thermal stability, as well as the aforementioned results, indicated that the bonding process of corn stalk rind and adhesive was extremely complex, featuring complicated physico-chemical changes. The adhesive filled the surface cracks and depressions on the corn stalk rind, which not only increased the thermal stability thereof, but also closely fixed the corn stalk rind through a pastern nail-like bonding effect.

CONCLUSIONS

1. Bonding adhesive and corn stalk rind increased the ignition temperature and thermal stability of corn stalk rind and reduced the thermal decomposition of hemicelluloses and cellulose. The range of ideal hot-pressing temperatures was suggested as being below 200 °C, which not only was conducive to reducing thermal decomposition of hemicelluloses and cellulose in bonding and solidification of corn stalk rind, but also decreased the separation of organic components in the adhesive. Furthermore, the

epidermis of corn stalk rind can be used for improving fire-resistance, which decreases its production cost, and increases the future usability of plate blanks.

2. In the hot-pressing of corn stalk rind after gluing, temperatures of between 90 °C and 200 °C were favorable to the softening of the lignin in the corn stalk rind and to solidifying the adhesive. When the temperature was higher than 220 °C, the rate of loss of weight rapidly increased, accelerating the thermal decomposition of the hemicelluloses and cellulose in the corn stalk rind after gluing.
3. The bonding process of the corn stalk rind and adhesive was extremely intricate, with complex physico-chemical changes therein; moreover, the adhesive filled the cracks and depressions in the surface of the corn stalk rind, which improved the thermal stability of the corn stalk rind and closely bound it through a pastern nail-like bonding effect.

ACKNOWLEDGMENTS

This work was supported by the Training Programme for Key Outstanding Young Teachers in Higher Education Institutions in Henan province (Grant No. 2016GGJS-231), the Special Fund for China Agriculture Research System (Grant No. CARS-03, and Grant No. CARS-04-PS-23), and the Special Fund for Henan Agriculture Research System (Grant No. S2017-02-G07), China.

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Article submitted: September 20, 2017; Peer review completed: February 2, 2018; Revised version received and accepted: February 4, 2018; Published: February 22, 2018.
DOI: 10.15376/biores.13.2.2748-2758