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Research on the Preparation of Wood Adhesive Active Fillers from Tannin-/Bentonite-Modified Corn Cob

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Abstract: The artificial plywood industry in our country relies heavily on industrial flour as a filler for adhesives. Using abundant corn cob powder as the main raw material, corn cob powder was modified by impregnation with a sodium-based bentonite/bayberry tannin and used as filler for urea–formaldehyde resin (UF) adhesive, with NH_4Cl as the curing agent and poplar veneer as the raw material to prepare plywood. The results showed that the modified corn cob powder with a particle size of 250 mesh was uniformly dispersed in the UF adhesive. When used as a filler, the modified corn cob powder effectively prevented the premature curing of the UF adhesive and significantly reduced its viscosity. Compared with flour filler, the bonding strength of the prepared plywood increased by 12.1%–19.6% while the formaldehyde emission decreased by 12.7%–27.8%. The cold pressing performance of the plywoods prepared with modified corn cob flour was comparable to the performance of plywood produced with industrial flour.

Keywords: corn cob; bayberry tannin; sodium-based bentonite; adhesive filler

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1. Introduction

With the swift growth of China's construction and furniture industries, the artificial plywood industry has emerged as a key foundational sector in the country [1]. This industry is responsible for producing construction building materials and furniture materials. Presently, the primary adhesives employed for artificial plywood in China are formaldehyde-based synthetic resin adhesives. These include urea–formaldehyde resin adhesive, phenol-formaldehyde resin adhesive, and melamine resin adhesive. Together, these three types of adhesives account for over 80% of total adhesive consumption within the wood processing industry [2]. The urea–formaldehyde resin adhesive, in particular, enjoys widespread use in the domestic artificial plywood industry due to its notable advantages, such as corrosion resistance, a colorless cured adhesive layer, ease of application, excellent process performance, low cost, superior bonding performance, and excellent insulation properties. When utilizing urea–formaldehyde resin adhesive for pressing plywood, a curing agent is typically added during the adhesive adjustment process. Additionally, a certain proportion of filler is commonly incorporated [3]. By adding filler to the urea–formaldehyde resin adhesive, adhesive consumption and associated costs can be reduced. Furthermore, this aids in enhancing the initial tackiness of the adhesive [4], preventing excessive adhesive penetration into the wood, and mitigating resulting adhesive deficiency. In addition, the inclusion of filler helps to diminish the internal stress arising from the volume shrinkage of the adhesive during the curing process [5]. This, in turn, improves the durability of the bonding strength and extends the service life of the artificial plywood.

Fillers that are commonly used for urea–formaldehyde resin adhesives possess specific characteristics. They are generally chemically inactive, neutral or close to neutral in nature, possess good water miscibility, and can cure after water evaporation. These fillers exhibit stable viscosity over time and do not significantly prolong the curing time of the adhesive [6]. Importantly, they have minimal impact on bonding strength and durability. Additionally, they are readily available as powder, cost-effective, and have a plentiful supply of raw materials. Various fillers are utilized for plywood production both domestically and internationally. These include wheat flour, coconut shell powder, bark powder, mineral powder, soybean powder, wood powder, and lightweight calcium carbonate, among other mineral components [7]. In particular, domestically, flour is widely employed as a filler for urea–formaldehyde resin adhesive within the plywood industry, with an annual consumption of approximately 300,000 tons. However, this is extensive use of wheat flour in non-food industries. Hence, it is crucial from both economic and societal perspectives to explore cheaper fillers that can effectively reduce formaldehyde emissions [8,9] while being a viable alternative to flour. The utilization of such fillers would help diminish grain consumption in non-food industries.

Corn is a highly important grain, with the largest global plantation and highest yield. Corn cob contains a large amount of hemicellulose, cellulose, and lignin, with rich carbon content. Under dry weight conditions, the crude fiber content is approximately 33% [10]. Among various agricultural byproducts, corn stands out due to its exceptionally high hemicellulose content and significant value in terms of utilization [11]. However, the current efficiency in utilizing corn cobs is remarkably low, resulting in the disposal or incineration of approximately 500,000 tons of corn cobs in China annually. This practice not only contributes to environmental pollution but also wastes valuable renewable resources. In the specific case of utilizing corn cob powder as a filler for urea–formaldehyde adhesive, challenges arise. The powder tends to absorb the adhesive, leading to thickening [12]. Furthermore, it exhibits poor dispersibility within the adhesive solution, causing it to sink or float on the surface.

Tannins are secondary metabolites that have evolved in vascular plants as a means of self-protection. They are found in various plant tissues, including bark, roots, leaves, flowers, and fruits. Among these, bark contains the highest concentrations of tannins, with levels ranging from 20% to 40% in many coniferous tree barks [13]. The presence of tannins in plants helps defend against oxidative stress caused by UV damage and other environmental factors. They also play a crucial role in preventing cell structure damage by neutralizing harmful free radicals and protecting against bacterial and fungal infections [14,15]. In China, bayberry tannin (BT) is a prominent and commercially valuable type of tannin. It is widely available and comparatively inexpensive. The structure diagram is shown in Figure 1.

Bentonite is a naturally occurring clay with montmorillonite as its primary component. The layered two-dimensional grid structure of montmorillonite confers excellent properties to bentonite, including strong adsorption capacity, ion exchange capability, and expansibility [16]. In China, bentonite resources are abundant and widely distributed across more than 20 provinces, resulting in its increasing importance in development and utilization. Sodium-based bentonite, which is obtained through sodium modification of calcium-based bentonite, exhibits superior qualities. These include a higher cation exchange capacity, improved dispersibility, reproducibility, and thermal stability [17]. Furthermore, sodium-based bentonite has a high water-absorption rate and expansion ratio, as well as good thixotropic properties, viscosity, and lubricity of colloidal suspensions. This type of bentonite serves as a fundamental material for the deep processing of bentonite. It has proven effective in treating various pollutants in wastewater, particularly in the enrichment and fixation of heavy metals in large-volume wastewater [18,19]. Sodium-based bentonite also demonstrates efficacy in adsorbing anilines and nicotine in soil, as well as formaldehyde in the air. The structure diagram is shown in Figure 2.

Therefore, this study aims to investigate the feasibility of using sodium-based bentonite and bayberry tannin to modify corn cob powder as a filler material for urea–formaldehyde resin. The goal is to find an alternative to industrial flour fillers for the preparation of urea–formaldehyde resin adhesives and provide technical support.

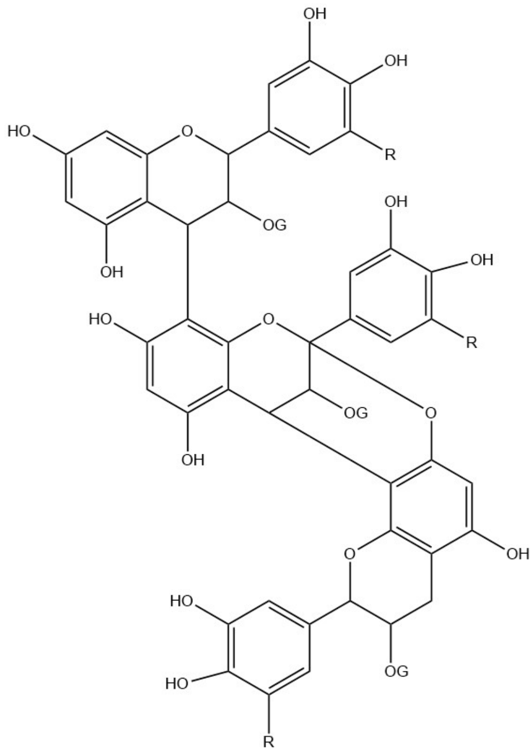

Figure 1. The structure of bayberry tannin.

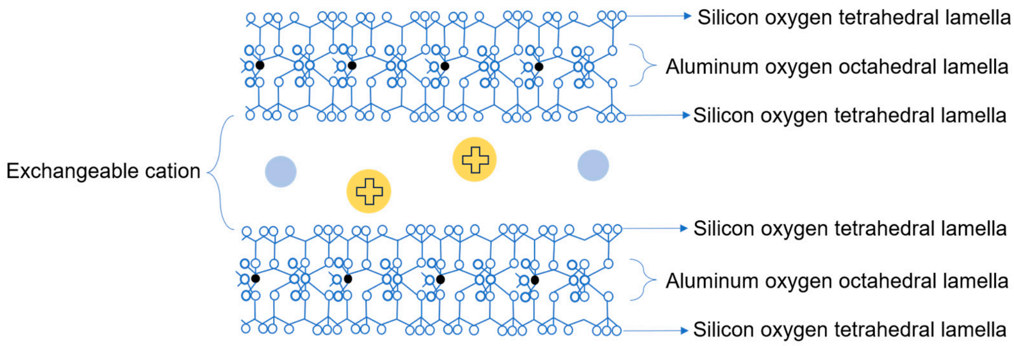

Figure 2. The structure diagram of bentonite.

2. Materials and Methods

2.1. Materials and Reagents

Corn cob: the corn kernels were stripped and dried until the moisture content was 10%, and the pieces were cut into 3 cm × 1 cm × 2 cm (length × width × height), produced in Linyi City, Shandong Province; urea–formaldehyde resin adhesive: milky white, viscosity 125.3 mPa·s, solid content 50%, purchased from China Nanjing Taier Chemical Co., Ltd.; bayberry tannin: 250 mesh, purchased from China Zhengzhou Haizhou Chemical Products Co., Ltd.; sodium-based bentonite: 1500 mesh, purchased from China Hubei Mineral Products Factory; flour: 250 mesh, loose packing density is 0.219 g/cm^3; deionized water, etc., are purchased; poplar veneer: width 300 mm × 300 mm × 15 mm, moisture content 10%.

2.2. Equipment and Instruments

Electric hot-air drying oven, constant-temperature water bath, rotary viscometer, ultrafine pulverizer, vibrating sieve, universal testing machine, Fourier transform infrared spectrometer (FTIR), X-ray diffraction instrument (XRD), scanning electron microscope (SEM), etc. The experimental equipment used in this chapter is shown in Table 1.

Table 1. Experimental instruments and equipment.

Equipment Name	Equipment Type	Manufacturer
vacuum pressure impregna-tion tank	XYR 8-00	China Weihai Xinyuan Chemical Machinery Co., Ltd.
Electronic scales	FA1104D4N	China Shanghai Jinghong Experimental Equipment Co., Ltd.
Electric hot-air drying oven	101A-2ET	China Shanghai Experimental Instrument Factory Co., Ltd.
FTIR	VERTEX 80V	BRUKER company from Switzerland.
SEM	Quanta200	FEI company from the United States.
XRD	D8ADVANCE	Bruck AXS GMBH

2.3. Test Methods

2.3.1. Preparation of Modified Corn Cob Powder

The corn cob blocks were weighed and then placed in a vacuum pressure impregnation tank. The tank was evacuated to a negative pressure of −0.09 MPa. Then, a 40% solution of sodium-based bentonite in water was injected into the impregnation tank through a silica gel tube, maintaining the negative pressure for 40 min. The vacuum valve was closed, and nitrogen gas was injected into the tank to reach a pressure of 1.5 MPa, maintained for 40 min. The pressure was released, and the water in the solution was filtered out. The dried corn cob pieces were then weighed, and according to Equation (1), and the weight gain rate was calculated to be 52%.

$$\mathrm{WPG} = (\mathrm{m2} - \mathrm{m1})/\mathrm{m1} \times 100\% \tag{1}$$

In the equation, WPG represents the weight gain rate of the modified corn cob, expressed as a percentage. m1 and m2 represent the dry mass of the corn cob before and after impregnation, respectively, measured in grams. For the second impregnation, a 40% solution of bayberry tannin in water was used. The same procedure as mentioned above was repeated. The impregnated corn cob was dried, weighed, and the weight gain rate was calculated to be 41%. For the third impregnation, dried sodium-based bentonite-impregnated corn cob pieces and a 40% solution of bayberry tannin in water were used. The procedure was repeated. The impregnated corn cob was dried, weighed, and the weight gain rate was calculated to be 45%. The modified and unmodified corn cob powders were then pulverized using an ultrafine pulverizer and sieved into different particle sizes (150, 200, 250, and 300 mesh). The powders were placed in sealed bags for future use.

2.3.2. Preparation of Modified UF Adhesive with Corn Cob Powder

Different particle sizes (150, 200, 250, and 300 mesh) and different amounts (0%, 5%, 10%, 15%, 20%, 25% of the mass of UF adhesive) of modified corn cob powder and unmodified corn cob powder were added to the UF adhesive. The mixture was thoroughly mixed and set aside for later use. An equal amount of flour was added to the UF adhesive and mixed evenly as a control group.

2.3.3. Preparation of Plywood

A 5-layer plywood panel made from UF adhesive with modified corn cob powder (filler content of 20% and particle size of 250 mesh) was prepared using poplar veneer. The adhesive was applied to both sides of the veneers at a rate of 280 g/m^2. As a control sample, a plywood panel was also prepared using UF adhesive with 20% flour filler. Three specimens were prepared for each condition as shown in Table 2. The preparation process involved the following steps: adhesive coating, veneer assembly, 20-min curing, hot pressing, and cooling. The hot-pressing process was conducted at a pressure of 1.2 MPa, a temperature of 130 °C, and a duration of 10 min. The experimental procedure is shown in Figure 3.

Table 2. Formulation for the production of plywood.

	1	2	3	4	5
Poplar veneer	flour	unmodified corn cob	bentonite-modified corn cob	tannin-modified corn cob	bentonite- + tannin-modified corn cob
Additive Amount (%)	20	20	20	20	20
Granularity (mesh)	250	250	250	250	250

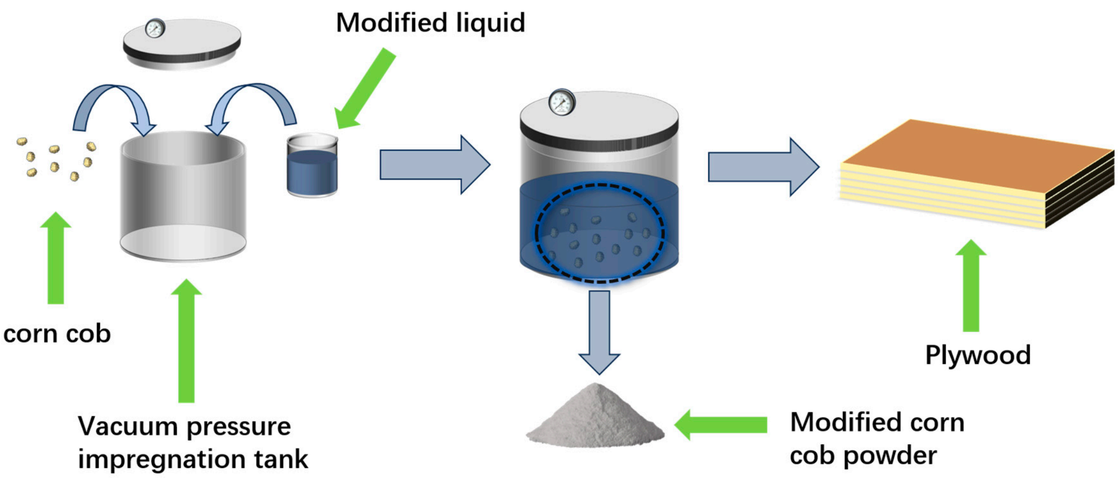

Figure 3. Experimental flow chart.

2.4. Performance Characterization

2.4.1. Performance Characterization of Corn Cob Powder

(1) Microscopic morphology

The distribution of sodium-based bentonite and bayberry tannin within the corn cob powder (250 mesh) was observed using SEM.

(2) Chemical properties

① An X-ray diffractometer was used to perform characterization analysis of the crystal phase and crystal structure of unmodified and modified corn cob powder (both with a particle size of 250 mesh). The diffractogram of the powder was analyzed to identify the diffraction peaks.

② Fourier Transform Infrared Spectroscopy was used to conduct analysis of the chemical functional groups in unmodified and modified corn cob powder (both with a particle size of 250 mesh). The characteristic peaks in the spectra of the powder were analyzed.

2.4.2. Adhesive Property Characterization

(1) Weighed amounts of unmodified and modified corn cob powder (both with a particle size of 250 mesh) as well as flour, in proportions of 0%, 5%, 10%, 15%, 20%, and 25% by weight of UF resin, were added to 60 g of UF resin and stirred evenly.

① The increase in volume of the UF adhesive after the addition of different fillers was compared.

② Following the testing method outlined in GB/T14074-2017 [20], the viscosity and curing time of the UF adhesive with different fillers were measured.

(2) Different particle sizes of modified corn cob powder and unmodified corn cob powder, as well as flour, with a mass of 20% of the resin, were added separately to 50 g of UF

resin and stirred evenly. The mixture was then dried in a drying oven at 60 °C for 1 h until it was partially cured into blocks. The blocks were removed and cut into 3 mm thick slices, which were then placed back in the drying oven and heated until fully cured. The cured slices were observed under a scanning electron microscope to examine the distribution of the fillers in the UF adhesive.

2.4.3. Characterization of Plywood Performance

Unmodified and modified corn cob powder (both with a particle size of 250 mesh) and flour were mixed into the UF resin with a mass ratio of 20% to prepare plywood, with the mixture stirred evenly.

(1) According to GB/T17657-2013 [21], the bonding strength of Type II plywood is determined by testing the bonding strength of specimens. The test uses Type A specimens, with a total of 4 groups and 3 specimens per group.
(2) According to GB/T17657-2013, the free formaldehyde emission of plywood is determined using the desiccator method. The test includes 4 groups, with 3 specimens in each group.

3. Results

3.1. Properties of Modified Corncob Powder

(1) Microscopic morphology

Figure 4 shows the SEM images of unmodified and modified corn cob powder. From Figure 4, it can be clearly observed that both bentonite and tannin have successfully deposited within the porous structure of the modified corn cob powder. The sodium-based bentonite appears as individual square-shaped particles, while the bayberry tannin exhibits an elliptical spherical shape.

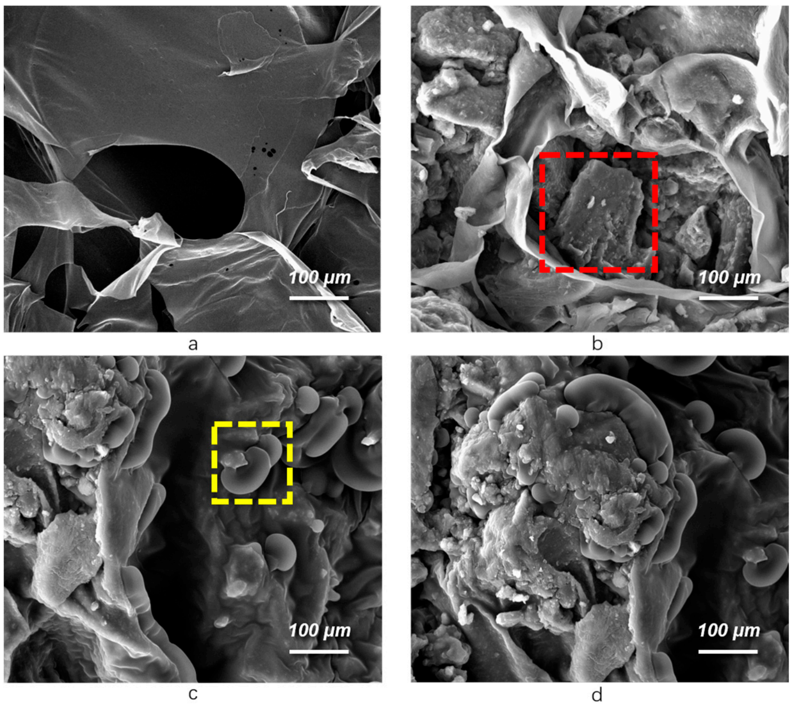

Figure 4. SEM of unmodified corn cob and modified corn cob ((**a**): unmodified corn cob; (**b**): bentonite-modified corn cob; (**c**): tannin-modified corn cob; (**d**): bentonite- + tannin-modified corn cob). In the red box is sodium-based bentonite; In the yellow box is bayberry tannin.

(2) The crystal structure of unmodified and modified corn cob powder was determined and analyzed using an X-ray diffractometer, and the results are shown in Figure 5A.

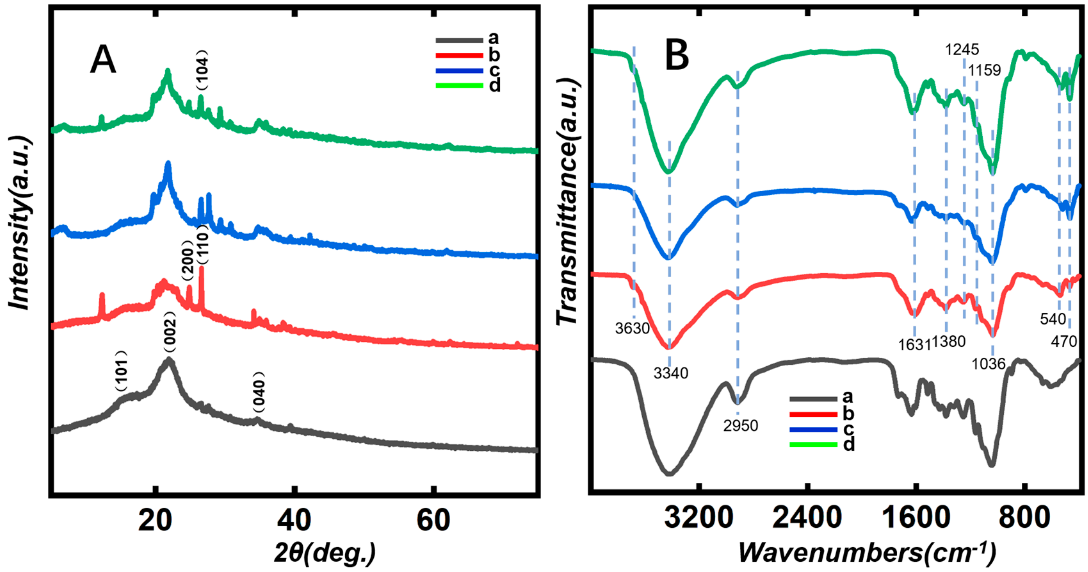

Figure 5. (**A**) XRD patterns of modified and unmodified corn cob powder; (**B**) FTIR spectra of modified and unmodified corn cob powder (a: unmodified corn cob; b: bentonite-modified corn cob; c: tannin-modified corn cob; d: bentonite- + tannin-modified corn cob).

Figure 5A shows the diffraction peaks observed at 2θ angles of 16.1°, 21.9°, and 34.6°, which correspond to the typical crystal planes (101), (002), and (040) of cellulose I in the corn cob powder [22,23]. After modification, these typical crystal planes of cellulose I showed slight shifts. The diffraction peak observed at a 2θ angle of 24.7° corresponds to the crystal plane (200) of NaO, the diffraction peak observed at a 2θ angle of 26° corresponds to the crystal plane (104) of $CaCO_3$, and the diffraction peak observed at a 2θ angle of 26.6° corresponds to the crystal plane (110) of SiO_2 [24]. After modification with bayberry tannin, new diffraction peaks appeared at 27.6°, 29.3°, and 30.9°, corresponding to the tannin's diffraction peaks. This phenomenon can be attributed to the interaction between the modification agent and water, which causes the expansion of the inner cell walls of the corn cob. As a result, the modification agent can more easily penetrate into the non-crystalline regions of the cell walls, leading to the expansion of the non-crystalline regions, and possibly even the crystalline regions. Ultimately, this leads to a decrease in the relative crystallinity of the corn cob.

(3) The chemical functional groups of unmodified and modified corn cob powder were analyzed using Fourier-transform infrared spectroscopy (FTIR), and the results are shown in Figure 5B. The absorption peak at 3340 cm^{-1} in the FTIR spectrum corresponds to the hydroxyl groups involved in the hydrogen bonding of corn cob [25]. The peak height of the hydroxyl absorption peak at 3300–3400 cm^{-1} increased from around 0.73 to 0.84 compared to the unmodified corn husk. The decrease in volume and intensity indicates the successful deposition of the modifier inside the corn husk. Additionally, an absorption peak appeared at 2950 cm^{-1}, which corresponds to the stretching vibration of -CH_2 functional group. This is mainly due to the asymmetric stretching vibration of C-H bonds in corn husk [26,27].

In the high-frequency region, the sodium-based bentonite exhibits stretching vibrations of Al-OH at 3630 cm^{-1}, whereas in the mid-frequency region, the absorption peak at 1631 cm^{-1} is attributed to the bending vibration of interlayer water molecules (H-O-H). The absorption peak range between 1380 cm^{-1} and 1631 cm^{-1} corresponds to the benzene ring skeleton vibration in the tannin structure [28]. The vibration peak at 1036 cm^{-1} is attributed to the stretching vibration of the C=O bonding. The absorption peaks at 1245 cm^{-1} and 1159 cm^{-1} mainly arise from the deformation vibration of C-H bonds. In the low-wavenumber region, there are two distinct bending vibration bands at 530 cm^{-1} and 470 cm^{-1}. The bending vibration near 470 cm^{-1} corresponds to Si-O-Si, while the bending vibration near 530 cm^{-1} corresponds to Si-O-Al [29,30]. These observations further confirm that the modified corn cob powders, obtained through a two-step vacuum impregnation method, successfully deposit the modifiers into the cell cavities of the corn cob.

3.2. Adhesive Properties

3.2.1. Micromorphology

The distribution of untreated corn cob and modified corn cob in the UF adhesive is shown in Figure 6.

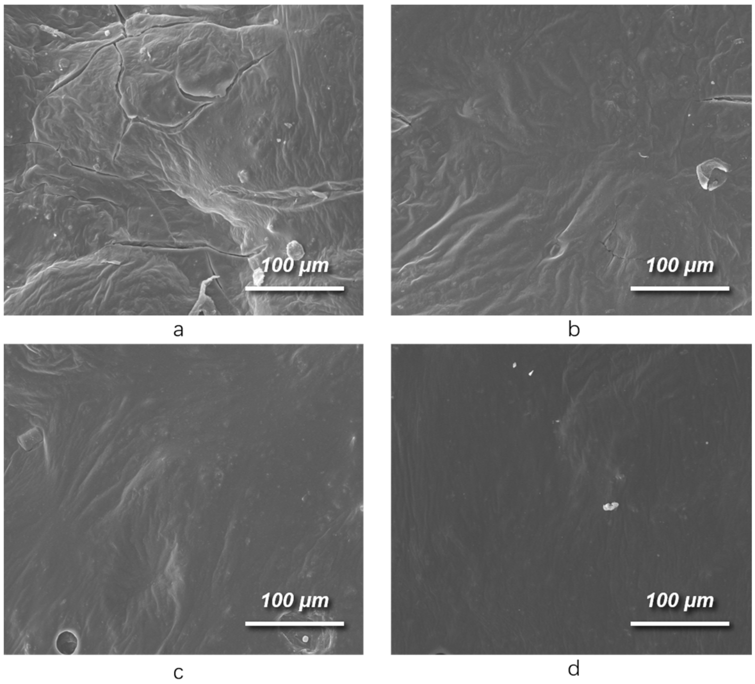

Figure 6. Distribution of unmodified corn cob and modified corn cob in UF solution ((**a**): unmodified corn cob; (**b**): bentonite-modified corn cob; (**c**): tannin-modified corn cob; (**d**): bentonite- + tannin-modified corn cob).

Figure 6 shows that, with the addition of modified additives, the dispersion of corn cob in the UF adhesive improves, resulting in a smoother surface after curing. Additionally, comparing the cured untreated corn cob with modified corn cob, it was observed that the untreated corn cob had obvious cracks and protrusions on the surface. However, with the addition of the modified additives, the dispersion of the modified corn cob in the adhesive improved, resulting in the disappearance of cracks and reduced protrusions on the surface of the cured adhesive. In particular, when both bentonite- and tannin-modified additives were added simultaneously, the surface of the cured adhesive became flat and smooth, indicating the best dispersion. Overall, both bentonite and tannin can improve the dispersion of corn cob in the urea–formaldehyde adhesive, and the best dispersion is achieved when both additives are used together.

3.2.2. The Viscosity of UF Adhesive after Adding Fillers of Different Particle Sizes

Figure 7 demonstrates that, as the particle size of both untreated and modified corn cob powder decreases from 150 mesh to 250 mesh, the viscosity of the UF adhesive filled with the powder gradually increases. The viscosity of the UF adhesive reaches its peak when 250 mesh untreated and modified corn cob powders are utilized as fillers. However, when the particle size of both untreated and modified corn cob powders continues to decrease to 300 mesh, the viscosity of the UF adhesive decreases. The viscosity of the UF adhesive reaches its highest point when the particle size of the powder is 250 mesh, and is significantly higher compared to the viscosity of other particle sizes of both untreated and modified corn cob powders, even up to double or several times higher. This indicates that 250 mesh is the appropriate particle size for using modified corn cob powder as a filler in urea–formaldehyde adhesive.

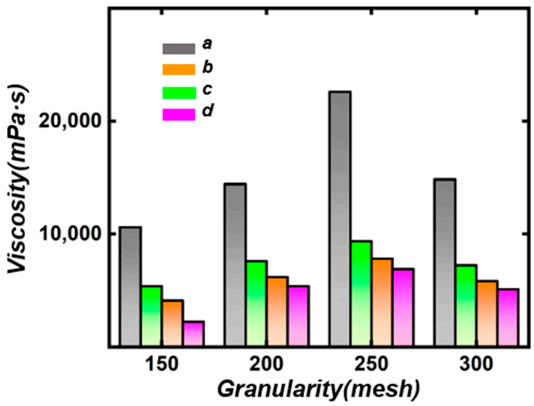

Figure 7. Effect of particle size on UF viscosity (a: untreated corn cob; b: bentonite-modified corn cob; c: tannin-modified corn cob; d: bentonite- + tannin-modified corn cob).

3.2.3. The Viscosity of UF Adhesive after Adding Fillers in Different Proportions

The viscosity of UF adhesive after adding untreated and modified corn cob powders and flour into the UF adhesive is shown in Figure 8. As the amount of untreated and modified corn cob powders and flour increases, the viscosity of the UF adhesive also increases, indicating that the addition of untreated and modified corn cob powders and flour has a thickening effect on the urea–formaldehyde adhesive. However, when the amount of untreated corn cob powder increases, the viscosity of the UF adhesive increases sharply, resulting in poor flowability. Excessive viscosity can make the UF adhesive too thick, leading to difficulties and uneven application. On the other hand, modified corn cob powders have a significant thinning effect. When the amount of bentonite-modified corn cob powder is 15%–20%, the viscosity of the UF adhesive ranges from 4520 mPa·s to 9360 mPa·s. When the amount of tannin-modified corn cob powder is 15%–20%, the viscosity of the UF adhesive ranges from 3640 mPa·s to 7840 mPa·s. When the amount of bentonite- + tannin-modified corn cob powder is 15%–20%, the viscosity of the UF adhesive ranges from 3180 mPa·s to 6900 mPa·s. When the amount of flour is 15%–20%, the viscosity of the UF adhesive ranges from 4660 mPa·s to 9540 mPa·s. In addition, at this range of modified corn cob powder addition, the viscosity of the UF adhesive is most suitable for adhesive application.

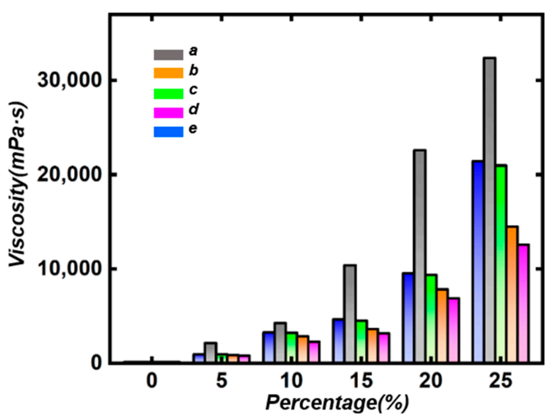

Figure 8. Effect of dosage on UF adhesive viscosity (a: untreated corn cob; b: bentonite-modified corn cob; c: tannin-modified corn cob; d: bentonite- + tannin-modified corn cob; e: flour).

3.2.4. The Curing Time of UF Adhesive after Adding Fillers with Different Particle Sizes

According to Figure 9, it can be observed that, when the addition amount is 20%, the curing time of UF adhesive filled with untreated and modified corn cob powders is longer than that of UF adhesive filled with flour. During the hot-pressing process of plywood, the pressing time should be appropriately extended to ensure the complete curing of the glue layer and to ensure the bonding strength of the plywood. As the particle size of untreated and modified corn cob powders decreases from 150 mesh to 250 mesh, the change trend of the UF adhesive is not significant, but overall it shows a decreasing and then increasing trend. When the particle size of untreated and modified corn cob powders is 250 mesh, the curing time of the UF adhesive is the shortest. After further reducing the particle size, the curing time of the UF adhesive slightly increases. Therefore, when the particle size of the powder is 250 mesh, it has the least impact on the curing time of the UF adhesive.

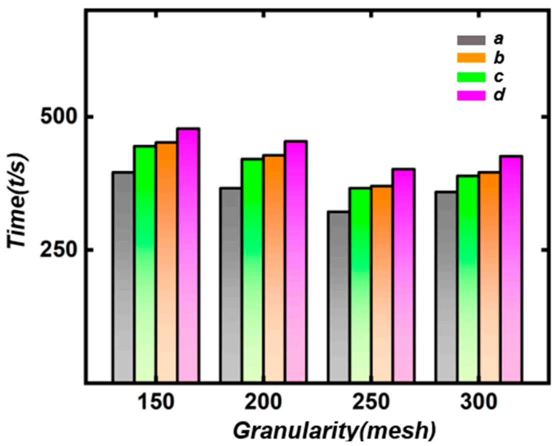

Figure 9. Effect of particle size on UF curing time (a: untreated corn cob; b: bentonite-modified corn cob; c: tannin-modified corn cob; d: bentonite- + tannin-modified corn cob).

3.2.5. The Curing Time of UF Adhesive after Adding Fillers with Different Proportions

The curing time of the UF adhesive was studied after adding different proportions of untreated and modified corn cob powders, as well as flour, as fillers. The curing time results are shown in Figure 10. After adding untreated and modified corn cob powders, as well as flour, the curing time of the UF adhesive is longer compared to when no fillers are added. The curing time increases with the increasing addition of untreated and modified corn cob powders. However, the change is not significant with the increasing addition of flour. When the addition amount of flour reaches 25%, the curing time of the UF adhesive slightly decreases. It can be observed that flour, as a filler for urea–formaldehyde adhesive, provides a relatively stable curing time for the UF adhesive. In contrast, untreated and modified corn cob powders as fillers result in a longer curing time, indicating that they slow down the curing rate of the UF adhesive and effectively prevent premature curing. Among the modified corn cob powders, the combination of bentonite and tannin shows the most significant effect, suggesting that when bentonite and tannin are used as modification agents for corn cob powder as a filler for urea–formaldehyde adhesive, they have the best effect in preventing premature curing of the adhesive.

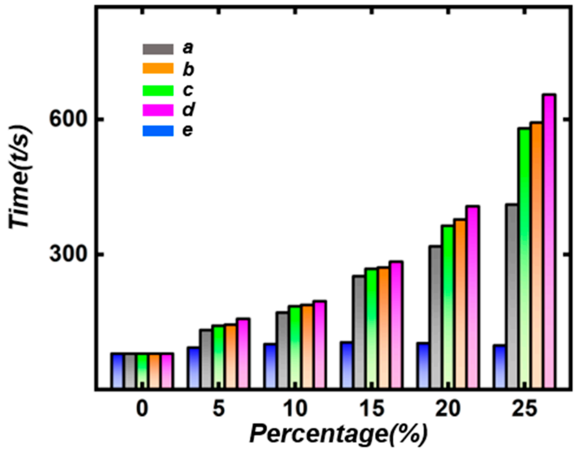

Figure 10. Effect of adding amount on curing time of UF (a: untreated corn cob; b: bentonite-modified corn cob; c: tannin-modified corn cob; d: bentonite- + tannin-modified corn cob; e: flour).

3.2.6. The Volume Increase in UF Adhesive after Adding Different Fillers

The higher the viscosity of the adhesive, the thicker the adhesive solution, and the smaller the volume, resulting in a lower volume increase. The original volume of the adhesive is 200 mL. Fillers such as untreated and modified corn cob powder (both with a particle size of 250 mesh) at a concentration of 20% of the adhesive mass, as well as flour, were added. To calculate the average volume change, we can refer to Table 3. The table shows that the UF adhesive with bentonite-modified corn cob powder as a filler has the largest volume change, while the UF adhesive with untreated corn cob powder as a filler has the smallest volume change. The reason for this is that untreated corn cob powder easily absorbs the adhesive, resulting in thickening of the mixture, leading to a smaller volume change. On the other hand, the combination of bentonite and tannin modification effectively reduces the viscosity of the corn cob powder, resulting in some thinning and achieving a greater volume increase. Overall, the effect of using the combination of bentonite and tannin modification as a filler is superior to using flour for achieving volume increase.

Table 3. The volume increment of UF adhesive after adding 20% of different fillers (mL).

Fillers	Flour	Unmodified Corn Cob	Modified Corn Stover with Bentonite	Modified Corn Stover with Tannin	Bentonite + Tannin Modified Corn Stover
Volume of the adhesive (mL)	230 ± 7	210 ± 8	244 ± 7	237 ± 6	241 ± 8

3.3. *Performance of Plywood*

The table presented (Table 4) displays the testing results for the density, bonding strength, and formaldehyde emission of plywood produced with UF adhesive. Modified corn cob powder and flour were used as fillers with a loading amount of 20% and a particle size of 250 mesh. The values shown in the table are the average results obtained from five experimental groups.

From Table 4, it can be observed that when modified corn cob powder is used as a filler, the bonding strength is higher than when flour is used as a filler, and it meets the national standard requirement (0.7 MPa). This is because modified corn cob powder has a higher content of cellulose and hemicellulose, and the finely ground 250 mesh modified corn cob powder has good filling properties, reducing stress at the bonding interface and improving bonding strength. Additionally, corn cob powder contains a large amount of cyclic substances that react with urea–formaldehyde resin at high temperatures, increasing cross-linking density and improving the bonding strength of the plywood. Furthermore, when modified corn cob powder is used as a filler, the formaldehyde emission is lower compared to using flour as a filler. This is because the increment properties of modified corn cob powder are superior to flour, resulting in less adhesive application. Bayberry tannins contain catechins, which can react with formaldehyde to eliminate a portion of it. At the same time, bentonite has excellent adsorption properties and exhibits a good adsorption effect on formaldehyde, resulting in a reduction in the released amount of formaldehyde. In terms of fillers using modified corn cob powder, the bonding strength is higher when bentonite- + tannin-modified corn cob powder is used compared to single modification, and the formaldehyde emission is lower. Therefore, the combination of bentonite- and tannin-modified corn cob powder is more suitable as a filler for UF adhesive in plywood preparation.

Table 4. The bonding strength and formaldehyde emission of plywood prepared with modified corn cob powder and flour as fillers at a filler content of 20% were evaluated.

Fillers	Density/(g·cm^{-3})	Adhesive Strength/MPa	Formaldehyde Emission Level/(mg·L^{-1})
Flour	230 ± 7	210 ± 8	244 ± 7
Modified corn stover with bentonite	0.62 ± 0.05	1.32 ± 0.06	1.24 ± 0.05
Modified corn stover with tannin	0.72 ± 0.04	1.48 ± 0.04	1.10 ± 0.04
Bentonite + tannin modified corn stover	0.71 ± 0.06	1.58 ± 0.04	0.97 ± 0.06

3.4. Analysis of Pre-Pressing Effect

The pre-pressing effects of the four groups of specimens are shown in Figure 11. The results of the pre-pressing test of the plywood indicate that after being cold pressed for 60 min in the pre-press machine, all four panels achieved complete consolidation and could not be separated by hand. Additionally, after being left for 30 min, no delamination occurred, suggesting that the pre-pressing performance of the plywood prepared with modified fillers meets the requirements.

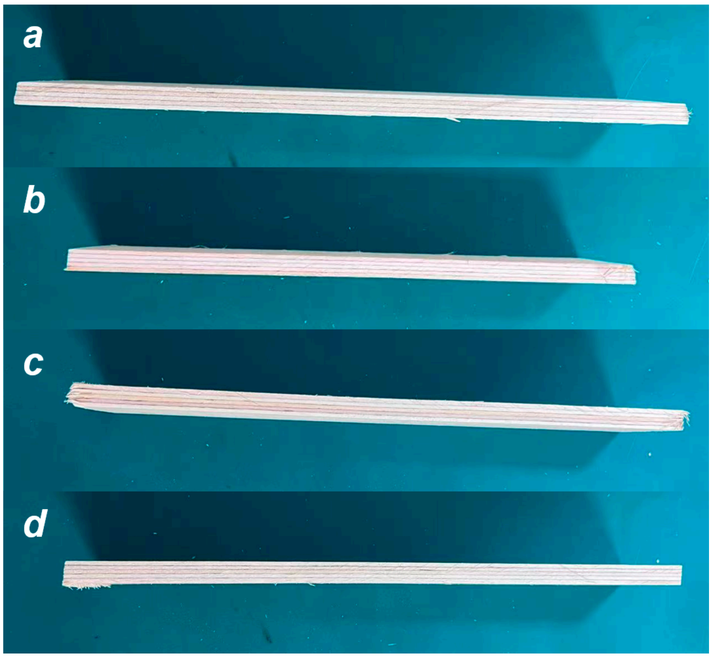

Figure 11. Cold-pressing effect of plywood prepared with UF adhesive using modified corn cob powder and flour as fillers ((**a**): flour; (**b**): modified corn cob with bentonite; (**c**): modified corn cob with tannin; (**d**): bentonite- + tannin-modified corn cob).

4. Conclusions

(1) Both bentonite and tannin can improve the dispersibility of corn cob in urea–formaldehyde (UF) adhesive solution. The best dispersibility is achieved when both additives are used simultaneously.

(2) Compared to flour and unmodified corn cob powder, modified corn cob powder has excellent thickening properties. The optimal addition amount ranges from 15% to 20%, with a mesh size of 250 being most suitable for the adhesive coating process of plywood.

(3) When compared to flour, the use of modified corn cob powder as a filler can prolong the curing time of UF adhesive, effectively preventing pre-curing. The resulting plywood exhibits bonding strength that meets the requirements of GB/T9846-2015 [31], with an improvement of 12.1% to 19.6%. It also reduces formaldehyde emission by 12.7% to 27.8%. Among them, the combination of bentonite- and bayberry tannin-modified corn cob powder shows the best performance as a filler.

(4) Plywood prepared with modified corn cob powder as a filler demonstrates excellent cold pressing results and meets the requirements for cold-pressing performance of plywood.

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