Two Modified Treatment Methods for Pretreated Corn Stalk and Its Composites with Modified Lignosulfonate

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Effects of two different modified treatments were investigated relative to the chemical and mechanical properties of pretreated corn stalk particles and their composites prepared with a modified lignosulfonate (ML) binder. Corn stalk particles (CP) first were prepared by treating corn stalk particles with oxalic acid in ultrasonic conditions (pretreated corn stalk particles, PCP). These particles were then modified by treatment with either laccase-vanillin system with ultrasound (LU) or polyethylenimine-glutaraldehyde with ultrasound (PU), and the surface chemistries of the modified PCP and mechanical properties of LU-PCP/ML composites and PU-PCP/ML composites, such as modulus of rupture (MOR), modulus of elasticity (MOE), internal bonding strength (IB), 24-h thickness swelling (TS), and crystallinity were compared. Both modified treatments dramatically enhanced the mechanical properties of the composites. The MOR, MOE, and IB of the PU-PCP/ML composites were improved by up to 148%, 81%, and 62%, respectively, compared to LU-PCP/ML. Moreover, the 24-h TS of the LU-PCP/ML composites was reduced by 16%. These results show that the pretreatment method of CP and ultrasonic collaborative treatment of PCP can effectively improve the properties of its composites. Modified PCP with PU was more favorable for surface chemical and mechanical properties.

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Keywords: Corn stalk; Pretreatment; Laccase-vanillin system; Polyethylenimine-glutaraldehyde; Ultrasound; Chemical and mechanical properties

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INTRODUCTION

Corn stalk is approximately 90% cheaper than all other agricultural fiber used to date for preparation of composites (Nyambo *et al.* 2010; Shah 2013). Corn stalk is also more abundant than other natural fibers because it is a common agricultural waste product, and using these fibers to create green composites is not only a low-cost and environmentally friendly solution for waste disposal, but also allows farmers to make a profit on their waste products (Jarabo *et al.* 2013; Williams *et al.* 2017). In addition, extracting fibers from corn stalks consumes relatively little energy and is environmentally friendly (Reddy and Yang 2005; Zini and Scandola 2011).

Currently, corn stalk waste is used as feed, bundled into bales for animal bedding, or in most cases simply left in the fields. The stalks left in the field are then burned, which produces large amounts of smoke, leads to air pollution, and increases the risk of traffic accidents by reducing the visibility. Air pollution and smog are already major concerns in

northern China, and any means of reducing air pollution is highly desirable. In addition, from the perspective of sustainable development, the use of waste materials or by-products, such as corn stalks, is more advantageous than the use of some other natural fibers, such as sisal, jute, bamboo, ramie, flax, and hemp, that require large land areas to grow (Zhou *et al.* 2010; Chen *et al.* 2016; Luo *et al.* 2016).

The waxy layer and ash content on the surface of corn straw affect the interfacial compatibility of corn straw and other materials in composite boards. As such, researchers have investigated various pretreatment methods to improve the compatibility of straw with other materials, including hydrothermal treatments, NaOH treatments, oxalic acid treatment (Bin *et al.* 2022), soaking the straw in an acetic acid solution, steam blasting, and microwave treatments (Martelli-Tosi *et al.* 2017). To further increase the surface activity of straw, more advanced activation modification methods have also been developed, such as biological oxidation treatments and chemical bionic modification methods (Abraham *et al.* 2020).

Laccase is a bio-derived oxidation system that is highly efficient (Widsten and Kandelbauer 2008) and has promising application potential for the treatment of corn straw. Moreover, the addition of several small molecules to the reaction can greatly improve the efficiency and oxidation rate using laccase (Rahikainen *et al.* 2013). Accordingly, the use of laccase is an effective biological pretreatment for raw materials that replaces expensive synthetic chemicals with cheaper, more environmentally friendly reagents (Hu *et al.* 2016). Likewise, polyethylenimine (PEI) is a water-soluble polymer with very strong positive ionic charge that contains a large number of highly active secondary and primary amines that can be used to cross-link to the hydroxyl groups in cellulose. The PEI is also known to react with carbonyl groups to form covalent bonds and contains both hydrophobic and polar group regions (De La Orden and Urreaga 2006). As such, PEI has been shown to react with many kinds of substances and is widely used as a binder, adsorption medium, and surface modifier (Geng and Li 2006; Yuan and Guo 2017).

While previous studies (Li *et al.* 2019) have used PEI or laccase to directly treat corn stalk particles (CP), the waxy layer on the straw surface affected the bond properties of the treated CPs. Therefore, here the authors compare the comprehensive effectiveness of different pretreatment methods on CPs ranging from the surface chemistries of the particles to the mechanical properties of the corresponding composites (Bin *et al.* 2022). Different from the authors' previous research (Li *et al.* 2019; Yuan *et al.* 2019), on the basis of pretreatment, an improved enzymatic method and PEI modified treatment conditions were explored and ultrasonic collaborative treatment was introduced. In this study, two modified treatments were performed on pretreated corn particles (PCP), and then activated PCP were the reacted with modified lignosulfonate (ML) to form composites. The effects of modified treatments of laccase-vanillin system or polyethylenimine-glutaraldehyde with ultrasound on the properties of the PCP and PCP/ML composites are discussed in detail.

EXPERIMENTAL

Materials

Corn straw were obtained from Anda (Heilongjiang province, China) and were separated using a skin separator (XZ2020, Xingtai Hengkong Jiacheng Machinery Manufacturing Development, China). The skins were reduced to particles using a flaker

(FW-100 high-speed shredder, Changzhou, China). The corn stalk particles (CP) were dried to a moisture content of 5% and then filtered through 40-mesh to 60-mesh for separation. The average chemical compositions of CP were determined to be 17.7% lignin, 45.6% cellulose, 24.5% hemicelluloses, 9.3% extractives, and 2.9% ash. Lignosulfonate was obtained from Shenyang Xingzhenghe Chemical Company (Shenyang, China). Polyethylenimine (PEI) was obtained from Shanghai UN Chemical (Shanghai, China). The PEI molecular weight was 75,000 g/mol, and it was dispersed in water to form a 50 wt% aqueous solution. Laccase was obtained from Wuhan Yuancheng Technology Development Co., Ltd. (Wuhan, China). All other chemicals were of analytical grade.

Material Synthesis and Composite Preparation

Pretreatment of corn stalk particles (CP)

The PCP was prepared following the authors' reported procedure (Bin *et al.* 2022). A slurry containing 3 g of CP dispersed in a 5% oxalic acid solution was prepared such that the final CP mass concentration was 3%. The slurry was then ultrasonicated at 50 °C for 1 h. The resulting PCP was dried at 60 °C before use in subsequent processes.

The relative content of epidermal wax components of CP raw materials revealed 87.6% of fatty acids, followed by 7.39% of primary alcohols, 4.13% of alkanes, and 0.92% of diketones, and that of PCP was 77.9% of fatty acids, followed by 6.98% of primary alcohols, 8.89% of alkanes, and 6.23% of diketones. The fatty-acid content of wax exhibited a decreasing trend, and the relative contents of fatty acids reached the minimum after the oxalic acid + ultrasound treatment.

Modification of pretreated corn stalk particles

Laccase-vanillin system with ultrasound modified (LU) treatment: The absorbance of the ABTS and laccase solutions were measured using a spectrophotometer at 30 °C to determine the enzyme concentrations. Accordingly, the laccase activity was determined to be 3500 U/g. The laccase activation system was prepared by adding a predetermined amount of laccase and vanillin to a buffer solution containing acetoacetate and sodium acetate. To modify the PCP, the particles were then added to this laccase solution to form a slurry with a solid concentration 3%. The slurry was ultrasonicated in air for 45 min. The activation was performed at 45 ± 3 °C. After activation, the slurry was dried at 60 ºC for 24 h to recover the activated solids. The PCP activated by treatment with laccase-vanillin system is referred to as LU-PCP in the manuscript.

PEI-glutaraldehyde with ultrasound (PU) modified treatment: A slurry containing 3% by mass PCP in a solution containing 50% PEI was prepared. The slurry was ultrasonicated at 50 °C for 1 h, and then, a predetermined amount of solution containing 50% glutaraldehyde was added. The mixture then was ultrasonicated for an additional 30 min. After modification, the slurry was dried at 60 °C for 24 h to recover the solids. In this article, PCP activated with PEI-glutaraldehyde with ultrasound will be referred to as PU-PCP for short.

Preparation of modified lignosulfonate (ML)

The ML was prepared following a procedure in literature (Yuan *et al.* 2014). First, 1 g of lignosulfonate was dissolved in 10 mL of distilled water, and the pH of the solution was adjusted to pH 10. Then, 10 mL of H_2O_2 (20 wt%) was added to the lignosulfonate solution, and the mixture was stirred at 60 °C for 30 min. Thereafter, the solution was concentrated to 30 wt% and referred to as ML.

Preparation of composites

The modified PCP was placed into a mixer. After mixing at high speed for 1 min, the desired amount of the ML solution and liquid paraffin were slowly added. The mixture was stirred until uniform and then allowed to rest for 3 min. The different components were manually added to a mold of 250 mm × 250 mm. The target density of composites was determined to be 0.84 g/cm^3 ± 0.04 g/cm^3 with a target thickness of 5 mm, and then the samples were hot-pressed at 160 °C under 3.0 MPa of pressure for 5 min. The composites of the resulting PCP/ML, LU-PCP/ML, and PU-PCP/ML are listed in Table 1, and a schematic of the fabrication process is shown in Fig. 1.

Table 1. Summary of the Compositions of the Composites and Their Abbreviated Names

Sample Designation		Modified Treatment Condition	
General	Specific	Laccase Concentration (U/g·PCP)	PEI Dosage (wt%)
PCP/ML	PCP/ML	No treatment	No treatment
LU-PCP/ML	LU1-PCP/ML	75	-
	LU2-PCP/ML	85	-
	LU3-PCP/ML	95	-
PU-PCP/ML	PU1-PCP/ML	-	2.0
	PU2-PCP/ML	-	2.5
	PU3-PCP/ML	-	3.0

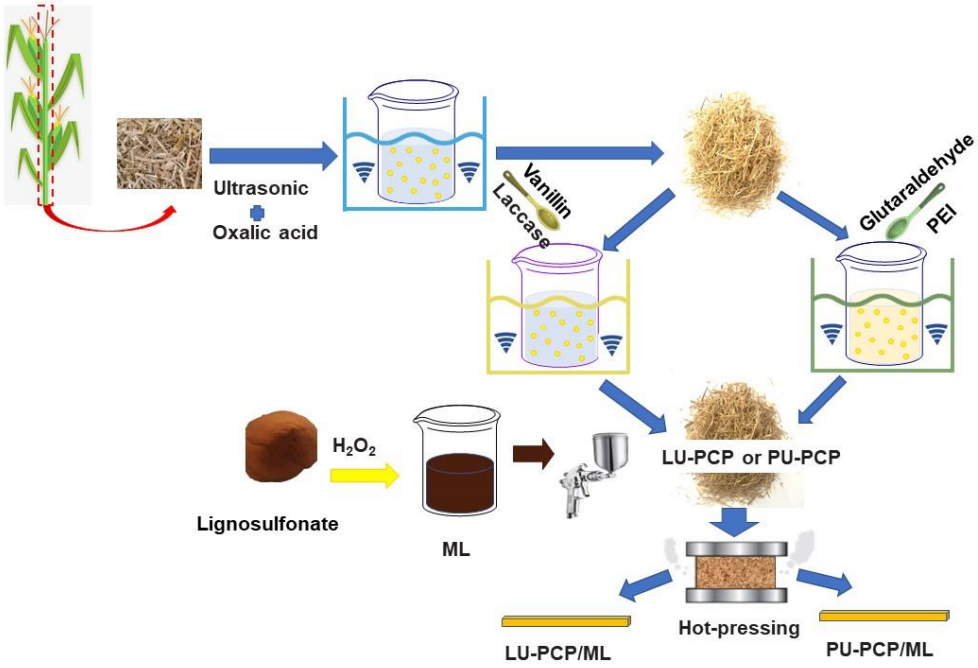

Fig. 1. Schematic illustration of fabrication processes of the LU-PCP/ML and PU-PCP/ML composites

Mechanical and dimensional characterization

The mechanical and dimensional properties of the composites were measured according to Chinese National Standard GB/T 17657 (2013) after the composites were conditioned at 20 ± 2 °C and 65 ± 5% relative humidity (RH). A sample with dimensions

of 200 mm × 50 mm was subjected to a three-point static bending test to measure modulus of rupture (MOR) and modulus of elasticity (MOE) values at a loading speed of 5 mm/min. Samples with dimensions of 50 mm × 50 mm were pulled apart in the vertical direction to measure the internal bond (IB) value at a loading speed of 2 mm/min. Five samples of each composite were measured for reproducibility. The 24 h thickness swelling (24h TS) was measured as the percentage increase in thickness and weight of the sample after 24 h of immersion in water at room temperature. For these TS measurements, 8 specimens with dimensions of 50 mm × 50 mm were analyzed. The load-bearing particleboard properties were defined as MOR $\geqslant$ 15 MPa, MOE $\geqslant$ 2200 MPa, IB $\geqslant$ 0.45 MPa, and 24 h TS $\leqslant$ 22% according to GB/T 4897 (2015).

Materials characterization

Fourier transform infrared spectroscopy (FTIR; Thermo Fisher Scientific, Waltham, MA, USA) was used to characterize the functional groups in the samples. The FTIR spectra were recorded from 4000 to 500 cm^{-1} with a resolution of 4 cm^{-1}.

X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Waltham, MA, USA) was performed using a MgK X-ray source (1253.6eV). The C, N, O, and Si elemental compositions on the surface of the samples were measured. The passing energy was 20 eV, and the samples were analyzed at a vacuum pressure of 3.2×10^7 Pa.

X-ray diffraction (XRD, X'Pert Powder, Alemlo, Netherlands) measurements were performed to determine the crystal structure and relative crystallinity of the different samples. The data were measured over 2θ angles ranging from 10° to 45° and scanned at a rate of 5°/min. The crystallinity indexes of the samples were calculated in accordance with previous literature (Segal *et al.* 1959).

Scanning electron microscopy (SEM) images were recorded to evaluate surface morphologies of PCP subjected to the different activation treatments as well as the corresponding PCP/ML composites. Images were collected on a Sirion 200 instrument (FEI, Hillsboro, OR, USA). The samples were coated with a thin layer of gold before imaging to increase the conductivity of the surfaces. The SEM images were collected with a 12.5 kV beam voltage.

RESULTS AND DISCUSSION

FTIR Analyses of the PCP with Different Modified Treatments

The FTIR spectra of PCP as well as the PCP activated by treatment with either laccase (85 U/g·PCP) or PEI (2 wt%) are presented in Fig. 2. The absorbance peaks in the region of 1500 to 1600 cm^{-1} are characteristic of the aromatic rings in the lignin and are characteristic functional groups for corn straw. As shown in Fig. 2a, the spectrum for PCP contains a band near at 3320 cm^{-1} that originates from the stretching of the O-H bonds, a band at 2896 cm^{-1} due to the stretching vibrations of the C-H bonds, and a band at approximately at 1699 cm^{-1} that corresponds to the vibrations from the H-O-H bonds in the absorbed water (Nasir *et al.* 2013; Barczewski *et al.* 2020).

After modification with laccase-vanillin system with ultrasound (LU) in Fig. 2b, the intensity of the peak's characteristic of the aromatic ring groups of LU-PCP between 1602 and 823 cm^{-1} decreased, suggesting the laccase treatment effectively oxidized the aromatic rings in the lignin (Nasir *et al.* 2013). The intensity of the C-O peaks from the

primary alcohol stretching vibrations at 1030 cm^{-1} also weakened, which indicated that laccase treatment also effectively epoxidized the hydroxyl groups in the lignin (Jin *et al.* 1991; Felby *et al.* 1997). A new band at 1110 cm^{-1} was present in the spectrum of LU-PCP that was characteristic of C-C or C-O stretching vibrations. Meanwhile, the intensities of the bands at about 1726 cm^{-1} and 1159 cm^{-1}, corresponding to C=O stretching vibrations and C-O-C vibrations, respectively, weakened (Wu *et al.* 2011).

As can be seen in Fig. 2c, peaks characteristic of PEI and glutaraldehyde were present in the FTIR spectrum of PU-PCP. The spectrum for PU-PCP showed absorbance peaks around 1686 and 2846 cm^{-1} that were characteristic of the C=O and C-H groups in glutaraldehyde (Ji *et al.* 2018). These peaks suggested an aldehyde reaction occurred between the PEI and PCP during the treatment. The spectrum of the PU-PCP presents also contained the peaks seen in the spectra for the as-prepared PCP (a) and LU-PCP (b), as well as additional bands around 3305 cm^{-1} from the stretching vibrations of the N-H bonds in PEI. A peak observed at 1620 cm^{-1} due to the flexing of the primary amine ($-NH_2$) groups in the polymer was also present (Park *et al.* 2018; Pineda *et al.* 2021).

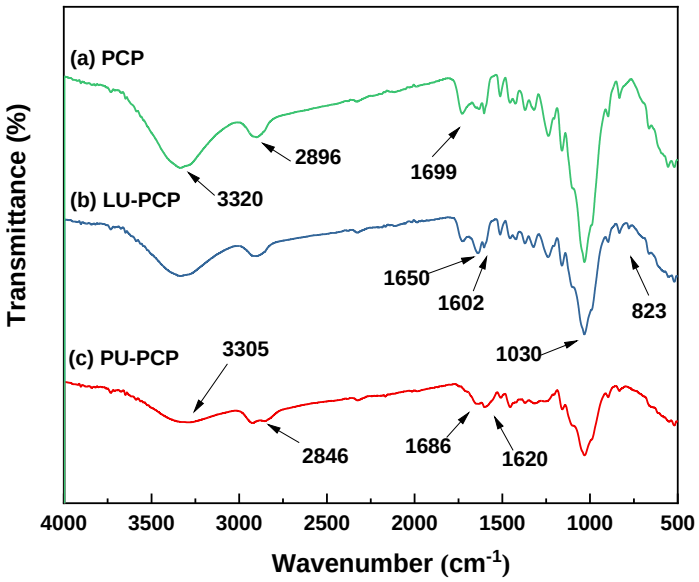

Fig. 2. FTIR spectra of the (a) as-prepared PCP and PCP treated with (b) laccase (85 U/g·PCP) and (c) PEI (2 wt%)

XPS Analyses of the PCP with Different Modified Treatments

The XPS technique was used to study the surface properties of the treated PCP (DiFlavio *et al.* 2007; Kuzmenko *et al.* 2017). The results showed that the surfaces contained carbon, oxygen, nitrogen, and a small amount of Si (Table 2). The Si was present in the samples mainly as SiO_2 (103.2 eV). It is worth mentioning that the PU modified treatment effectively reduced the SiO_2 content, while the laccase treatment had little effect on the SiO_2 content. The possible reason is that PU forms polymer on the surface of CP, and SiO_2 was covered (Geng and Li 2006). But the laccase activation object is the lignin of CP, will not affect SiO_2 content (Yuan and Guo 2017). Likewise, the PEI treatment considerably increased the N content on the surface of the particles, while the laccase treatment had little effect on the N content. The large increase in N content was consistent with the amino groups in the PEI binding to the PCP surface and was in good agreement with the FTIR results of PU-PCP discussed above.

Table 2. Surface Elemental Compositions of the Different Samples

Samples	Oxygen Content (%)	Carbon Content (%)	Si Content (%)	N Content (%)
PCP	23.8±0.8	72.7±1.6	0.63±0.02	2.87±0.12
LU1-PCP	28.6±1.1	68.4±1.4	0.68±0.02	2.32±0.08
LU2-PCP	29.6±0.9	67.4±1.2	0.88±0.03	2.12±0.09
LU3- PCP	29.1±1.2	67.7±0.9	0.54±0.01	2.66±0.10
PU1-PCP	13.4±0.3	74.5±1.1	0.44±0.01	11.66±0.30
PU2-PCP	11.3±0.1	77.1±1.5	0.35±0.01	11.25±0.22
PU3-PCP	10.8±0.2	78.9±1.3	0.37±0.01	9.93±0.21

The C1s spectra (Fig. 3) of the PCP samples were fit to four types of carbon atoms, namely C–C/C-H bonds (the peak at 284.5 eV, C1), oxygen-containing bonds such as C–O (285.3 eV, C2), C=O/O-C-O bonds (286.4 eV, C3), and O-C=O bonds (287.8 eV, C4) (Orelma *et al.* 2016). The relative area under the C1 peak for the as-prepared PCP was 45.9 ±0.9%. The C1 peak areas of LU1-PCP, LU2- PCP, LU3-PCP, PU1-PCP, PU2-PCP, and PU3-PCP were 45.9±1.2%, 48.1±1.4%, 48.0±1.1%, 56.1±1.8%, 59.7±2.1%, and 61.3± 1.9%, respectively. The increase in C1 peak area corresponding to C-C and C-H groups suggested that the degraded lignin on the surface of corn straw polymerized during the activation treatment, which increased the overall content of phenoxy groups. Meanwhile, C4 peaks corresponding to O-C=O bonds were only seen in the samples treated with laccase activation system, indicating LU treatment increased the carboxylic acid content in the samples.

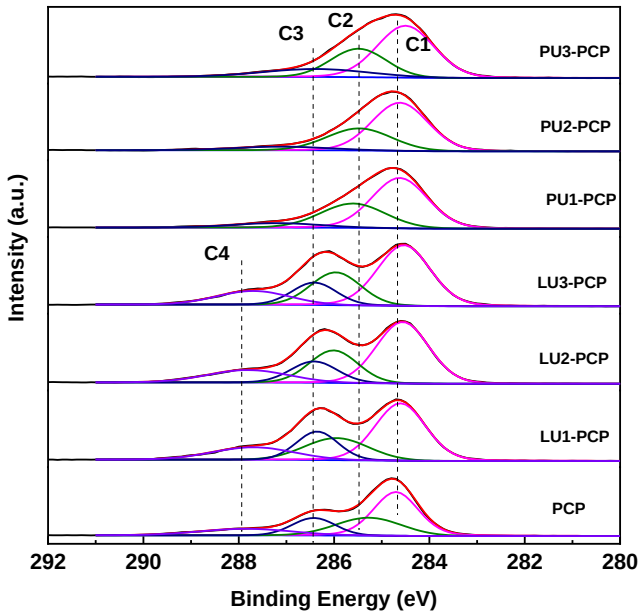

Fig. 3. XPS C 1s spectra of PCP after different modified treatments

XRD Analyses of the PCP with Different Modified Treatments

The XRD patterns of PCP and modified PCP samples are shown in Fig. 4. Diffraction peaks were seen at 2θ = 16.8° and 22.2°, which corresponded to the lattice planes of cellulose I. Therefore, both the laccase and PEI modified treatments retained the

crystallinity of the as-prepared PCP. The crystal structures of the treated materials were also consistent with that seen in natural cellulose (Poletto *et al.* 2014).

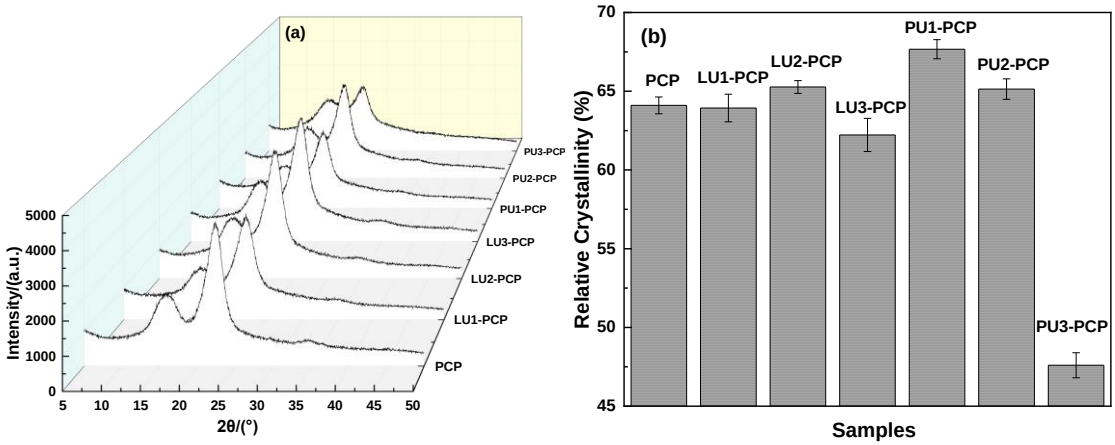

Fig. 4. XRD patterns and relative crystallinity of PCP after different modified treatments

Further analysis of the XRD patterns showed that the crystallinity of PCP was 64%. While the modified treatments did not affect the crystal structure, they did greatly affect the relative crystallinity of the different PCP samples. With an increase in the laccase concentration used in the modified treatment, the crystallinity of LU1-PCP, LU2-PCP, and LU3-PCP ranged from 64%, 65%, and 62%, respectively. Meanwhile, the crystallinity of the modified PCP decreased with an increase in the PEI dosage, and the crystallinity of PU1-PCP, PU2-PCP, and PU3-PCP were 67%, 65%, and 61%, respectively. The non-linear trend in relative crystallinity with laccase concentration perhaps suggested that as the lignin was degraded, it dissolved in the surrounding solution, which increased the crystallinity. However, when the laccase concentration was too high, the lignin degradation products adsorbed on the surface of straw and could form an amorphous coating with decreased the overall crystallinity of the materials (Chen *et al.* 2023). Meanwhile, the PU modified treatment increased the numbers of aldehyde groups and Schiff bases in the corn straw, which might increase the crystallinity of the modified material. However, the addition of too much PEI could form an amorphous substance on the surface of the straw, which resulted in the observed decrease in the crystallinity of the materials (Johar *et al.* 2012).

Morphologies of PCP Surfaces with Different Modified Treatments

The SEM revealed the morphological features of raw material CP, the as-prepared and activated PCP samples. It can be seen in Fig. 5a that the raw material CP has a rough surface. The surface of PCP with pretreatment is smooth, which may have been due to the the waxy surface layer partially removed (Bin *et al.* 2022) in Fig. 5b. On this basis, the surface of the corn straw modified with LU showed more distinct structures, which may have been due to the continuous degradation of intermolecular lignin in Fig. 5c. As shown in Fig. 5d, the number of cross-links on the PCP surface after PU treatment increased. The morphology of the corn straw was less distinct, and there was a thick coating on the straw surface, which was in good agreement with the XRD results discussed above (Johar *et al.* 2012).

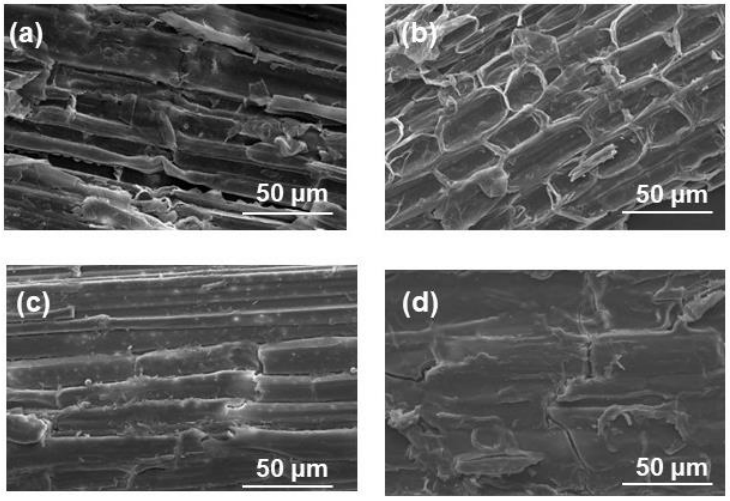

Fig. 5. SEM images of CP(a), PCP(b), and the activated PCP (c: LU-PCP, d: PU-PCP)

Effect of Modified Treatments on the Peeled Surface Structure of PCP/ML Composites

Images of the surfaces peeled from the PCP/ML, LU-PCP/ML, and PU-PCP/ML composites are shown in Fig. 6. Figure 6a shows that there were obvious voids between the PCP in the composites, suggesting that the bonding between PCP and ML was poor. Figure 6b shows improved interfacial bonding, where the voids between LU-PCP fibers were smaller. The improved bonding suggested that the laccase modified treatment increased the number of hydrogen and chemical bonds formed between the LU-PCP and ML. Figure 6c shows a representative image of a surface peeled from a PU-PCP/ML composite. Notably, there were almost no voids between the corn straw particles. These findings suggested that the interfacial bonding between PU-PCP and ML was much stronger compared to the other composites, and this strong bonding was attributed to the quinone-tanning process between PU-PCP and ML (Li and Geng 2004; Zini and Scandola 2011).

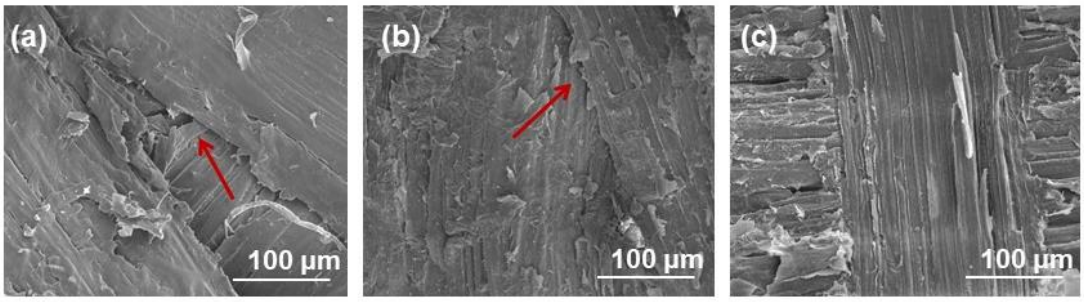

Fig. 6. The peeling surfaces of (a) PCP/ML, (b) LU-PCP/ML, and (c) PU-PCP/ML composites

Effect of Modified Treatments on Mechanical and Dimensional Properties of the Composites

As shown in Fig. 7, at optimal modified conditions using a laccase concentration of 75 or 85 U/g·PCP, an increase in the MOR, MOE, and IB, and a decrease in the 24 h TS of the corresponding composites were observed. However, when the concentration of laccase was further increased to 95 U/g·PCP, the MOR, MOE, and IB of the composite

decreased while the 24 h TS increased. The highest MOR was measured for the LU2-PCP/ML composite, and the MOR was 72% higher than that of the PCP/ML composite. The highest MOE was observed for the LU2-PCP/ML composite and was 105% higher than that of PCP/ML composite. The highest IB was also observed for the LU2-PCP/ML composite and was 114% higher than that of PCP/ML composite. The lowest 24 TS was observed for the LU2-PCP/ML composite and was 30% lower than that of PCP/ML composite. Together, these results show that the LU2-PCP/ML composite had the best comprehensive properties.

Table 3. Surface Elemental Compositions of the Different Samples

Samples	Oxygen Content (%)	Carbon Content (%)	Si Content (%)	N Content (%)
PCP	23.8±0.8	72.7±1.6	0.63±0.02	2.87±0.12
LU1-PCP	28.6±1.1	68.4±1.4	0.68±0.02	2.32±0.08
LU2-PCP	29.6±0.9	67.4±1.2	0.88±0.03	2.12±0.09
LU3- PCP	29.1±1.2	67.7±0.9	0.54±0.01	2.66±0.10
PU1-PCP	13.4±0.3	74.5±1.1	0.44±0.01	11.66±0.30
PU2-PCP	11.3±0.1	77.1±1.5	0.35±0.01	11.25±0.22
PU3-PCP	10.8±0.2	78.9±1.3	0.37±0.01	9.93±0.21

As the PEI dosage increased from 2.0 to 3.0% during the activation treatment, the MOR, MOE, and IB values of the corresponding composites decreased, while the 24h TS increased. The highest MOR, MOE, and IB were measured for the PU1-PCP/ML composite, and these values were 327%, 269%, and 246% higher than the PCP/ML composite, respectively. Moreover, the lowest 24h TS was also observed in the PU1-PCP/ML composite and was 42% than that of the PCP/ML composite.

These findings highlight that both modified treatments considerably enhanced the mechanical properties of the corresponding PCP/ML composites. Moreover, compared with the composite prepared with CP activated by PEI-glutaraldehyde alone in the authors' previous study (Bin *et al.* 2022), the MOR, MOE, and IB of the PU-PCP/ML composites prepared here were 83%, 48%, and 218% higher, respectively, and the 24h TS was reduced by 12%. Lastly, the pretreatment method of CP and ultrasonic collaborative treatment of PCP were able to effectively improve the properties of its composites. Together these results show that both the mechanical and dimensional properties of the PU-PCP/ML composite were immensely improved.

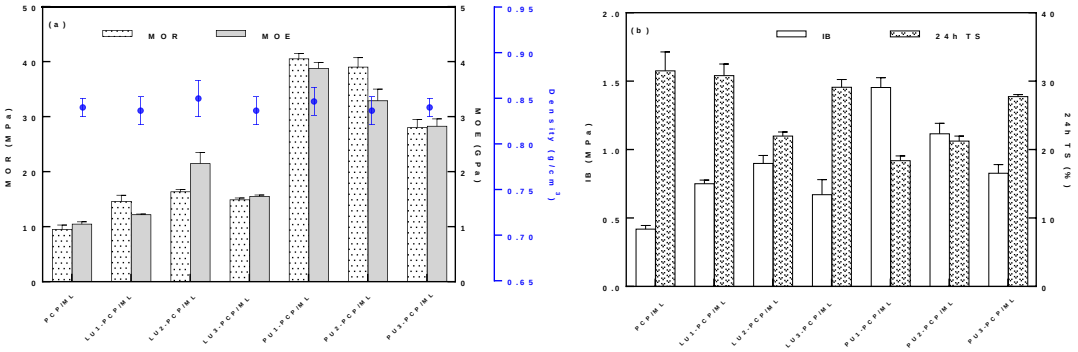

Fig. 7. Effect of modified treatment on the mechanical and dimensional properties of composites: (a) MOR and MOE, (b) IB and 24h TS

CONCLUSIONS

The effects of two different modified treatments on the chemical and mechanical properties of pretreated corn stalk particles and the corresponding composites prepared with a modified lignosulfonate (ML) binder were discussed.

1. The optimal laccase treatment used 85 U/g·PCP, and the optimal poly(ethyleneimine) (PEI) treatment used a 2.0 wt% solution. The modulus of rupture (MOR), modulus of elasticity (MOE), and internal bond strength (IB) of the polyethyleneimine-glutaraldehyde with ultrasound pretreated corn stalk particles with a modified lignosulfonate binder (PU-PCP/ML) were 148%, 81%, 62% higher, respectively, compared to the LU-PCP/ML composite, and 24h TS was 16% lower.
2. The pretreatment method of corn stalk particles (CP) and ultrasonic collaborative treatment of pretreated corn stalk particles (PCP) can effectively improve the properties of its composites.
3. The adhesion was stronger in the PU-PCP/ML composites compared to the laccase-vanillin system with ultrasound (LU-PCP/ML) composites, which implied that the interfacial bonding between the PU-PCP and ML was the strongest.
4. The modification of PCP with PU modified treatment is more efficient than treatment with LU activation treatment in terms of both the surface chemistry of the fibers and mechanical properties of its composites.

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