

Effect of nano-SiO₂ on the performance of starch/polyvinyl alcohol blend films

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Abstract

In this paper, several starch/polyvinyl alcohol (PVA)/nano-silicon dioxide (nano-SiO₂) biodegradable blend films were prepared by a solution casting method. The physical and biodegradable properties of this film were also studied. From the results, SPS5 was found to have the best tensile strength at about 15.0 MPa, and its elongation at break was 120%. With the increase in nano-SiO₂ content, the water resistance of the films was also improved. Additionally, SPS5 had the best optical transparency in all of the films. The soil burial test showed that the addition of nano-SiO₂ has no significant influence to the biodegradability of the films. Moreover, the results indicated that an intermolecular hydrogen bond and a chemical bond C—O—Si were formed in the nano-SiO₂ and starch/PVA. Therefore, the miscibility and compatibility between starch and PVA were increased, and the physical properties of the additional nano-SiO₂ were improved.

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Keywords: Biodegradable film; Nano-silicon dioxide; Corn starch

1. Introduction

Starch has been considered as a suitable source material because of its inherent biodegradability, ready availability, and relatively low cost. However, as compared to most petroleum-based polymers, the poor mechanical properties and relatively high hydrophilic nature of starch prevent its use in widespread applications (Funke, Berghaller, & Lindhauer, 1998; Lu, Tighzerta, Dole, & Erre, 2005; Hull-eman, Janssen & Feil, 1998). For this reason, blends of starch with other biodegradable synthetic polymeric materials have been investigated for numerous packaging applications.

Starch/polyvinyl alcohol (PVA) blend plastics are one of the most popular biodegradable plastics, and are widely used in packaging and agricultural applications (Follain, Joly, Dole, & Bliard, 2005; Xiao & Yang, 2006; Zhai,

Yoshii, & Kume, 2003; Zhai, Yoshii, Kume, & Hashim, 2002). Polyvinyl alcohol is a biodegradable synthetic material which has the advantages of good film formation, strong conglutination, and high thermal stability. In recent years, PVA has been applied more and more in the materials industry. However, the mechanical properties and water resistance of the native starch/PVA film are still lower than those of other polymers made from petroleum.

In this experiment, the starch/PVA blend film was prepared by a casting method, and nano-SiO₂ was used to improve the properties of starch/PVA blend films. Many studies indicate that nano-materials can improve the performance of polymer materials such as plastic and rubber, but relevant studies regarding starch polymers modified by nano-SiO₂ have not yet been reported (Zou et al., 2007; Yang et al., 2006).

By studying the effect of nano-SiO₂ on the structure and properties of starch film in our laboratory, we were able to discover the mechanism for improving the properties of a starch-based biodegradable film using nano-SiO₂.

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2. Experimental method

2.1. Materials

Corn starch (ST) was provided by Huanglong Food Ltd. of Gongzhuling City (moisture content 11.7%, protein 0.23%, fat 0.075%, and ash content 0.08%), while polyvinyl alcohol (PVA) was produced and provided by Chongqing Inorganic Chemical Reagent Factory (DP 1799 ± 50 , NaOH $\leq 0.2\%$, acetic acid remnant $\leq 0.13\%$, volatilization content $\leq 9.0\%$, and transmissivity $\geq 90\%$). Tetraethyl orthosilicate (TEOS) and the ethanol used, which were of analytical grade, were purchased from Aldrich. The water used was distilled and deionized water. Then glycerine and other reagents, which were all of analytical grade, were used as received.

2.2. Preparation of the films

Aqueous 8 wt.% ST/PVA solutions were prepared by dissolving 6 g of ST and 4 g PVA in 125 ml water and refluxing these at 90 °C for 30 min. Then 2.5 g of glycerine was mixed, and the mixture was stirred for 90 min before casting into a plexiglass plate placed on a leveled flat surface. After the blends were allowed to dry at 50 °C in an oven for 12 h, the fully dried membranes were peeled away from the glass plate, then they were heated in a thermosetting oven at 95 °C for 1 h to induce crosslinking reaction.

The ST/PVA/nano-SiO₂ composites were prepared by the addition of a TEOS mixture to the 8 wt.% ST/PVA solutions. The TEOS mixture was prepared by mixing H₂O, HCl, and TEOS in a molar ratio of 4:0.1:1, which was stirred at room temperature for 2 h. The TEOS was added at a different weight to the polymer weight. Then the ST/PVA/TEOS solutions were mixed together along with 2.5 g of glycerine for each composition, and the mixture was stirred at 90 °C for 2 h. The solutions were then poured onto a plexiglass plate. The cast solutions were allowed to dry at 50 °C for 12 h. After which, the fully dried membranes were peeled away from the glass plate, and then were heated in a thermosetting oven at 95 °C for 1 h to induce the crosslinking reaction. The experimental conditions used to prepare the films and the nomenclatures used for each sample are shown in Table 1.

2.3. Mechanical properties of the films

The tensile strength and elongation at break of the films were measured on the electron tensile tester CMT-6104 (Shenzhen Sans Test Machine Co., Ltd., China) according to Chinese standard method GB/T4456-96 (Polyethylene Blown film for packaging, 1996). The films were cut into 120 × 15 mm strips, with the gauge length (i.e., the distance between the two clamps) set at 80 mm, a tensile rate (i.e., the rate of extending the travel of the clamp) of 250 mm/min, a return rate (i.e., the rate of return travel of the clamp) of 200 mm/min, and a breaking load of 200 N.

Table 1
Experimental conditions of films

Sample	ST (g)	PVA (g)	Glycerine (g)	SiO ₂ (g)	Water (ml)
SPS0	6	4	2.5	0	125
SPS1	6	4	2.5	0.05	125
SPS2	6	4	2.5	0.10	125
SPS3	6	4	2.5	0.15	125
SPS4	6	4	2.5	0.20	125
SPS5	6	4	2.5	0.25	125
SPS6	6	4	2.5	0.30	125
SPS7	6	4	2.5	0.35	125
SPS8	6	4	2.5	0.40	125
SPS9	6	4	2.5	0.45	125
SPS10	6	4	2.5	0.50	125

2.4. Water absorption and water solubility of the films

Dried films were immersed in distilled water at room temperature (25 °C). After the equilibrium (24 h), moisture on the surface of the film was removed, and the weight of the films was measured. The water absorption (W_a) in the film was calculated as follows:

$$W_a = (W_e - W_0)/W_0$$

where W_e is the weight of the film at the adsorbing equilibrium, and W_0 is the first dry weight of the film. The swelled films were dried again for 24 h at 60 °C. Then their water solubility (W_s) was calculated by the following equation:

$$W_s = (W_0 - W_d)/W_0$$

where W_d is the dry weight of the swelled film (Park, Chough, Yun, & Yoon, 2005).

2.5. Water vapor transmission rate (WVTR) and water vapor permeability (WVP) of the films

The water vapor transmission of the films was measured using the ASTM method. A glass cup with 10 g of CaCl₂ was closed with a sample of film firmly fixed on top. The films were cut circularly with a diameter of 8 cm and then were sealed using melted paraffin. The cups were weighed with their contents and were placed in a desiccator containing saturated KCl solution in a beaker at the bottom, providing an RH of 0.8434 at 25 °C. The cups were weighed every 24 h until a steady increase in weight was achieved. The water vapor transferred through the films and absorbed by the desiccant was determined from the weight gain of the cup. The water vapor transmission rate (WVTR) and water vapor permeability (WVP) were calculated as follows:

$$WVTR = \frac{\Delta W}{\Delta t \times A}$$

$$WVP = \frac{WVTR}{\Delta P} L$$

where $\Delta W/\Delta t$ is the amount of water gain per unit time of transfer, A is the area exposed to water transfer (m²), L is the film thickness (m), and ΔP is the water vapor pressure

difference between both sides of the film (Pa) (Li, Kennedy, Peng, Yie, & Xie, 2006; Kaya & Kaya, 2000).

2.6. Soil burial test

The films were placed in a box, buried in soil containing 28% moisture, and then were placed in a desiccator where the relative humidity and temperature were adjusted to 75% and 25 °C, respectively. At a 10-day interval, the samples were taken out, washed with water, and dried to a constant weight. The weights of the recovered samples were determined (Ishigaki, Kawagoshi, Ike, & Fujita, 1999; Lee, Youn, Yun, & Yoon, 2007).

2.7. Optical transperance analysis

The percentage of the films light transmittance (T) was measured by using a Shimadzu UV-160A spectroscope (Shimadzu, Kyoto, Japan) at different wavelengths (400 nm, 500 nm, 600 nm, 700 nm, and 800 nm).

2.8. FT-IR analysis

The powdered samples were blended with potassium bromide and laminated, and the IR spectra were recorded with a Nicolet (USA) Nexus 470 FTIR spectrometer. The wave range, from 4000 cm^{-1} to 400 cm^{-1} , was scanned 32 times for spectrum integration. The scanning resolution was 4 cm^{-1} .

3. Results and discussion

3.1. Mechanical properties of the films

Because polymer materials, such as films, may be subjected to various kinds of stress during use, the determination of the mechanical properties involves not only scientific but also technological and practical aspects. The dependence of the tensile strength on the nano-SiO₂ content of the blend films is shown in Fig. 1. The tensile strength of the SPS0 film was 9.03 MPa. When the nano-SiO₂ was added into the starch and polyvinyl alcohol blend solution, the tensile strength of the resulting blend film increased along with an increase in nano-SiO₂ content, and it reached a maximum point at about 2.5 wt% of the nano-SiO₂ content (SPS5), thus achieving 15.0 MPa. When the nano-SiO₂ content exceeded 2.5%, the tensile strength of the blend film decreased along with an increase in nano-SiO₂ content, but it was still much higher than that of the SPS0 film. The remarkable increase in the tensile strength of the blend films indicated the presence of intermolecular interactions between nano-SiO₂ and starch or nano-SiO₂ and polyvinyl alcohol in the blend films.

The dependence of the elongation at break on the nano-SiO₂ content of the blend films is shown in Fig. 1. The elongation at break of the blend film decreased slowly along with an increase in nano-SiO₂ content.

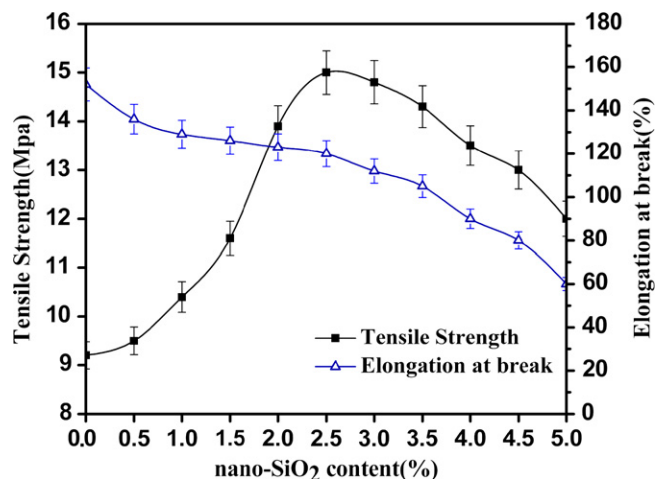


Fig. 1. The dependence of the mechanical properties on the nano-SiO₂ content of the blend films.

3.2. Water absorption and water solubility of the films

One of the major drawbacks in the use of a starch-based material is its water absorption tendency, and any improvement in water resistance is therefore highly important. The water absorption of the SP and SPS films is shown in Fig. 2. It can be seen that the water absorption of the blend film decreased with an increase in nano-SiO₂ content. The water absorption of the SPS0 film was 109.32%, while the SPS5 had the lowest water absorption at about 27.00%. When the nano-SiO₂ content varied from 3 to 5%, the water absorption of the film increased, but it was still much lower than that of the SPS0 film. The reason was because of the network structure formed by combining nano-SiO₂ with starch/PVA, which prevented the water molecules from dissolving and improved the water resistance of the film.

Fig. 2 also shows the water solubility of the films, and as can be seen from the figure, the film has a low water solubility, and the water solubility of the blend film decreased with an increase in nano-SiO₂ content.

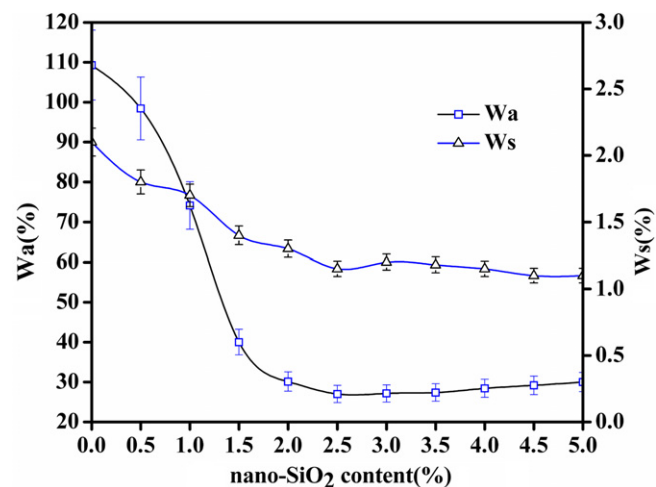


Fig. 2. The water absorption and water solubility of the films.

3.3. WVTR and WVP of the films

WVTR is a measure of the ease of moisture to penetrate and pass through a material. The film WVTR was calculated, and the results are shown in Fig. 3. The figure indicates that an increase in nano-SiO₂ decreased WVTR in the whole. Then the WVP of the films also shows the same trend (Fig. 4), that is, the WVP of the films decreased with an increase in nano-SiO₂ content. Then when the nano-SiO₂ content exceeded 2.0%, the content of nano-SiO₂ has no significant effect on the WVP of the films. This might indicate the existence of intermolecular interactions and a decrease in the mobility of both the ST and PVA when the nano-SiO₂ was added to the solution.

3.4. Biodegradability of the films

The weight loss of the SPS0 and SPS5 films is shown in Fig. 5. From this figure, it can be seen that the weight loss of SPS0 and SPS5 was slightly changed when the soil burial

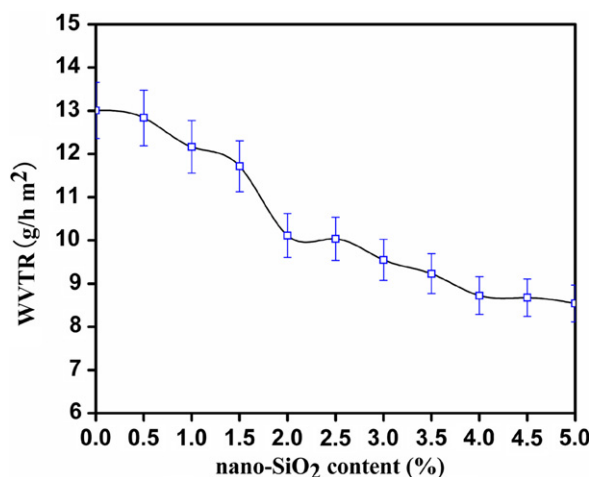


Fig. 3. Water vapor transmission rate (WVTR) of films.

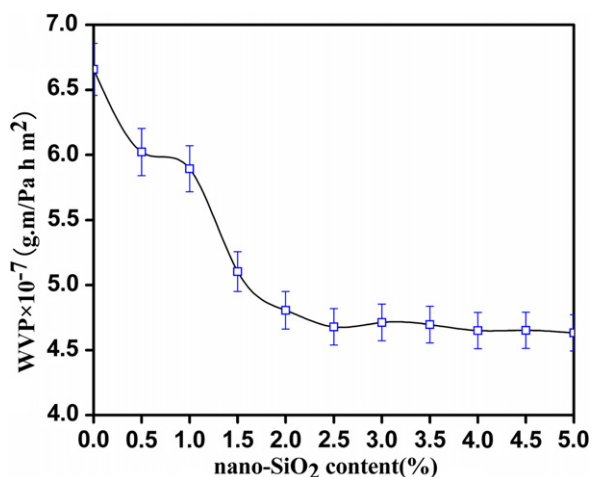


Fig. 4. Water vapour permeability (WVP) of films.

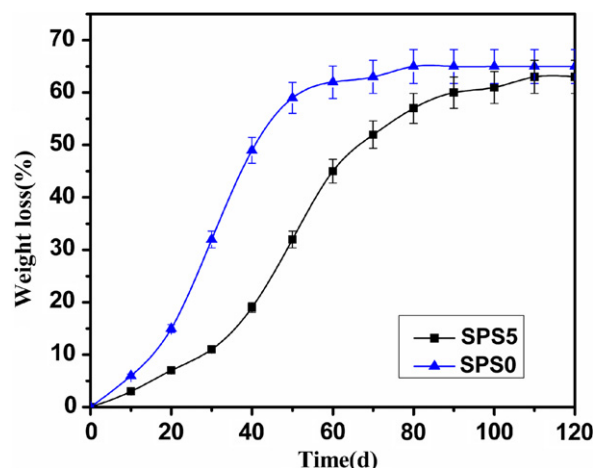


Fig. 5. The weight loss of SPS0 film and SPS5 film in 120 days.

time was under 30 days. Then from 30 to 80 days, the weight loss of SPS0 and SPS5 had a significant increase. When the soil burial time was 120 days, the SPS0 and SPS5 had a close weight loss. This might indicate that nano-SiO₂ has no significant influence on the biodegradability of the films. Additionally, nano-SiO₂ made the miscibility and compatibility increase and form a dense structure between the ST and PVA, which in turn reduced the infiltration velocity of the microorganisms. With the increase in degradable time, the compactness of the films was destroyed. Therefore, the two films exhibited the same weight loss at a later stage.

3.5. Optical transparence of the films

Generally, the transparency of films is an indicator of the miscibility of polymer blends. The optical transparence ($T\%$) at different wavelengths for the films is shown in Table 2. As indicated in the table, all of the films' transmittance increased with the increase in wavelengths. SPS5 had the best optical transparence among all of the blend films, indicating that SPS5 has the best miscibility among all the blend films.

Table 2

The optical transparence ($T\%$) at different wavelengths for the films

Sample	Wavelengths				
	400 nm	500 nm	600 nm	700 nm	800 nm
SPS0	41	46	47	51	53
SPS1	47	51	50	53	57
SPS2	52	55	59	64	65
SPS3	55	59	62	66	69
SPS4	57	61	63	67	71
SPS5	65	68	70	73	73
SPS6	62	66	71	68	73
SPS7	63	65	75	71	70
SPS8	61	63	66	68	68
SPS9	60	62	63	62	66
SPS10	54	58	61	65	61

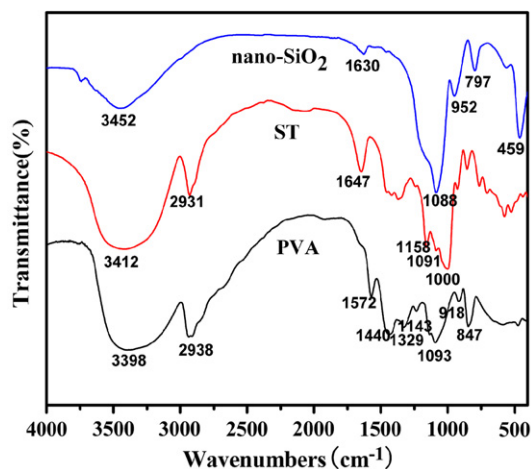
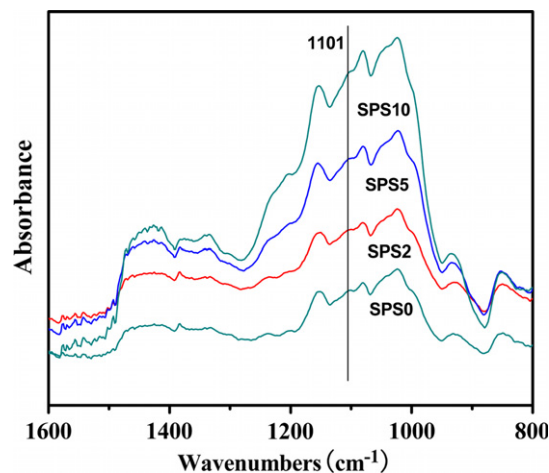
Fig. 6. The IR spectra of nano-SiO₂, ST, and PVA.

Fig. 7. The IR spectra of films.

3.6. FT-IR analysis

The IR spectra of nano-SiO₂, ST, and PVA are shown in Fig. 6.

The strong and wide absorption band at 3452 cm⁻¹ of the nano-SiO₂ samples indicated that there were plenty of —OH on the surface of the nano-SiO₂. The absorptions at 1088 cm⁻¹, 797 cm⁻¹, and 459 cm⁻¹ were attributed to the antisymmetric stretching vibration, symmetric stretching vibration, and flexural libration vibration of Si—O—Si, respectively.

From the spectra of ST, the strong and broad absorption peak at 3412 cm⁻¹ was assigned to the characteristic absorption peak of the stretching vibration of —OH and the hydrogen bonds' association in —OH groups. The bands at 1158 cm⁻¹ and 1091 cm⁻¹ were attributed to the stretching vibration of C—O in the C—O—H groups, and the band at 1000 cm⁻¹ was attributed to the stretching vibration of C—O in the C—O—C groups. Meanwhile, the characteristic absorptions of starch also appeared at 1455 cm⁻¹, 1388 cm⁻¹, and 851 cm⁻¹.

For pure PVA, as with almost all organic compounds, an absorption band can be seen at 2931 cm⁻¹ due to the stretching vibrations of the CH and CH₂ groups. The bands attributed to the CH and CH₂ deformation vibrations were present at the 1300–1500 cm⁻¹ range. Also very intensive, the broad hydroxyl band occurs at 3000–3600 cm⁻¹, and an accompanying C—O stretching exists at 1000–1260 cm⁻¹.

Fig. 7 shows the IR spectra of films at 1600–800 cm⁻¹. SPS0 has no peak at the 1101 cm⁻¹, but SPS2, SPS5, and SPS10 all have a peak at the position. The peak at 1101 cm⁻¹ may be attributed to the C—O—Si group that formed between nano-SiO₂ and ST, or nano-SiO₂ and PVA.

The peak position for the O—H stretching of the films is also shown in Fig. 8. The absorption band around 3440 cm⁻¹ shifted to a lower wave number with the increase in nano-SiO₂ content, indicating an increase in intermolecular hydrogen bonds between nano-SiO₂ and

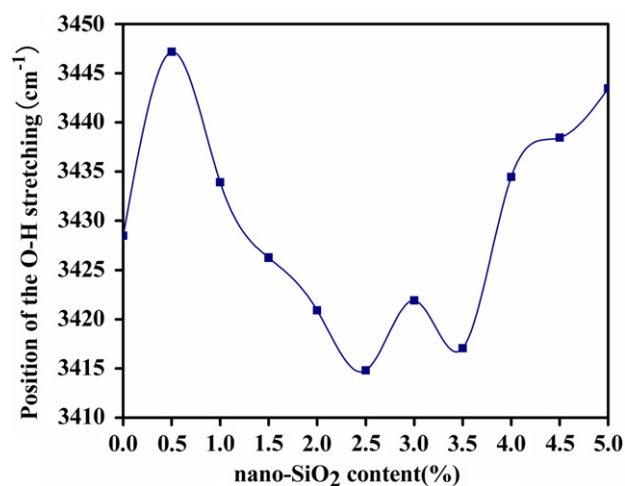


Fig. 8. Peak position for the O—H stretching of films.

ST, or nano-SiO₂ and PVA, especially the nano-SiO₂ content at 2.5 wt%.

4. Conclusions

In this work, the properties of a starch-based biodegradable film were improved through the addition of nano-SiO₂. The result of the experiment shows that the mechanical properties of the film were enhanced by the addition of nano-SiO₂. SPS5 was found to have the best tensile strength at about 15.0 MPa, and its elongation at break was 120%. With the increase in nano-SiO₂ content, the water resistance of the films was also improved. Moreover, SPS5 had the best optical transparency among all the films. The soil burial test showed that the addition of nano-SiO₂ has no significant influence on the biodegradability of the films.

From the IR analysis, we can see that with the increase in nano-SiO₂ content, there was also an increase in the intermolecular hydrogen bonds between nano-SiO₂ and ST, or nano-SiO₂ and PVA, especially the nano-SiO₂ con-

tent at 2.5 wt%. Furthermore, there may be an C—O—Si bond formed between nano-SiO₂ and ST, or nano-SiO₂ and PVA. The nano-SiO₂ and starch/PVA blend also formed a network structure to prevent the water molecule from dissolving, which greatly increased the water resistance and mechanical properties of the film.

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