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Abstract: This study sought to improve the utilization of sorghum straw resources and promote the industrial production of new biomass materials. Herein, we fabricated SSP/ZnO/PVA nanocomposite films from sorghum straw powder (SSP), corn starch, polyvinyl alcohol (PVA), and nanostructured ZnO via the casting method. Then, we used response surface methodology to examine the effects of the mass concentrations of SSP, glycerol (Gly), and nanostructured ZnO, as well as the starch-PVA mass ratio on the tensile strength (TS) and water vapor permeability (WVP) of the SSP/ZnO/PVA nanocomposite films. The optimum preparation conditions were as follows: SSP mass concentration of 2.0 g/150 mL, Gly mass concentration of 2.5 g/150 mL, starch-PVA mass ratio of 6:4.5, and nanostructured ZnO mass concentration of 0.7 g/150 mL. The TS and WVP of the prepared films were 47.57% higher and 27.07% lower, respectively, than those of ZnO/PVA composite films without SSP. Scanning electron microscopy and atomic force microscopy showed that the SSP/ZnO/PVA nanocomposite films had smooth surfaces and dense cross-sections, without obvious delamination or phase separation. Fourier transform infrared spectroscopy, X-ray diffraction, and thermogravimetric analyses revealed that SSP was highly compatible with the ZnO/PVA matrix. Thus, SSP addition could improve the crystallinity, thermal stability, and matrix interactions of SSP/ZnO/PVA nanocomposite films.

Keywords: sorghum straw powder; nanostructured ZnO; polyvinyl alcohol; nanocomposite film; physical properties; structural characterization

1. Introduction

In recent years, in order to reduce the environmental burden of traditional petroleumbased materials, the use of biomass-based materials, such as cellulose and starch, to prepare degradable films has become the focus of a great deal of active research. As a common biomass resource, sorghum straw is widely distributed throughout close to 50 countries and regions around the world. The annual output of sorghum straw in China alone is as high as four million tons. At present, sorghum straw is mainly used as animal feed, soil fertilizer, and industrial raw material. However, sorghum straw presents certain drawbacks as a feed material; for instance, the straw has high anti-nutritional factor and prolamin contents, as well as low lysine contents. Sorghum straw is used in limited amounts as a material for soil enhancement and industrial purposes. Large amounts of leftover sorghum straw are thus discarded or incinerated. Besides wasting sorghum straw resources, this practice also threatens the ecological environment. The key to the rational utilization and improvement of the comprehensive values of sorghum straw lies in the study of its energy and industrial utilization technology [1].

Polyvinyl alcohol (PVA) is a nontoxic and biodegradable film-forming polymer resin [2,3]. However, it also contains a large number of hydrophilic –OH groups, which gives PVAbased composites a high water vapor transmission rate (WVTR) and, thus, limits their



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). applications in the field of materials science. The combination of nanoparticles with PVA leads to materials featuring large filler interface areas, enhanced molecular mobility, and reduced hydrophilicity [4]; thus, the performance of nanoparticle-modified PVA is enhanced [5]. Nanostructured ZnO is nontoxic and highly stable. It can improve the mechanical and barrier properties of polymers [6–8] when used as a nanostructured filling material.

oil/chitosan membranes could positively alter the mechanical and barrier properties of the resultant films. Biomass materials have broad application prospects owing to their environmentally friendly and renewable properties. Although some edible biomass materials offer excellent performance, their use in applications not intended for consumption is not recommended because of their edible value. Non-edible biomass materials also have more natural advantages in terms of materials and properties, and their production can save energy, reduce emissions, and exploit green resources [10]. Sorghum straw is rich in cellulose, hemicellulose, and lignin [11,12]. Given its relatively large specific surface area, high specific strength, and low density, it is suitable for use as a reinforcement material for polymer-based composite films [13,14]. Therefore, sorghum straw can be mixed with an environment-friendly polymer to not only form a composite material with improved performance but also enhance the comprehensive utilization value of sorghum straw [15,16]. Recently, multicomponent composites based on biomass-derived carbon materials have been extensively studied. For example, Hou et al. [17] used $CoFe_2O_4$, polyaniline and discarded grapefruit peels as the matrix to prepare a new type of biomass material with the advantages of high absorption strength, absorption bandwidth, and light weight through simple carbonization and polymerization processes. Sun et al. [18] demonstrated that adding corn stalk nanocellulose into corn phosphate starch films can improve the tensile strength (TS) and barrier properties of the resultant films. Kunanopparat et al. [19] and Dobircau et al. [20] found that hemp straw and cotton fibers can improve the physical properties of wheat starch films. El Halal et al. [21] revealed that adding barley husk fibers has a positive effect on the TS and water vapor permeability (WVP) of starch films. Da Silva et al. [22] demonstrated that eucalyptus nanocellulose can enhance matrix interactions in cassava starch films, leading to positive effects on their mechanical and water resistance properties. Oliveira et al. [23] observed via scanning electron microscopy (SEM) that eucalyptus cellulose can be effectively dispersed in protein-based films and improve their TS and reduce their elongation at break. Numerous studies on the preparation of biomass materials after the extraction of cellulose from straw have been published [24,25]; however, cellulose extraction not only

Sanuja et al. [9] showed that the application of nanostructured ZnO to neem essential

In this study, sorghum straw was pretreated to solve the above problem. The preprocessed sorghum straw powder (SSP) was directly mixed with corn starch and PVA and then added with glycerol (Gly) and nanostructured ZnO to prepare nanocomposite films. The preparation conditions were optimized to improve the properties of the resultant films. Next, the microstructure, crystal structure, and spectral and thermal properties of the nanocomposite films were investigated using SEM, atomic force microscopy (AFM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), and thermogravimetric analysis (TGA). The results of this work could improve the utilization of sorghum straw resources and provide a useful reference to promote the industrial production of new biomass materials.

increases the difficulty of the process but also reduces the utilization efficiency of the straw. Moreover, directly mixing straw with the polymer leads to biomass materials with poor mechanical properties and stability, which in turn limit their industrial applications [26].

2. Materials and Methods

2.1. Materials and Reagents

The materials used in this study included corn starch (edible grade; Angel Yeast Co., Ltd., Yichang, China), sorghum straw (Anda Agricultural Science and Technology Park, Daqing, China), nanostructured ZnO (particle size, 30 ± 10 nm; analytical grade;

Shanghai Aladdin Co., Ltd., Shanghai, China), PVA ([CH₂CH(OH)]*n*; molecular weight, 75,000–79,000 g/mol; average degree of polymerization, 1750 \pm 5; Shanghai McLean Biochemical Technology Co., Ltd., Shanghai, China), and Gly (C₃H₈O₃; purity \geq 99%). Other chemical reagents (analytical grade) used in the experiments were provided by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

2.2. Instruments and Equipment

The instruments and equipment used in the study included a JD100-3B electronic balance (Shimadzu Corp, Shanghai, China), a 101-2A electric blast drying oven, a HWS24 thermostatic water bath, a BPMJ thermostatic incubator (Zhengzhou Pushton Electronic Instruments Co., Ltd., Zhengzhou, China), KH-500DE digital control ultrasonic cleaner, a DFY-200C high-speed universal pulverizer (Shanghai LNB Instrument Co., Ltd., Shanghai, China), a JJ-1 electric blender (G&G International Co., Ltd., Changzhou, China), an XLW electronic tensile tester, a TSY-T1L water vapor transmission rate testing system, and a BMH-1 3 spiral micrometer (Labthink Instruments Co., Ltd., Jinan, China). In addition, a Merlin scanning electron microscope (Carl Zeiss, Oberkochen, Germany), an AVATAR360 spectrometer (Thermo Nicolet Corp., Shenzhen, China), a MiniFlex600 X-ray diffractometer (Rigaku Corp., Tokyo, Japan), a Q50 thermogravimetric analyzer (TA Instruments, Suzhou, China), and JPK atomic force microscope (Bruker, Saarbrücken, Germany) were used for characterization, as well as a laboratory-made plexiglass film former.

2.3. Methods

2.3.1. Pretreatment of Sorghum Straw

The sorghum straw was cut into sections, washed, dried, crushed, and filtered through a 100-mesh sieve to obtain raw straw powders. The powder was dispersed in distilled water at a solid-to-liquid ratio of 1:10 (g/mL). The mixture was boiled for 15 min, cooled, and filtered. Next, NaOH (mass concentration, 10 g/100 mL) was added to the filter residue at a liquid-to-solid ratio of 5:1 (mL/g). The mixture was subjected to ultrasonic-assisted treatment at 180 W and 75 °C for 60 min and then suction-filtered. The filter residue was washed with neutral distilled water and added with NaClO at a liquid-to-solid ratio of 2:1 (mL/g). The mixture was washed to neutrality and 75 °C for 45 min and then suction-filtered. The residue was washed to neutrality and freeze-dried to obtain SSP. The flow chart of the sorghum straw pretreatment process is shown in Figure 1.

2.3.2. Preparation of SSP/ZnO/PVA Nanocomposite Films

Based on the methods of Zhong et al. [27] and Ortega-Toro et al. [28], certain amounts of nanostructured ZnO and SSP were added to 150 mL of distilled water. The mixture was ultrasonically dispersed, added with starch and PVA, magnetically stirred, and then added with Gly. The mixture was then heated under stirring in a water bath at 85 °C for 45 min and degassed with ultrasonic waves. Some of the slurry was cast on a self-made glass plate to form a film. The film was then dried at 60 °C for 4 h, removed from the plate, and placed in an incubator set to a temperature of 25 °C with a relative humidity of 60% for over 24 h. Finally, the properties of the nanocomposite films were tested. Figure 2 presents a flow chart of the preparation process of the nanocomposite films.







Figure 2. Flow chart of the preparation process of SSP/ZnO/PVA nanocomposite films.

2.3.3. Determination of the Properties of the Nanocomposite Films Thickness Determination

The film thickness (mm) was measured from four symmetric edge points and the center point of the film according to GB/T 6672-2001 *Plastic Film and Sheeting—Determination of Thickness*. The results of this test were averaged.

TS Determination

TS was measured according to GB/T 1040.3-2006 *Tensile Property Testing of Films and Sheets* and then calculated according to Equation (1):

$$TS/MPa = \frac{F}{B \times d}$$
(1)

where F is the maximum tension (N) the film can bear before it breaks, B is the film width (mm), and d is the film thickness (mm).

WVP Determination

WVP was determined in accordance with GB 1037-1988 Test method for water vapor permeability of plastic films and sheets—cup method and GB/T 16928-1997 Test method for packaging materials—moisture permeability and calculated according to Equations (2) and (3):

WVTR =
$$\frac{1}{A} \cdot \left(\frac{\Delta m}{t}\right)$$
 (2)

WVP/
$$(10^{-12} \text{ g/(cm \cdot s \cdot Pa)}) = \frac{\text{WVTR} \times \text{d}}{\Delta P} \times 100,$$
 (3)

where A is the area of the test cup rim (cm²), $\Delta m/t$ is the mass change of the film per unit time (g/s), d is the film thickness (cm), and ΔP is the difference in vapor pressure between the two sides of the film (Pa).

2.3.4. Single-Factor Experimental Design

Nanocomposite films were prepared as described in Section 2.3.2. The single-factor experimental design is shown in Table 1; here, the fixed level was set to an SSP mass concentration of 2 g/150 mL, Gly mass concentration of 2.5 g/150 mL, starch–PVA mass ratio of 7:3, and nanostructured ZnO mass concentration of 0.6 g/150 mL.

	Factor						
Level	SSP Mass Concentration/ (g/150 mL)	Gly Mass Concentration/ (g/150 mL)	Starch–PVA Mass Ratio/ (w/w)	Nanostructured ZnO Mass Concentration/ (g/150 mL)			
1	1	1.5	9:1	0.2			
2	1.5	2	8:2	0.4			
3	2	2.5	7:3	0.6			
4	2.5	3	6:4	0.8			
5	3.0	3.5	5:5	1.0			

Table 1. Factors and levels used in the single-factor experiments.

2.3.5. Response Surface Experimental Design

According to the results of the single-factor test, Design-Expert software 13.0 and the Box–Behnken test design were adopted to formulate a four-factor, three-level Box–Behnken experimental design. The experimental factors used were SSP mass concentration (X_1), Gly mass concentration (X_2), starch–PVA mass ratio (X_3), and nanostructured ZnO mass concentration (X_4). The response values were TS (Y_1) and WVP (Y_2). The factors and levels used in this study are shown in Table 2.

Table 2. Factors and levels used in the response surface design.

Tester	Level			
ractor	-1	0	1	
X_1 —SSP mass concentration/(g/150 mL)	1.5	2	2.5	
X_2 —Gly mass concentration/(g/150 mL)	2	2.5	3	
X_3 —starch–PVA mass ratio/(w/w)	7:3	6:4	5:5	
X ₄ —nanostructured ZnO mass concentration/(g/150 mL)	0.4	0.6	0.8	

2.3.6. Microstructural Observation and Characterization SEM

The samples were cut into squares or rectangles (5 mm \times 5 mm or 5 mm \times 1 mm), fixed, and sprayed with gold. The surface and cross-sectional morphologies of the nanocomposite films were observed using SEM at an accelerating voltage of 5 kV.

AFM

The samples were cut into squares (10 mm \times 10 mm) and then fixed on the testing platform. The measurements were performed in tapping mode with a scan area of 1 μ m \times 1 μ m, scan frequency of 0.55 Hz, and cantilever elastic constant of 26 N/m.

XRD

The samples were cut into squares (20 mm \times 20 mm) and then placed in the test chamber of the X-ray diffractometer with a Cu K α X-ray source. Step measurements were performed with a tube current of 40 mA, tube voltage of 40 kV, scanning range of 5°–50°, step angle of 0.020°, and sampling time of 0.1 s.

FT-IR

Attenuated total reflectance FT-IR analysis was conducted to examine the chemical interactions in the films. The samples were placed under the test probe, and the corresponding spectra were measured over the wavelength range of $500-4000 \text{ cm}^{-1}$ with a scan count of 16 and resolution of 4 cm⁻¹.

TGA

A 5–10 mg sample was placed in an aluminum crucible for TGA. An empty aluminum crucible was used as the control, and nitrogen (99.999%) was used as the protective gas. The thermal properties of the samples were tested at a heating rate of 10 $^{\circ}$ C/min in the temperature range of 50–500 $^{\circ}$ C.

2.4. Statistical Analysis

At least three parallel replicates were tested for each sample. The data were analyzed using SPSS 19.0 software and Duncan's method at a significance level of p < 0.05. Origin 9.0 was employed for all illustrations, and the response surface test results were subjected to linear regression and variance analysis using Design-Expert (p < 0.05).

3. Results and Discussion

3.1. Effect of SSP Mass Concentration on the Physical Properties of the Nanocomposite Films

Figure 3 shows that, as the SSP mass concentration increases, TS first increases and then decreases, whereas WVP first decreases and then increases. When the SSP mass concentration is 2.0 g/150 mL, TS reaches a maximum value of 31.32 MPa, and WVP reaches a minimum value of 1.273×10^{-12} g/(cm·s·Pa). When added at an appropriate amount, SSP is fully dispersed in the matrix and promotes the formation of strong intermolecular hydrogen bonds, enhances matrix interactions, and increases the density of the film structure, leading to an increase in TS. In addition, SSP forms numerous channels through which water vapor in the matrix can effectively diffuse, thereby increasing WVP [29]. However, when excess SSP is continuously dispersed into the matrix, the dense matrix structure becomes loose owing to the agglomeration of SSP and cracks appear. In this case, water molecules can easily penetrate the matrix, decreasing TS and increasing WVP. Thus, an SSP mass concentration of 2.0 g/150 mL was chosen as the central level for the response surface test.



Figure 3. Effect of SSP mass concentration on the physical properties of the nanocomposite films.

3.2. Effect of Gly Mass Concentration on the Physical Properties of the Nanocomposite Films

As shown in Figure 4, as the Gly mass concentration increases, TS first increases and then decreases, whereas WVP first decreases and then increases. When the Gly mass concentration is 2.5 g/150 mL, TS reaches a maximum value of 29.13 MPa, and WVP reaches a minimum value of 1.243×10^{-12} g/(cm·s·Pa). The increase in TS and decrease in WVP can be explained by the conformational change of starch molecules when a certain temperature and shear force are applied to the matrix.



Figure 4. Effect of Gly mass concentration on the physical properties of the nanocomposite films.

In this case, the starch molecules change from a helical conformation to a random coil one, leading to the penetration of Gly molecules into the interior of the starch granules. The film-forming substances in the matrix become entangled with each other and form intermolecular hydrogen bonds, which enhance their interactions and hinder the permeation of water vapor. However, as the Gly mass concentration gradually increases, changes in the hydrogen bonds in the matrix occur. These changes weaken the interaction forces, enlarge the structural voids, loosen the film structure, and increase the hydrophilicity of the film [18]; thus, TS decreases, and WVP increases. Based on these results, a Gly mass concentration of 2.5 g/150 mL was used as the central level for the response surface test.

Figure 5 demonstrates that, as the PVA content in the matrix increases, TS first increases and then decreases, whereas WVP first decreases and then increases.



Figure 5. Effect of starch–PVA mass ratio on the physical properties of the nanocomposite films.

When the starch–PVA mass ratio is 6:4, TS reaches a maximum value of 31.32 MPa, while WVP reaches a minimum value of 1.213×10^{-12} g/(cm·s·Pa). These results are due to the addition of PVA to the matrix as a reinforcing agent, which promotes the formation of strong intermolecular hydrogen bonds and enhances interactions among the film-forming substances. As the crystallinity of the film decreases and its structure becomes more compact, the passage of water molecules is inhibited; thus, TS increases, and WVP decreases. However, as the PVA content gradually increases, the number of hydrophilic groups in the system increases accordingly, and the intermolecular hydrogen bonds are destroyed. Thus, the interactions in the system are reduced, and the film structure becomes loose. Moreover, the formation of hydrophilic groups increases the sensitivity of the matrix to water molecules. As a result, TS decreases, and WVP increases. Based on these findings, a starch–PVA mass ratio of 6:4 was applied as the central level for the response surface test.

3.4. Effect of Nanostructured ZnO Mass Concentration on the Physical Properties of the Nanocomposite Films

As shown in Figure 6, as the nanostructured ZnO mass concentration in the matrix increases, TS first increases and then decreases, whereas WVP first decreases and then increases. When the nanostructured ZnO mass concentration is 0.6 g/150 mL, TS reaches a maximum value of 30.22 MPa, while WVP reaches a minimum value of 1.223×10^{-12} g/ (cm·s·Pa). These changes can be attributed to the increased adsorption and bonding of nanostructured ZnO, which features a small particle size, to the matrix.

The presence of nanostructured ZnO endows the matrix with a certain interfacial adhesion property, which promotes stress transfer, thereby allowing the film to bear a certain load. In addition, the nucleation of nanostructured ZnO could increase the crystallization area of the composite system, which improves its crystallization performance, reduces the availability of channels through which water vapor can permeate, and, hence, enhances the water-blocking performance of the film. These findings are consistent with the XRD results. The combination of nanostructured ZnO with PVA leads to the formation of a large filler interface area, which can alter the molecular fluidity of the matrix and reduce its hydrophilicity by combining with –OH [4]. Therefore, TS increases, and WVP decreases. As the amount of nanostructured ZnO added to the films increases, the particles tend to agglomerate in the matrix, destroying its original dense structure and causing the interior to become loose. These changes lead to a stress concentration and permit water molecules to

permeate into the film. Therefore, TS decreases, and WVP increases. Based on these results, a nanostructured ZnO mass concentration of 0.6 g/150 mL was chosen as the central level for the response surface test.



Figure 6. Effect of nanostructured ZnO mass concentration on the physical properties of the nanocomposite films.

3.5. Response Surface Test Results

3.5.1. Response Surface Test Design and Results

Considering the results of the single-factor tests, a four-factor, three-level response surface test was conducted; here, SSP mass concentration (X_1) , Gly mass concentration (X_2) , starch–PVA mass ratio (X_3) , and the nanostructured ZnO mass concentration (X_4) were taken as the test factors, and TS (Y_1) and WVP (Y_2) were taken as the response values. The results are shown in Table 3. Design-Expert was used to perform quadratic polynomial regression fitting of the experimental data in Table 3 and obtain the regression equations of TS (Y_1) and WVP (Y_2) as follows.

 $TS (Y_1) = 30.928 + 1.2742 X_1 + 0.9975 X_2 + 3.9725 X_3 + 0.9708 X_4 - 1.0875 X_1 X_2 + 1.2175 X_1 X_3 + 0.9725 X_1 X_4 - 0.7875 X_2 X_3 + 0.4225 X_2 X_4 + 1.7625 X_3 X_4 - 3.9419 X_1^2 - 1.6794 X_2^2 - 5.3419 X_3^2 - 3.2844 X_4^2$

 $WVP (Y_2) = 1.2140 - 0.1058 X_1 - 0.0183 X_2 + 0.1425 X_3 + 0.0099 X_4 + 0.0100 X_1 X_2 + 0.0100 X_1 X_3 - 0.0025 X_1 X_4 + 0.0025 X_2 X_3 - 0.0175 X_2 X_4 + 0.0099 X_3 X_4 + 0.2972 X_1^2 + 0.1484 X_2^2 + 0.1647 X_3^2 + 0.1259 X_4^2$

As shown in Table 4, the variances of the TS and WVP models are extremely significant (p < 0.0001), but the lack of fit is not significant (p > 0.05). The high correction coefficients obtained ($\mathbb{R}^2 \operatorname{Adj}_{TS} = 0.9725$ and $\mathbb{R}^2 \operatorname{Adj}_{WVP} = 0.9503$) indicate that the constructed regression equations can be used to explain the changes in the response values and that the values predicted by the models fit the actual values well. In the TS model, p < 0.01 for the primary and quadratic terms and $0.01 for the interaction terms (except <math>X_2$ and X_4). In the WVP model, p < 0.01 for the primary (except X_2) and quadratic terms, and p > 0.05 for the interaction terms. In addition, the dispersion coefficients of the two models are low ($\operatorname{CV}_{TS} = 2.90\%$, $\operatorname{CV}_{WVP} = 2.93\%$), thus indicating that the entire experiment has high accuracy and good reliability. The influence of various factors on the TS and WVP of the nanocomposite films showed the order starch–PVA mass ratio (X_3) > SSP mass concentration (X_1) > Gly mass concentration are the main factors affecting the TS and WVP of the nanocomposite films.

Test Number	X ₁	X ₂	X ₃	X ₄	Y ₁ /MPa	$Y_2/(10^{-12} \text{ g/(cm \cdot s \cdot Pa)})$
1	-1	-1	0	0	21.25	1.81
2	1	$^{-1}$	0	0	26.45	1.56
3	$^{-1}$	1	0	0	26.19	1.73
4	1	1	0	0	27.04	1.52
5	0	0	-1	-1	18.43	1.34
6	0	0	1	-1	22.95	1.62
7	0	0	-1	1	17.98	1.36
8	0	0	1	1	29.55	1.68
9	-1	0	0	-1	22.75	1.72
10	1	0	0	-1	23.3	1.51
11	$^{-1}$	0	0	1	22.41	1.76
12	1	0	0	1	26.85	1.54
13	0	-1	-1	0	18.04	1.41
14	0	1	-1	0	22.35	1.36
15	0	-1	1	0	27.29	1.68
16	0	1	1	0	28.45	1.64
17	$^{-1}$	0	-1	0	17.69	1.65
18	1	0	-1	0	17.38	1.44
19	-1	0	1	0	23.37	1.91
20	1	0	1	0	27.93	1.74
21	0	-1	0	-1	25.52	1.49
22	0	1	0	-1	25.16	1.52
23	0	-1	0	1	25.82	1.51
24	0	1	0	1	27.15	1.47
25	0	0	0	0	31.23	1.12
26	0	0	0	0	31.06	1.26
27	0	0	0	0	31.35	1.15
28	0	0	0	0	29.98	1.29
29	0	0	0	0	31.02	1.25

 Table 3. Box–Behnken design with experimental results.

Table 4. Analysis of variance for the fitted regression model.

6]	ГS	WVP	
Source	F Value	p Value	F Value	p Value
Model	71.69	< 0.0001 **	39.23	< 0.0001 **
X_1 —mass concentration/(g/150 mL)	37.06	< 0.0001 **	67.78	< 0.0001 **
X ₂ —Gly mass concentration/(g/150 mL)	22.71	0.0003 **	2.03	0.1757
X_3 —starch–PVA mass ratio/(w/w)	360.21	< 0.0001 **	122.88	< 0.0001 **
X ₄ —nanostructured ZnO mass concentration/(g/150 mL)	21.51	0.0004 **	0.61	0.4496
X_1X_2	9.00	0.0096 **	0.20	0.6602
X ₁ X ₃	11.28	0.0047 **	0.20	0.6602
X_1X_4	7.20	0.0179 *	0.013	0.9122
X_2X_3	4.72	0.0475 *	0.013	0.9122
X_2X_4	1.36	0.2633	0.62	0.4450
X_3X_4	23.64	0.0003 **	0.2	0.6602
X_1^2	191.72	< 0.0001 **	288.86	< 0.0001 **
X_2^2	34.80	< 0.0001 **	72.05	< 0.0001 **
X_3^2	352.09	< 0.0001 **	88.70	< 0.0001 **
X_4^2	133.10	< 0.0001 **	51.86	< 0.0001 **
Lack of Fit	2.07	0.2525	0.10	0.9983

Note: ** Variance is highly significant, p < 0.01; * Variance is significant, p < 0.05.

3.5.2. Response Surface Methodology

The response surface plots of the effects of PVA mass ratio and SSP mass concentration on the TS of the nanocomposite films are shown in Figure 7. When the SSP mass concentration is

held constant but the PVA content increases, the TS of the nanocomposite films first increases and then decreases. When the PVA mass ratio is fixed, the TS of the nanocomposite films first increases and then decreases with increasing SSP mass concentration. TS reaches a maximum value when the SSP mass concentration is 2–2.25 g/150 mL and the PVA mass ratio is 6:4–5:5. Moreover, the interaction between these two factors is extremely significant.



Figure 7. Effects of starch–PVA mass ratio and SSP mass concentration on the TS of the nanocomposite films.

The response surface plots illustrating the effects of PVA mass ratio and SSP mass concentration on the WVP of the nanocomposite films are shown in Figure 8. When the PVA content is low, the SSP mass concentration has a significant effect on WVP. The WVP of the nanocomposite films first decreases and then increases with increasing SSP mass concentration. When the SSP mass concentration is 2–2.25 g/150 mL and the PVA mass ratio is 6:4–5:5, the slope of the response surface is extremely steep, WVP shows a minimum value, and the interaction between these two factors is not significant.



Figure 8. Effects of starch–PVA mass ratio and SSP mass concentration on the WVP of the nanocomposite films.

3.5.3. Optimization and Verification of the Preparation Process of the SSP/ZnO/PVA Nanocomposite Films

Design-Expert was used to simultaneously solve the two regression equations. The maximum value of the TS of the nanocomposite films was 31.48 MPa, and the minimum value of WVP was 1.34×10^{-12} g/(cm·s·Pa). The optimal preparation process included an

SSP mass concentration of 1.96 g/150 mL, Gly mass concentration of 2.52 g/150 mL, starch– PVA mass ratio of 6:4.5, and nanostructured ZnO mass concentration of 0.7 g/150 mL. To verify the reliability of the model further, we modified the optimal preparation conditions based on actual operations and used an SSP mass concentration of 2.0 g/150 mL, Gly mass concentration of 2.5 g/150 mL, starch–PVA mass ratio of 6:4.5, and nanostructured ZnO mass concentration of 0.7 g/150 mL. Three parallel experiments were performed under these conditions, and the resultant nanocomposite films showed a TS of 31.41 MPa and WVP of 1.32×10^{-12} g/(cm·s·Pa), which are close to the predicted values. These findings reveal that the regression model fits the data well and that the optimization results are reliable.

3.5.4. Comparison Results

Compared with those of ZnO/PVA nanocomposite films without SSP, the TS and WVP of the SSP/ZnO/PVA nanocomposite films increased by 47.57% and decreased by 27.07%, respectively.

3.6. Structural Characterization of the SSP/ZnO/PVA Nanocomposite Films 3.6.1. SEM Analysis

Figure 9 shows the SEM images of the surface (a1 and b1) and cross-section (a2 and b2) of the SSP/ZnO/PVA and ZnO/PVA nanocomposite films prepared under optimal conditions. The dispersion state of each phase and bonding between phase interfaces in the SSP/ZnO/PVA and ZnO/PVA systems are good. In addition, the surface of the SSP/ZnO/PVA nanocomposite film is relatively flat, and most areas of the film show a uniform formation. Protrusions that are invisible to the naked eye develop owing to the agglomeration of SSP over a small area. No obvious particles or protrusions are observed on the smoother surface of the ZnO/PVA film without SSP. The cross-sections of the SSP/ZnO/PVA and ZnO/PVA films are relatively dense, and no noticeable delamination or phase separation could be observed. This finding indicates that SSP has good compatibility with various film-forming substances and will not negatively affect the physical properties of the nanocomposite films [30].



Figure 9. SEM images of SSP/ZnO/PVA and ZnO/PVA nanocomposite films: **(a1)** SSP/ZnO/PVA membrane surface (3000× magnification); **(a2)** SSP/ZnO/PVA membrane cross-section (500× magnification); **(b1)** ZnO/PVA film surface (3000× magnification); and **(b2)** SSP/ZnO/PVA film cross-section (500× magnification).

3.6.2. AFM Analysis

The AFM images of SSP/ZnO/PVA and ZnO/PVA are shown in Figure 10a and Figure 10b, respectively. The surface of the ZnO/PVA film is flat, with an average roughness (Ra) of 16 nm and root-mean-square roughness (Rq) of 21.32 nm. By comparison, SSP/ZnO/PVA had an Ra of 19.44 nm and Rq of 26.91 nm. These results indicate that adding SSP increases the roughness of the surface of the nanocomposite films. Oliveira et al. [23] also observed that adding eucalyptus cellulose as a reinforcing agent increased the surface roughness and opacity of protein-based films.



Figure 10. AFM images of (a) SSP/ZnO/PVA and (b) ZnO/PVA.

3.6.3. FT-IR Analysis

When two or more substances are mixed, their interactions can be evaluated by FT-IR [29]. Figure 11 shows the infrared spectra of ZnO/PVA and SSP/ZnO/PVA measured over the wavenumber range of $500-4000 \text{ cm}^{-1}$. The absorption peaks at approximately 3326 and 3342 cm⁻¹ are generated by O–H and N–H bond stretching vibrations. Meanwhile, adding SSP broadens the absorption peaks of SSP/ZnO/PVA at 3342 cm⁻¹, suggesting that the hydrogen bonding between SSP and the ZnO/PVA nanocomposite film system is strengthened. The absorption peaks at approximately 2983 and 1467 $\rm cm^{-1}$ are generated by the C-H symmetric stretching vibration, and the absorption peaks near 1697 and 1703 cm⁻¹ are the C=C stretching vibration, the C–O stretching vibration, and the stretching of the C–C skeleton. Vibrational absorption peaks appear at approximately 1180 and 1134 cm⁻¹. Comparing the FT-IR spectra of ZnO/PVA and SSP/ZnO/PVA nanocomposite films reveals that most of the absorption peaks of SSP/ZnO/PVA nanocomposite films are generally broader and at higher wavenumbers, confirming that adding SSP strengthens the hydrogen bonding between the membrane molecules and improves the compatibility between various substrates, thereby enhancing the TS and barrier properties of the nanocomposite membrane.



Figure 11. FT-IR images of ZnO/PVA and SSP/ZnO/PVA.

3.6.4. XRD Analysis

Differences in the crystalline structures of polymers can be reflected by their XRD patterns, as changes in the size and shape of the grains in the crystalline region affect the half-peak width, peak height, and peak position in these patterns. Figure 12 shows the XRD patterns of ZnO/PVA and SSP/ZnO/PVA.



Figure 12. XRD patterns of ZnO/PVA and SSP/ZnO/PVA.

The diffraction patterns of SSP powder at $2\theta = 16^{\circ}$, 22° , and 32° are basically consistent with the characteristic peaks of type I cellulose. In addition, the relatively weak peaks at $2\theta = 17^{\circ}$, 25° , and 27° are generally consistent with the characteristic peaks of hemicellulose and lignin. Most of the amorphous hemicellulose and lignin are removed from the straw during preprocessing, thereby exposing more crystalline cellulose in SSP and effectively improving its crystallinity. The diffraction peaks of ZnO/PVA and SSP/ZnO/PVA at $2\theta = 31^{\circ}$, 34° , and 36° are generated by nanostructured ZnO crystals, while the diffraction peaks at $2\theta = 19^{\circ}$ are generated by PVA crystals. The diffraction peak at $2\theta = 21^{\circ}$ is due to matrix interactions and crystallization after adding SSP to the PVA system. The crystalline strength of SSP/ZnO/PVA is significantly higher than that of ZnO/PVA. The spectral comparison and analysis show that SSP addition promotes the crystallization of ZnO/PVA and SSP, resulting in strong interactions between the molecules and, hence, improving the

TS and barrier properties of the SSP/ZnO/PVA nanocomposite films [31]. This finding is basically consistent with the FT-IR analysis results.

3.6.5. TGA

TGA is an important method to evaluate the thermal stability of materials [32]. Figure 13a and Figure 13b shows the TG and DTG diagrams, respectively, of both ZnO/PVA and SSP/ZnO/PVA. The thermal weight loss process of the nanocomposite films could be divided into three stages. In the first stage (50–150 °C), the downward trend of the TG curve is relatively gentle, and the mass loss could be mainly attributed to the volatilization of small molecules, such as bound water and Gly, within the film [33–35].



Figure 13. (a) TG and (b) DTG diagrams of ZnO/PVA and SSP/ZnO/PVA.

The characteristics of the curve in this stage indicate that the film structure is dense, and the bound water content of the film is low. The sharp downward curve of the second weight loss stage (150–320 °C) indicates the extensive degradation of the samples. At this temperature range, glycosyl depolymerization, internal reorganization, and the "glass transition" phenomenon occur within the film [36]. At this stage, the ZnO/PVA nanocomposite film shows a mass loss of approximately 53%. Meanwhile, the mass loss of the SSP/ZnO/PVA nanocomposite film is approximately 51%, which is slightly less than that of the ZnO/PVA nanocomposite film, owing to the addition of SSP. In the third weight loss stage (320–500 °C), the mass loss of the film is slow and could be mainly attributed to the disruption of adjacent –OH and glycosidic bonds in the system. The TG curves also show that the decomposition rate of the SSP/ZnO/PVA membrane is relatively slow. This finding indicates that the strong interactions between SSP and ZnO/PVA delay the movement of molecular chains [37,38], which enhances the thermal stability of the film, consistent with the XRD and FT-IR results. After heat treatment at 500 °C, compared with the ZnO/PVA film without SSP, the SSP/ZnO/PVA film has a higher residual mass. This suggests that adding SSP to the ZnO/PVA system affects the thermal conductivity of the composite material by hindering thermal degradation, resulting in the hysteresis of the thermal degradation temperature [39]. The maximum pyrolysis temperature of the composite film is related to the depolymerization and pyrolysis of the biopolymer. Figure 13(b4) shows the DTG curves of the ZnO/PVA and SSP/ZnO/PVA nanocomposite films, which reveal the degradation behavior and the effect of blending components on the thermal properties of the films. In addition, the maximum pyrolysis temperature of ZnO/PVA is 308 °C, whereas that of SSP/ZnO/PVA is 310 °C, meaning that this material was improved by the presence of SSP. In general, the thermal decomposition temperatures of the ZnO/PVA and SSP/ZnO/PVA films exceed 150 °C, all of which have certain thermal stability. Combined with the TG and DTG curves, this finding shows that adding SSP gives the nanocomposite films higher thermal stability.

4. Conclusions

The SSP mass concentration, Gly mass concentration, starch–PVA mass ratio, and nanostructured ZnO mass concentration have different effects on the TS and WVP of SSP/ZnO/PVA nanocomposite films. A mathematical model based on single-factor experiments and the response surface analysis method was established to predict the effects of these factors on the TS and WVP of the SSP/ZnO/PVA nanocomposite films. The preparation conditions were also optimized. The nanocomposite films showed the best performance under the following conditions: SSP mass concentration of 2.0 g/150 mL, Gly mass concentration of 2.5 g/150 mL, starch–PVA mass ratio of 6:4.5, and ZnO mass concentration of 0.7 g/150 mL. The films obtained under these conditions showed a TS and WVP of 31.41 MPa and 1.32 \times 10^{-12} g/(cm s Pa), respectively, which are 47.57% higher and 27.07% lower, respectively, compared with those of ZnO/PVA nanocomposite films without SSP. The effects of starch–PVA, SSP, Gly, and nanostructured ZnO and their interactions on the performance of the films could be explained by the results of the response surface analysis. The influence of these factors on the TS and WVP of the nanocomposite films showed the order starch–PVA mass ratio > SSP mass concentration > Gly mass concentration > nanostructured ZnO mass concentration. SEM and AFM analyses revealed that the SSP/ZnO/PVA nanocomposite films have smooth surfaces with compact cross-sections and no obvious delamination or phase separation. These results indicate that SSP has good compatibility with the matrix. The structures of the nanocomposite films were characterized by FT-IR and XRD, and results confirmed that SSP addition enhances the interaction forces among the substrates of the SSP/ZnO/PVA nanocomposite film and, hence, its crystallinity. TGA revealed that the thermal decomposition temperatures of the ZnO/PVA and SSP/ZnO/PVA nanocomposite films exceed 150 °C. Nonetheless, all of the films had a certain amount of thermal stability, and together with the TG and DTG curves, the results indicate that adding SSP improves the thermal stability of the nanocomposite films. The results of this study provide a useful reference to improve the utilization rate of sorghum straw resources and promote the industrial production of new biomass materials.

In this study, PVA was selected as the reinforcing agent for the nanocomposite films. Although PVA is biodegradable, it is still derived from chemical materials and thus cannot fundamentally solve the energy problem. Therefore, future research could focus on the development of natural polymers and their derivatives with excellent compatibility with starch as the reinforcing agent to obtain green and environment-friendly composite films. Moreover, while this study used pretreated SSP, which can greatly improve the utilization rate of sorghum straw, the total utilization rate of this resource remains below 100%. Future researchers may also seek to develop approaches to improve the utilization of sorghum straw while ensuring the comprehensive performance of the resultant composite films. The experimental results of this study may be extended to include other types of straws (such as corn and wheat straws) so as to explore new methods of utilizing straw resources and facilitate the development of green environment-friendly materials.

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