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Nano-SiO₂-modified Xylan-PVOH-based Composite Films: Mechanical and Barrier Properties Investigation

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Hemicellulose from a wide range of sources and abundant reserves shows good biocompatibility, degradability, and renewability. Because of its low degree of polymerization and a large amount of hydroxyl groups, hemicellulose-based films exhibit low strength and tend to be hydrophilic, which hinders some potential applications. Therefore, hemicellulose-based films with improved strength and barrier properties are needed. In this study, nano-SiO₂ was incorporated into polyvinyl alcohol/xylan matrix for the purpose of preparing an inorganic-organic hybrid composite film with elevated mechanical and barrier performance. The addition of nano-SiO₂ can serve this purpose. A 1% nano-SiO₂ loading resulted in an increase of contact angle of the composite film from 89.6° to 110.4°, an increase of the tensile strength from 11.2 to 14.8 MPa, and a decrease of oxygen permeability from 1.83 to 0.27 $(cm^3 \cdot \mu m)/(m^2 \cdot d \cdot kPa)$, which corresponds to a contact angle that was increased by 23%, tensile strength increased by 32%, and oxygen permeability decreased by 85%. These results indicated that the nano-SiO₂ modified xylan film might have great application prospects as a barrier film in food packaging.

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INTRODUCTION

At a time of increasingly scarce global petrochemical resources and environmental problems caused by the widespread use of petroleum-based materials, the development and utilization of renewable and degradable biomass resources is urgent (Thakur *et al*. 2014; Tayeb *et al*. 2018; Shao *et al*. 2020). Biomass resources are natural energy carriers that store solar energy in the form of chemical energy. They are the most abundant renewable resources on the planet, including crop straw, wood, aquatic plants, *etc*. The effective development of biomass resources is expected to meet human demand for energy, fine chemicals, and materials. With regard to food packaging, commonly used packaging materials include glass, plastic, and metal, *etc*. The extensive use of conventional plastic materials inevitably produces a lot of packaging waste (Nesic *et al*. 2020). Therefore, the development of biodegradable or bio-based materials as packaging alternatives is an effective method to tackle the problem (Asgher *et al*. 2020).

Lignocellulosic biomass is mainly composed of cellulose, hemicellulose, and lignin, among which hemicellulose is the second most abundant polysaccharide. Hemicellulose is a main component of plant cell walls, accounting for 20 to 35% of the

total weight (Pauly and Keegstra 2008). Its properties, including good biocompatibility, degradability, and renewability, give hemicellulose a natural advantage in food packaging. However, its low degree of polymerization and the large number of hydroxyl groups in the main chain and side groups (Peng *et al*. 2011; Escalante *et al*. 2012) lead to poor mechanical and barrier properties, which are disadvantages for food packaging (Hansen and Plackett 2008). Therefore, physical or chemical modification of hemicellulose has long been a focus of research. Plasticizers and reinforcing agents improve the film-forming properties and mechanical properties of hemicellulose-based films. Commonly used plasticizers include glycerin and sorbitol (Mikkonen *et al*. 2012). Some chemical modification methods of hemicellulose include esterification (Egues *et al*. 2014; Gordobil *et al*. 2014), etherification (Hartman *et al*. 2006a; Velkova *et al*. 2015), crosslinking (Zoldners and Kiseleva 2013; Azeredo *et al*. 2015), and grafting (Borjesson and Westman 2016; Du *et al*. 2018).

Xylan is a major component of hemicellulose. This polar polymer with good oxygen barrier properties (Hartman *et al*. 2006b) has been studied for food packaging applications. Good mechanical and gas barrier properties are among the requirements for food packaging films to ensure the integrity and safety of food (Nesic *et al*. 2020). As mentioned earlier, hemicellulose films still have some disadvantages with regard to its use as food packaging, such as poor mechanical properties, high hydrophilicity, or poor barrier properties. In this context, extensive research has been directed to enhancing these properties of hemicellulose-based composite films (Reddy *et al*. 2013). An example of such attempts was the addition of nanoparticles. Xu *et al*. (2019) used nanocellulose to improve the mechanical properties of hemicellulose-based films. Chen *et al*. (2015) found improvements in barrier properties of hemicellulose-based composite films by blending with montmorillonite. At present, nano-silica (nano-SiO_2) has received extensive attention in the field of food packaging. For example, Zhang *et al*. (2018) prepared nano-silica/potato starch films; Kariminejad *et al*. (2022) studied the effect of nano-silica on the structure and physicochemical properties of polyvinyl alcohol (PVOH)/chitosan composite films.

Although nanoparticles could be used to improve the mechanical properties of hemicellulose films, intended for use as food packaging materials, the safety of nanomaterials has been considered a matter of concern. Packaging materials that come into contact with food should be inactive to ensure that they do not adversely affect food quality and human safety (Sothornvit 2019). The risk of nanomaterials to human body can be expected to depend on the size, morphology, toxicity, migration rate, and consumption of nanomaterials, but such issues are still under debate. Recently, the European Food Safety Agency (EFSA) issued a risk assessment guide on the application of nanoscience and nanotechnology in the food and feed chain in human and animal health. The physical and chemical properties, exposure assessment and hazard characterization of nanomaterials were introduced (More *et al*. 2021).

Nano-SiO_2 is a non-toxic, odorless, amorphous white powder. Nano-SiO_2 has the advantages of high stability and high food safety (Yu *et al*. 2012). Because nano-SiO_2 is cheaper than most other nanoparticles and is derived from readily available natural resources, it can be produced in existing production facilities. Nanocomposites show broad application prospects in food processing and preservation because of their lower cost and simpler preparation than current common multilayer food packaging (Mitrano *et al*. 2015; Zhang *et al*. 2016). Because of its high surface energy, nano-SiO_2 has a strong tendency to aggregate in water, but the inorganic anionic surfactant sodium hexametaphosphate (SHMP) changes the surface charge distribution of nanoparticles (Aruna *et al*. 2014),

reduces the aggregation of nanoparticles, and improves the dispersion in the hemicellulose-based composite film.

This article investigated xylan-based films for use in food packaging. To this end, polyvinyl alcohol (PVOH) was used as co-matrix and nano-SiO_2 was incorporated to form a physically cross-linked structure, using sorbitol as plasticizer. A solution-casting method was used to prepare a PVOH/xylan composite film. The effects nano-SiO_2 on the surface hydrophilicity, mechanical properties and gas barrier properties of the composite film were studied.

EXPERIMENTAL

Materials

Beech xylan (M_w is 20000 to 30000 g/mole, Shanghai Yuanye Bio-Technology Co., Ltd., Shanghai, China), PVOH (polyvinyl alcohol with a degree of polymerization of 1700 and alcoholysis degree 99%, Shanghai Titan Scientific Co., Ltd., Shanghai, China), *D*-sorbitol (M_w is 182.17 g/mole, particle size 50 nm, Shanghai Yuanye Bio-Technology Co., Ltd., Shanghai, China), nano-SiO_2 (M_w is 60.08, Shanghai Macklin Biochemical Technology Co., Ltd., Shanghai, China), sodium hexametaphosphate (M_w is 611.77 g/mole, Fuchen Chemical Reagent Co., Ltd., Tianjin, China) were used as received without further purification.

Preparation of Nano-SiO_2 Modified Hemicellulose-Based Composite Films

PVOH was completely dissolved in 0.05% sodium hexametaphosphate solution at 95 °C. A predetermined amount of nano-SiO_2 (0 to 2%, weight ratio, based on the total weight of PVOH and beech xylan) was dispersed in a 0.05% sodium hexametaphosphate solution, and then sonicated for 30 min at room temperature. The PVOH solution was cooled to 75 °C, and xylan and sorbitol were added. The mixture was stirred for 15 min, and nano-SiO_2 dispersion was added dropwise. After reaction at 75 °C for 2 h, the mixture was cooled to room temperature and sonicated for 30 min. The mixture was poured into a polystyrene dish (13 cm × 13 cm) and dried under ambient conditions to form a film. The composition of each film is shown in Table 1. Before all measurements, the dried films were placed in an oven at 25 °C for 48 h.

Table 1. Nomenclature and Composition of Films

Sample	Nano-SiO_2 Mass Fraction (%)	Mass of Beech Xylan (g)	Mass of PVOH (g)	Mass of Sorbitol (g)
H-0	0.0	1.2	0.4	0.4
H-0.4	0.4	1.2	0.4	0.4
H-0.7	0.7	1.2	0.4	0.4
H-1	1.0	1.2	0.4	0.4
H-1.2	1.2	1.2	0.4	0.4
H-1.5	1.5	1.2	0.4	0.4
H-2	2.0	1.2	0.4	0.4

Analytical Methods

Fourier transform infrared spectroscopy (FT-IR) was performed with a Nicolet LSJ20 infrared spectrometer (Waltham, MA, USA) with scanning range of 440 to 4000

cm^{-1}, 32 scans, and a resolution of 4 cm^{-1}.

For scanning electron microscope (SEM) analysis, the film sample was cut into a small square piece, and a thin layer of gold was plated on the surface. The surface morphology of the film was observed with a scanning electron microscope (Quanta 250 FEG, FEI, Hillsboro, OR, USA) using an acceleration voltage of 10 kV.

The X-ray diffraction (XRD) analysis of xylan and nano-SiO_2 modified and PVOH/xylan composite films were performed by using an X-ray diffractometer (D8 Advance, AXS, Bruker, Karlsruhe, Germany). The diffraction angle (2θ) varied in the range of 10 to 80° at a scanning speed of 5°/min.

The contact angle of the films was measured using a contact angle measuring instrument (OCA35, Data Physics Instruments, Charlotte, NC, USA). Water droplets of 2 µL were dropped on the surface of the film. The instrument software was used to capture the image of the droplet, and the contact angle was calculated from the image. Five different positions of each sample were measured, and the average value was reported as the contact angle of the sample (Zhao and Jiang 2018).

According to standard GB/T1040.2-2006 (2006), the film was cut into a rectangular sample of 10 mm × 80 mm. The thickness of the sample was measured using a thickness gauge. A microcomputer-controlled electronic universal testing machine (CMT6104, MTS Systems Co. Ltd., China) was used to test the tensile properties of the samples at a tensile speed of 5 mm/min with the distance between the clamps set at 60 mm. 5 rectangular specimens were cut from each film. Tensile strength and elongation at break of the film were the average of the test results of the 5 rectangular specimens.

According to China national standard GB/T 1038-2000 (2000), the oxygen permeability of the film was measured with a differential pressure gas permeameter (VAC-V2, Labthink) after the film sample was cut into slices with a diameter of 10 cm. Measurements were performed at 23 °C under relative humidity of 50%. The average value of 3 samples was taken.

Thermogravimetric analysis (TGA) was conducted on a thermogravimetric analyzer (STA7200, Hitachi, Tokyo) in temperature range of 40 to 600 °C with a heating rate of 20 °C/min, and a nitrogen flow rate of 20 mL/min.

RESULTS AND DISCUSSION

Preparation of Xylan-based Film

Xylan has a short molecular chain, low molecular weight, high glass transition temperature, and poor film-forming properties (Hanani *et al*. 2013). Blending xylan with other polymers improves its film-forming properties. Polyvinyl alcohol (PVOH) is a linear polymer containing a large number of hydroxyl groups. PVOH has high polarity and is suitable for blending with natural polymers (Chiellini *et al*. 2001). Its good mechanical properties, resistance to organic solvents, heat resistance, and gas barrier properties (Tang and Alavi 2011) offer this polymer unique advantages for food packaging. Incorporation of PVOH as co-substrate with other biopolymers has been reported.

Mixing PVOH with xylan to prepare a film can increase the possibility of application of xylan as film materials. Gao *et al*. (2014) blended xylan with PVOH to prepare composite films. Sorbitol was added to hemicellulose as a plasticizer to improve the processability of hemicellulose and the flexibility of hemicellulose-based composite films.

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Sodium hexametaphosphate was used to reduce the surface energy of nano-SiO_2 particles, and an ultrasonic disperser was also used to improve the dispersibility of nano-SiO_2 in the film, as shown in Fig. 1.
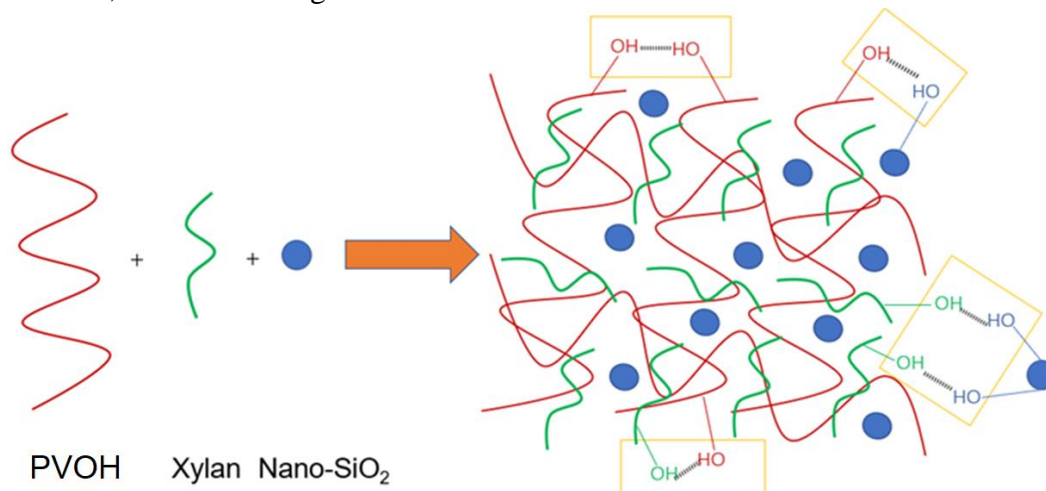

Fig. 1. Physical cross-linking reaction of the matrix (PVOH-Xylan) and nano-SiO_2

Structural Analysis

The FT-IR spectra of the nano-SiO_2 modified hemicellulose film are shown in Fig. 2. The peak at 3278 cm^{-1} is attributed to O–H stretching vibration in xylan and PVOH. The peak at 2939 cm^{-1} is assigned to the alkane C–H stretching vibration. The peak located at 1617 cm^{-1} originated from the stretching vibration of –COO– of uronic acid in hemicellulose (Chen *et al*. 2015). The stretching vibration of C–O accounts for the peak at 1037 cm^{-1}.
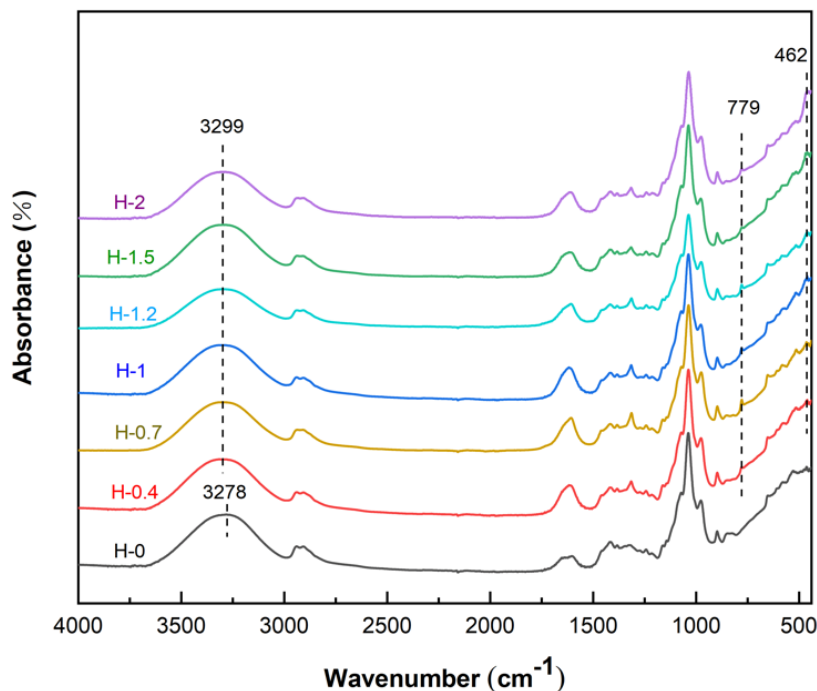

Fig. 2. FT-IR spectra of nano-SiO_2 modified xylan films

After the addition of nano-SiO_2, peaks at 779 cm^{-1} and 462 cm^{-1} emerged in the H-0.4 to H-2 composite films, which are an indication of Si–O–Si bond stretching vibration and bending vibration absorption (Rodgers *et al*. 2008). Another observation was the shift of hydroxyl absorption peak from 3278 cm^{-1} to higher (3299 cm^{-1}) in the nano-SiO_2/xylan/PVOH composite film, indicating the occurrence of hydrogen bonding interaction between the nano-SiO_2 particles and the film matrix.

Surface Morphology Analysis

The surface morphology of the hemicellulose-based composite film with different addition of nano-SiO_2 is shown in Fig. 3. The film without nano-SiO_2 addition (H-0) had a relatively smooth surface, with good compatibility between PVOH and xylan. With nano-SiO_2 addition, particle-shaped protrusions appeared on the surface of composite films, displaying rough surface morphology.
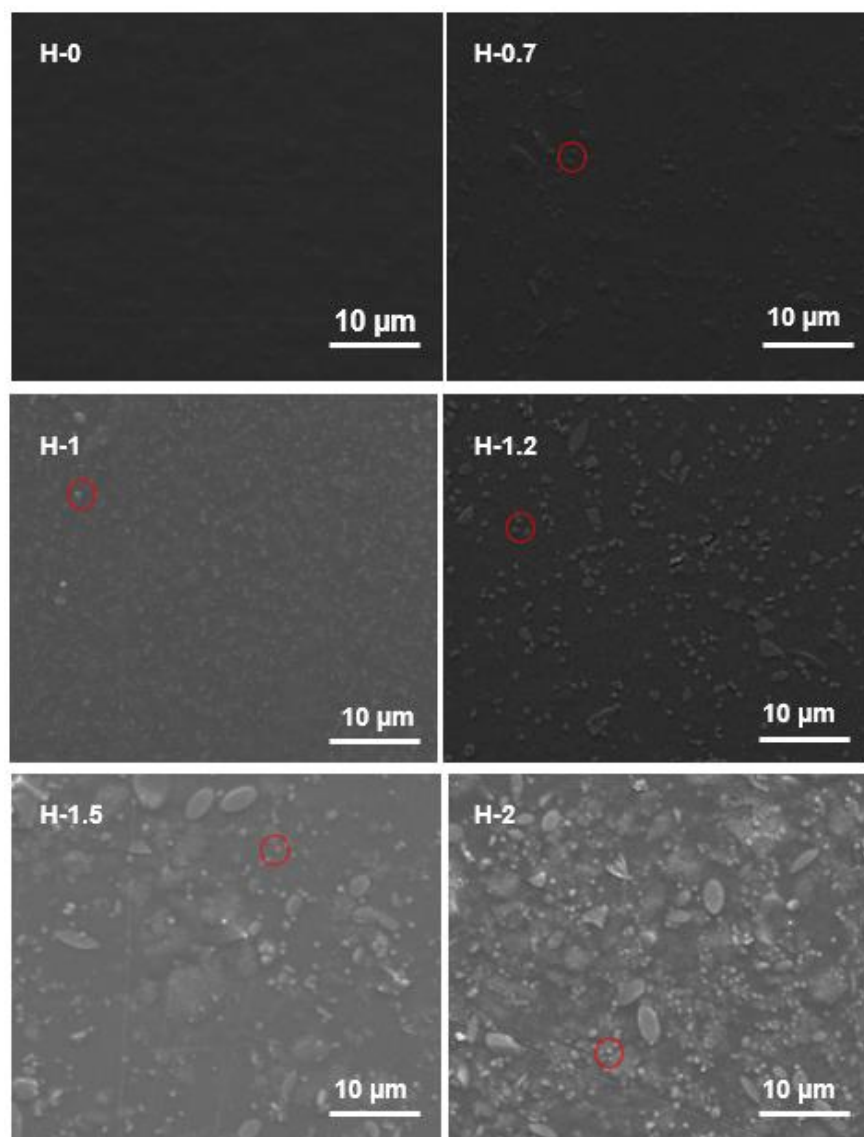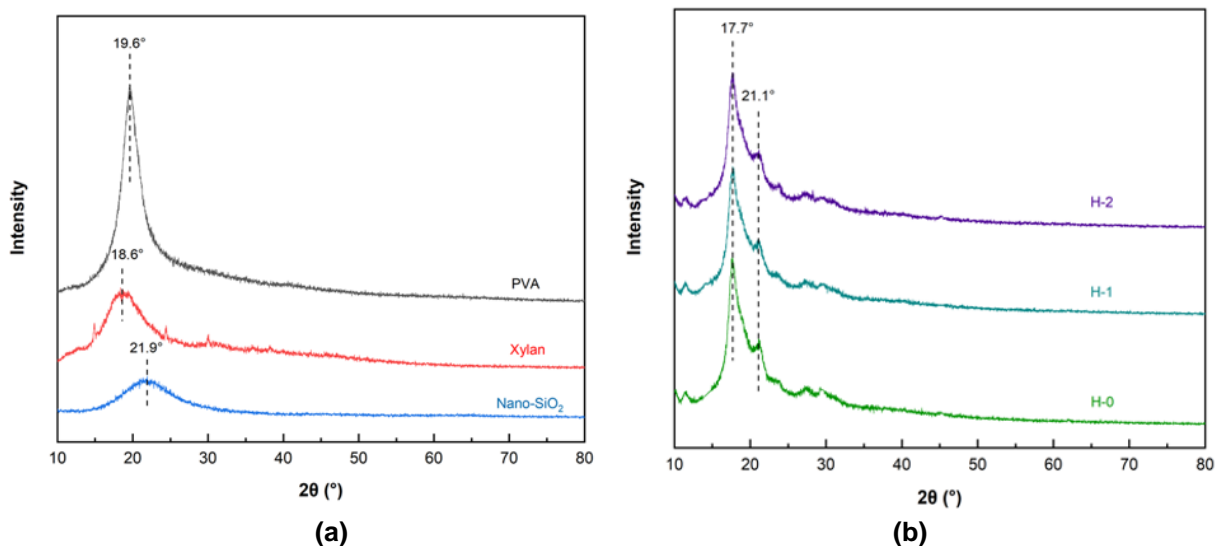

Fig. 3. SEM images of nano-SiO_2 modified xylan films

At an addition below 1.2%, nano-SiO_2 particles were dispersed in the film relatively uniformly. At a loading of 1.5%, nano-SiO_2 particles showed a certain degree of aggregation on the surface of the film, with the appearance of large size oval particles observed. At higher SiO_2 loading of 2%, the particles agglomeration phenomenon became more obvious. The higher the content of nano-SiO_2, the more attractive the nanoparticles were to each other. The formation of larger and more irregular clumps (Phothisarattana and Harnkarnsujarit 2022) resulted in an increased surface roughness. For non-homogeneous nanocomposites, the increase of the aggregate size of nanoparticles reduced the mechanical and barrier properties of the films (Kanmani and Rhim 2014; Dehghani *et al*. 2019).

XRD Analysis

The X-ray diffraction patterns of xylan, PVOH, nano-SiO_2, and hemicellulose composite films are shown in Fig. 4. The characteristic diffraction peak of xylan in hemicellulose composite films shifted from $2\theta = 18.6°$ to $2\theta = 21.1°$, and that of PVOH shifted from $2\theta = 19.6°$ to $2\theta = 17.7°$. This may be due to the change in crystal structure of the two polymers through hydrogen bonding during the formation of hemicellulose composite films (Liu *et al*. 2019b). Nano-SiO_2 had a wide diffraction peak at $2\theta = 21.9°$, indicating that it was amorphous (Tavakolian *et al*. 2021). After the addition of nano-SiO_2, no new crystallization peak appeared in the composite films H-1 and H-2, but the crystallization peak intensity of xylan/PVOH matrix at $2\theta = 17.7°$ and $21.1°$ decreased compared with that of H-0. PVOH and xylan were semi-crystalline due to the hydroxyl groups on the side chains. When the nano-SiO_2 interacted with the hydroxyl groups of the film matrix, the number of hydroxyl groups for forming intermolecular hydrogen bonds of xylan and PVOH decreased, leading to the decrease in crystallinity (Liu *et al*. 2019a).

Fig. 4. XRD patterns of PVOH, xylan and nano-SiO_2 (a) and nano-SiO_2 modified xylan films (b)

Surface Wettability

Advancing contact angles of the composite films were measured for evaluation of surface hydrophobicity. As shown in Fig. 5, the contact angles of H-0, H-0.4, H-0.7, H-1, H-1.2, H-1.5, and H-2 were 89.6°, 101.3°, 105.9°, 110.4° 105.1°, 100.2°, and 93.4°, respectively.

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Film surfaces with contact angles greater than 90° can be considered as hydrophobic surfaces. It can be seen from the figure that the advancing contact angle of the composite film was increased after nano-SiO_2 addition, and the hemicellulose-based composite film was a hydrophobic film. The content of nano silica increased from 0 to 1%, and the contact angle increased from 89.6 ° to 110.4 °. The change trend of the contact angle indicated that nano-SiO_2 was able to increase the surface hydrophobicity of the hemicellulose-based composite film. After adding nano-SiO_2 particles, some of the nano-SiO_2 particles appeared on the surface of the film, which might form a large number of micro/nano structures, increasing the surface roughness of the composite film (Song and Zheng 2013). At this point, the rough depressions on the film surface might be narrow and deep enough that each depression seemed bottomless, similar to a porous surface (Cassie and Baxter 1944; Hubbe *et al*. 2015). The depression between the nano-SiO_2 particles were filled with air, and the contact area between the film surface and the water droplets was further reduced. The tension between the surface of the film and the air layer was very low, which prevented the penetration of water droplets on the surface of the film (Mohammadi *et al*. 2012). However, when the amount of nano-SiO_2 exceeds 1%, the surface of the film was not uniform due to the agglomeration of nanoparticles on the surface of the film. In addition, nano-SiO_2 was hydrophilic. The surface of nano-SiO_2 with high content contained more hydrophilic hydroxyl groups. With the continuous increase of nano-SiO_2 addition, the improvement effect of nanoparticle on the hydrophobicity of xylan/PVOH composite films became weaker (Phothisarattana *et al*. 2022). This observation was consistent with the analysis of the surface morphology of the film in Fig. 3.
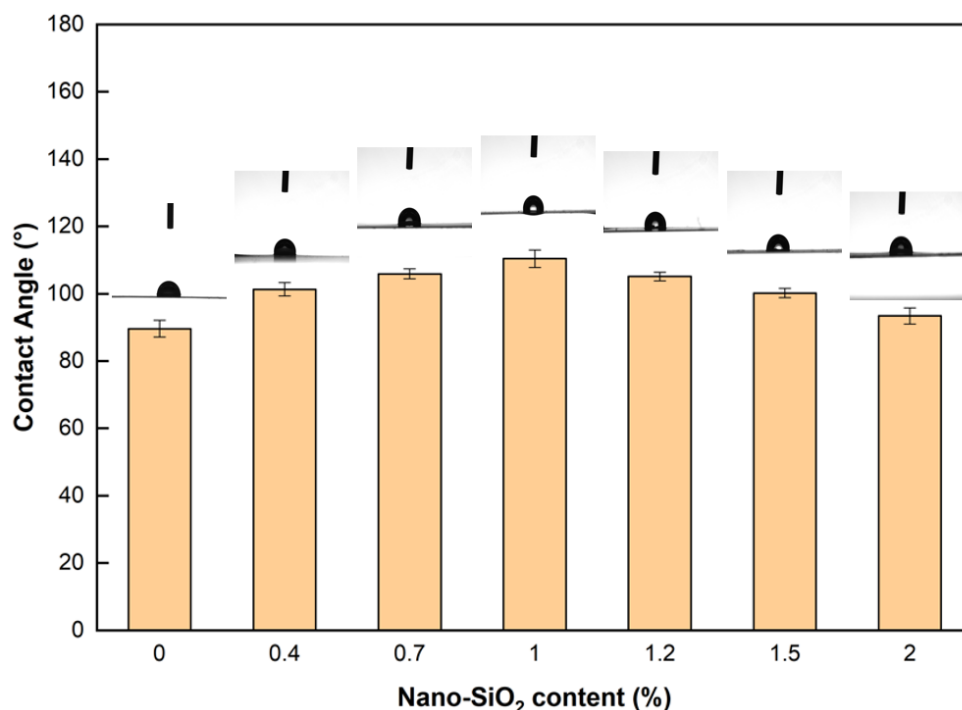

Fig. 5. Contact angle results of nano-SiO_2 modified xylan films

Mechanical Properties

Mechanical properties of the nano-SiO_2 modified xylan films were tested, and the results are shown in Table 2. At the initial stage (nano-SiO_2 addition less than 1%) tensile

strength values of the composite film were found to rise with increasing nano- SiO_2 addition, which declined at higher (above 1% nano-SiO_2 loadings. The elongation at break was found to change in the opposite way.

A maximal tensile strength of 14.78 MPa was achieved at 1% nano-SiO_2 loading, which is 32% higher than that of blank xylan/PVOH film. However, its elongation at break dropped to 4.65% at this nano-SiO_2 loading. Nano-SiO_2 of lower loadings (below 1.2%) showed good dispersion effect in composite film. The high surface energy and large specific surface area of the uniformly dispersed nano-SiO_2 particles could generate a huge interfacial area in the polymer matrix and improve the interfacial bonding force between the nanoparticles and the polymer matrix. At the same time, hydroxyl groups on the surface of small size rigid nano-SiO_2 particles and the hydroxyl groups in the polymer formed hydrogen bonds, which restricted the free movement of polymer chains (Wadaugsorn *et al*. 2022). The formation of hydrogen bonds raised the tensile strength (de Azeredo 2009; Liu *et al*. 2018) and reduced the flexibility of the film. Higher nano-SiO_2 loading reduced tensile strength but raised elongation at break of the composite film. Film H-2 showed a tensile strength of 10.95 MPa, and the elongation at break of 8.68%. At an addition of more than 1.5%, nano-SiO_2 exhibited a certain degree of agglomeration in the film matrix, resulting in stress concentration points, poor dispersion, and weakening of the interaction between nano-SiO_2 and polymer. In addition, the elongation at break of xylan composite films with nano-SiO_2 content more than 1.2% was higher than that of film H-0. At this level of addition, the agglomeration of nano-SiO_2 diminished the surface free energy, reduced the hydrogen bonding between nano-SiO_2 and xylan/PVOH matrix, displaying an effect similar to that of a plasticizer (Liu *et al*. 2019a). Large-size nano-SiO_2 aggregates increased the distance between xylan chains and PVOH chains, weakened the interaction between xylan and PVOH molecules, and made their molecular chains slide more easily.

Table 2. Tensile Test Results of the Nano-SiO_2 Modified Xylan Films

Sample	Thickness (μm)	Tensile Strength (MPa)	Elongation at Break (%)
H-0	82±3	11.19±0.85	5.24±0.99
H-0.4	84±2	11.43±0.47	4.25±1.42
H-0.7	87±2	12.38±0.19	4.09±1.85
H-1	92±3	14.78±0.37	4.65±0.94
H-1.2	93±1	13.59±0.36	6.18±0.72
H-1.5	96±3	11.18±0.47	7.19±1.40
H-2	98±4	10.95±0.36	8.68±1.21

Oxygen Barrier Properties

With regard to food packaging, the transmission of oxygen will lead to deteriorated food quality and shortened shelf life. Therefore, good oxygen barrier performance is a prerequisite for food packaging materials (Soni *et al*. 2016). Under the conditions of a temperature of 23 °C and a relative humidity of 50%, the oxygen permeability of the hemicellulose composite films with different nano-SiO_2 additions and some typical packaging materials are shown in Table 3.

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Table 3. Comparison of Oxygen Permeability of the Packaging Films in the Literature and this Work

Sample	Oxygen Permeability [$(cm^3 \cdot \mu m)/(m^2 \cdot d \cdot kPa)$]	Reference Citation
H-0	1.83*	-
H-0.4	1.13*	-
H-0.7	0.72*	-
H-1	0.27*	-
H-1.2	0.46*	-
H-1.5	0.66*	-
H-2	0.83*	-
TiO_2-KH550 nanoparticle-reinforced PVOH/xylan composite films	4.01	(Liu *et al.* 2018)
Cellulose nanofibers reinforced hemicellulose/chitosan films	5.21	(Tang and Alavi 2011)
Sodium trimetaphosphate crosslinked hemicellulose films	3.72	(Zhao *et al.* 2021)
Cellulose nanofibril films	72	(Borrega and Orelma 2019)
Quaternized hemicelluloses with chitosan and montmorillonite	10.95	(Chen *et al.* 2016)
Low-density polyethylene (LDPE)	772	(Zhong *et al.* 2007)
High-density polyethylene (HDPE)	237	(Zhong *et al.* 2007)
Ethylene vinyl acetate (EVA)	1431	(Zhong *et al.* 2007)
* Test conditions: 23 °C, 50% RH.		

As shown in Table 3, the oxygen permeability of the hemicellulose-based composite films was much lower than those of the common packaging materials LDPE, HDPE, and EVA, demonstrating that an appropriate amount of nano-SiO_2 addition can improve the oxygen barrier performance as indicated by the reduced oxygen permeability. At a 1% nano-SiO_2 addition, the oxygen permeability of the film reached the minimum [0.27 $(cm^3 \cdot \mu m)/(m^2 \cdot d \cdot kPa)$], which was 85% lower than that of the blank xylan/PVOH film. This was mainly due to the small size of nano-SiO_2, which was uniformly dispersed in xylan and PVOH matrix and filled the voids inside the composite film (Li *et al.* 2016). In addition, the nanoparticles were present in the molecular chains of xylan and PVOH and had strong intermolecular interactions with them (Rukmanikrishnan *et al.* 2021), reducing the mobility and free volume between the chains and making the film matrix more compact. However, the nano-SiO_2 particles of higher addition had serious agglomeration, and the agglomerated nanoparticles had more particle-particle interactions (Reddy *et al.* 2018). The oxygen barrier properties of the hemicellulose films were decreased due to the decrease of the compactness of the film.

An oxygen-barrier polymer can be defined as a polymer having an OP value of lower than 38.9 $(cm^3 \cdot \mu m)/(m^2 \cdot d \cdot kPa)$ at 23 °C (Hong and Krochta 2006). With an OP value of lower than 2 $(cm^3 \cdot \mu m)/(m^2 \cdot d \cdot kPa)$, nano-$SiO_2$ modified xylan film showed a great potential for application in food packaging.

Thermal Stability

A thermogravimetric analyzer (TGA) was used to study the thermal stability of nano-SiO_2 reinforced xylan film at 40 to 600 °C. As shown in Table 4 and Fig. 6, the weight loss of the film was mainly divided into the following three stages: 60 to 210 °C, 210 to 340 °C, and 340 to 520 °C. In the first stage of the film, the weight loss was caused by the

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evaporation of water vapor adsorbed on the surface of the film and the evaporation of internal moisture. Due to the strong hydrophilicity of nano-SiO_2 containing a large number of hydroxyl groups on the surface, the modified film contains relatively large amount of water. The weight loss of the modified film in the first stage was higher than that of the unmodified film. In the second stage the films showed the most weight loss due to degradation of the polymers (xylan, PVOH, and sorbitol) (Huang *et al*. 2018). The weight loss of the film at this stage was mainly due to the degradation of the side chains of xylan and PVOH. The weight loss of the film in the third stage was due to the carbonization of the polymer and the C–C backbone of xylan and PVOH was cleaved in this temperature range. At 600 °C, the unmodified film had the lowest carbon residue percentage of only 18.96%.

Table 4. Thermal Properties of the Nano-SiO_2 Modified Xylan Films

Sample	T_{max} (°C)			Carbon Residue at 600 °C (%)
	T_{max1} (°C)	T_{max2} (°C)	T_{max3} (°C)	
H-0	100.85	307.90	442.59	18.96
H-0.4	114.82	326.25	444.09	19.42
H-0.7	106.29	325.03	448.03	19.90
H-1	122.07	326.56	446.85	20.43
H-1.2	102.15	324.01	435.51	19.91
H-1.5	109.75	319.48	448.24	19.92
H-2	105.58	320.52	447.22	19.28
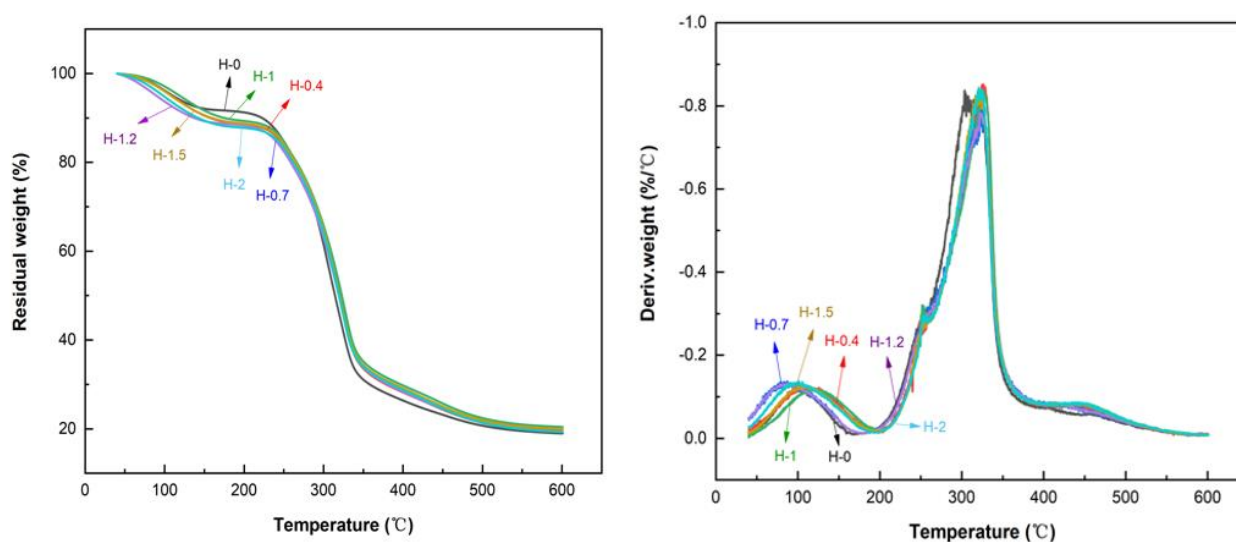
Fig. 6. Thermogravimetric (TGA) curves (left) and derivative thermogravimetry (DTG) curves (right) of nano-SiO_2 modified xylan film

In the second and third stages of weight loss, the thermal degradation temperature of the hemicellulose composite film with nano-SiO_2 particles was higher than that of the pure PVOH/xylan composite film. At a weight loss rate of 50%, unmodified film showed a degradation temperature of 313 °C, while the composite films exhibited degradation temperatures in the range of 318 to 322 °C. The temperature corresponding to the peak thermal decomposition rate of the xylan film (T_{max2} and T_{max3}) was increased after the addition of nano-SiO_2 particles. The nano-SiO_2 particles improved the thermal stability of

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the composite film in the second and third stages. This was mainly attributed to the generation of hydrogen bonding forces between nano-SiO_2, PVOH and xylan. A partial hydrogen bond network (Ahmadizadegan *et al*. 2018) formed inside the hemicellulose film, leading to an increase in the energy required for thermal degradation. Because nano-SiO_2 was not degraded at high temperature, the residual amount of the nano-SiO_2 modified xylan film at 600 °C was higher than that of the pure PVOH/xylan film.

CONCLUSIONS

1. The addition of nano-SiO_2 improved the mechanical strength and barrier properties of xylan/PVOH film because of the hydrogen bond interaction between nano- SiO_2 and xylan/PVOH matrix. A 1% nano-SiO_2 loading afforded the best improvement in the properties.

2. The uniform dispersion of nano-SiO_2 resulted in rougher surface and raised the static contact angle of composite (over 90°), which was considered an effective approach to the preparation of hydrophobic hemicellulose-based nanocomposite film.

3. The prepared composite film may be used as an alternative to, or substitute for traditional petrochemical-based food packaging materials due to the overall performance, especially good oxygen barrier properties.

ACKNOWLEDGMENTS

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