

Long-Chain Anhydride Modification: A New Strategy for Preparing Xylan Films

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ABSTRACT: Xylan, which is a widely abundant plant polymer, has been considered as an alternative for film preparation. Up to now, however, xylan films have suffered from brittleness, low mechanical strength, and humidity sensitivity. This paper describes a new and effective strategy to prepare xylan films with high mechanical strength and less moisture-sensitive properties by introducing long carbon chains into the xylan backbone. Furthermore, this work revealed some important details on the relationships between structure (molecular structure, aggregation behaviors, and surface morphology) and properties (film-forming performance, flexibility, tensile strength, and hydrophilicity) of xylan film. It was found that the hydrophobic carbon chains (2-octenylsuccinic anhydride half-ester groups) in the xylan backbone acted as steric hindrance and could effectively prevent xylan chains from aggregation. 2-Octenylsuccinic anhydride (2-OSA) modified xylan (2-OSA-X) demonstrated amorphous structure and had better film-forming performance than the unmodified xylan. 2-OSA-X films were smooth, flexible, and less moisture-sensitive and showed significantly increasing tensile strength at a low degree of substitution.

KEYWORDS: xylan, 2-octenylsuccinic anhydride, film, internal plasticization

INTRODUCTION

Polysaccharides obtained from agriculture and forestry have lately received much attention as alternatives to conventional plastic polymers derived from petroleum for future packaging materials.^{1–3} Among these polysaccharides, hemicelluloses, constituting 25–35% of lignocellulosic biomass, are considered to be inexhaustible and renewable resources for production of films and other biomaterials.^{3–5} Over the past few years preparing biocompatible films from xylan-rich and glucomannan-rich hemicelluloses has been attracting ever increasing attention due to (a) bioactivity and good oxygen barrier properties;³ (b) lower cost and easy availability from agriculture, forestry, and pulping industries or various biomass refinery processes; and (c) amorphous structure and easy dissolution in hot water, alkaline solution, or organic solvents such as DMSO and DMF/LiCl.^{6–8} Indeed, biomass refinery processes, in particular, biomass pretreatments, can recover large amounts of hemicelluloses, and preparing biocompatible films from these hemicelluloses will be a very important route to fully utilize these biopolymers.^{8–10}

Similar to cellulose, hemicelluloses consist of a large number of hydroxyl groups that can form considerable intermolecular and intramolecular hydrogen bonds, resulting in xylan chain aggregation or reordering in water evaporation during film formation.^{11–13} It was reported that hemicellulose films, for instance, xylan^{5,6,14} and spruce galactoglucomannan¹⁵ films, were semicrystalline and rather brittle due to strong hydrogen bonds. The high hydrophilicity and poor mechanical properties are the key limiting factors for the practical applications of hemicellulose films.

To improve film performance, plasticizers such as xylitol, sorbitol, glycerol, and biopolymers, for instance, chitosan, carboxymethyl cellulose, or even lignin, were introduced as external plasticizers to modify the molecular three-dimensional

organization.^{5,7,8,14} However, external plasticization does not significantly change the crystalline structure due to the strong hydrogen bonds, and thus the mechanical properties cannot be effectively improved.^{6,11} Also, exudation or volatilization of low molecular weight plasticizers in processing and application will lead to a dramatic decrease in various properties. In addition, the hydrophilic nature of hemicelluloses restricts the application of these films in high-humidity conditions.

Another route to improving the film performance of hemicelluloses is incorporation of reinforcements such as cellulose whiskers¹⁶ or cellulose microfibrils^{11,17} into the hemicellulosic matrix. Addition of these nano-reinforcements leads to a substantial improvement in the mechanical properties of films, which is mainly attributed to the strong mechanical strength and high specific ratio of the reinforcements, as well as the formation of a rigid hydrogen-bonded network. However, the reinforcing method does not alter the strong intermolecular and intramolecular hydrogen bonds, which become a key issue in obtaining flexible hemicellulose films with desirable mechanical properties.

Alkenylsuccinic anhydride, for example, dodecenylsuccinic anhydride, octadecenylsuccinic anhydride, and octenylsuccinic anhydride, modified starches have been of interest for many years.^{18,19} Such modified starches find applications as emulsifiers in food systems. Recently, long-chain succinic anhydride (*n*-octenylsuccinic anhydride, *n*-dodecenylsuccinic anhydride, and *n*-octadecenylsuccinic anhydride) modified xylns with a degree of substitution (DS) of 0.08–0.27 were prepared in ionic liquid.²⁰ However, there is no literature available on the

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application of long-chain succinic anhydride modified biopolymers in film preparation. In our continuance of preparing high-quality hemicellulose films and being inspired by octenylsuccinic anhydride (OSA) modified starch, which could form strong films at the oil–water interface and give emulsions that are resistant to reagglomeration,^{18,19} this work focused on preparing xylan films with enhanced mechanical and moisture-resistant properties from long-chain succinic anhydride modified xylan and investigating their structure and properties. For the first time we found that OSA modified hemicelluloses could produce internally plasticized films with high performance.

MATERIALS AND METHODS

Materials. Xylan was isolated from holocellulose of bamboo (*Dendrocalamus membranaceus* Munro, DmM) using 10% KOH at 30 °C for 10 h with a solid to liquid ratio of 1:20 (g/mL). The holocellulose was obtained by delignification of the extractive-free material (40–60 mesh) with sodium chlorite in acidic solution (pH 3.7–4.0) at 75 °C for 2 h. The obtained xylan was washed thoroughly with ethanol and vacuum-dried. The sugar analysis showed the following sugar composition (relative molar percent): 86.01% xylose, 7.21% arabinose, 4.53% glucose, 0.51% galactose, 1.12% glucuronic acid, and 0.62% galacturonic acid. Sorbitol was obtained from Shanghai Bio Life Science and Technology Co., Ltd. 2-Octenylsuccinic anhydride (2-OSA) and 2-dodecyl-1-succinic anhydride (2-DSA) were purchased from Tokyo Chemical Industry Co., Ltd. Laboratory-grade dimethyl sulfoxide (DMSO) was purchased from Sigma-Aldrich (Steinheim, Germany).

Sugar Composition. The sugar composition in the xylan was determined by high-performance anion exchange chromatography (HPAEC). The neutral sugars in XH were liberated by hydrolysis with 6% H₂SO₄ at 105 °C for 2.5 h. Afterward, the samples were filtered and injected into the HPAEC system (Dionex ISC 3000) with an amperometric detector, an ASS0 autosampler, and a CarboPA1 column (4 mm × 250 mm, Dionex). The uronic acid was eluted with 0.4 M NaOH for 20 min at a rate of 1 mL/min with postcolumn addition of 0.3 M NaOH at a rate of 0.5 mL/min. Calibration was performed with standard solutions of L-arabinose, D-glucose, D-xylose, D-glucose, D-mannose, D-galactose, glucuronic acid, and galacturonic acid.

Preparation of 2-OSA Modified Xylan and 2-DSA Modified Xylan. Xylan (1.98 g, equal to 0.015 mol of xylose units) was dissolved in DMSO (50 mL) at 90 °C for 60 min and then was cooled to room temperature. Afterward, the pH of the suspension was adjusted to 8.5 with triethylamine. The required amount of 2-OSA or 2-DSA was added slowly over 2 h at pH 8.5. The reaction was allowed to continue for 5 h at the same pH. The reaction was stopped by quenching in ethanol, and the precipitate was centrifuged and rinsed with ethanol and then dried overnight in a vacuum oven at ambient temperature. A series of such experiments was carried out in which reactant ratio (2-OSA or 2-OSA/xylose units) was varied in the range of 1:12 to 1:1, which were listed in Table 1. Molar amounts of xylan were calculated on the basis of xylose units ($M = 132$ g/mol) with two free OH groups. The degree of substitution (DS) of 2-OSA-xylan or 2-DSA-xylan, which is the average number of hydroxyl groups substituted per xylose unit, was determined by a titration method as previously described.²¹ Three samples of each modified xylan were titrated, and DS was calculated as an average of the obtained values.

Film Preparation. All free films were prepared by a casting method. 2-OSA-xylan or 2-DSA-xylan (1.00 g) was dissolved in 35 mL of deionized water at 80 °C, and then the solution was poured onto a polystyrene dish (12.5 × 12.5 cm) and allowed to dry in an oven at 80 °C to obtain 2-OSA-xylan or 2-DSA-xylan film. Externally plasticized (sorbitol plasticized) xylan film without chemical modification was also prepared as a control sample. Xylan (0.80 g), sorbitol (0.20 g), and deionized water (35 mL) were mixed under magnetic stirring at 80 °C for 60 min. The solution was then poured onto a polystyrene dish and allowed to dry at 23 °C and a relative humidity (RH) of 50%. Film thickness was measured using a micrometer (Lorentzen & Wettre, precision = 1 μm). Measurement was taken at 10 different locations on

Table 1. Film Samples and Film-Forming Performance

sample ^a	SA/xylan ratio ^b	DS	moisture content (wt %)	film formation
2-OSA-0		0	13.92 ± 0.8	cracks, smooth, cohesive, stiff
2-OSA-0.064	1:12	0.064	11.67 ± 0.5	continuous, smooth, flexible, elastic
2-OSA-0.098	1:8	0.098	10.63 ± 0.6	continuous, smooth, flexible, elastic
2-OSA-0.17	1:4	0.17	8.73 ± 0.6	continuous, smooth, flexible, elastic
2-OSA-0.22	1:2	0.22	7.57 ± 0.7	continuous, smooth, flexible, elastic
2-OSA-0.29	1:1	0.29	6.19 ± 0.4	continuous, smooth, flexible, elastic
2-DSA-0.081	1:8	0.081		fragments
2-DSA-0.15	1:4	0.15		fragments
2-DSA-0.19	1:2	0.19	7.24 ± 0.5	continuous, rough, flexible, elastic
2-DSA-0.27	1:1	0.27	5.90 ± 0.4	continuous, rough, flexible, elastic

^a2-OSA-0 is the control sample with sorbitol (20 wt %) as plasticizer. 2-OSA-0.064–0.29 are 2-OSA modified xylan with DS of 0.064–0.29, whereas 2-DSA-0.081–0.27 are 2-DSA modified xylan with DS of 0.081–0.27. ^bMolar ratio of 2-OSA or 2-DSA to xylose units.

each film, and the mean value was used in the calculations to determine the mechanical test measurement. The thicknesses of the films ranged between 60 and 80 μm.

FT-IR. FT-IR analysis was performed in an absorbance range of 4000–500 cm⁻¹ using a Bruker Vector 22 FT-IR in reflection mode.

Atomic Force Microscopy (AFM) Analysis. Surface morphologies of all films at the nanolevel were studied by AFM (Nanoscope III, Veeco Co. Ltd.). AFM scanning was conducted at four locations on each sample. Topographic (height) and phase images were recorded in tapping mode under ambient air.

Equilibrium Moisture Content. Three pieces of each film were conditioned at 50% RH and 23 °C for 7 days. The samples were then dried in an oven (105 °C) to reach constant mass and weighed again. The equilibrium moisture content was measured gravimetrically and calculated as the weight of water in the sample compared to the total weight.

X-ray Diffraction. Diffractograms were recorded in reflection mode in the angular range of 5–40° (2θ) by steps of 0.02° (2θ). The measurements were done with a diffractometer (Bruker, model D8 advance). The Cu Kα radiation generated at 40 kV and 40 mA was monochromatized using a 20 μm Ni filter. The scanning speed was 0.0385° s⁻¹.

Thermal Analysis. Thermal analysis was performed by using thermogravimetric analysis (TGA) and differential thermal analysis (DTA) on a simultaneous thermal analyzer (Pyris Diamond TG/DTA, PE Instrument). The apparatus was continually flushed with nitrogen. The sample weighed between 9 and 11 mg and was heated from room temperature to 600 °C at a heating rate of 10 °C/min.

Tensile Strength Testing. The tensile strength testing of film was carried out by using a tensile testing machine (Instron Universal Testing Machine 5565) with 100 N load cell at 50% RH and 23 °C. The samples were cut in the rectangular specimens with a width of 15 mm and length of 80 mm, and eight replicate specimens were tested from each film type. The initial distance between the grips was 30 mm, and the separation rate of the grips was kept constant at 4 mm/min.

Contact Angle Measurement. Hydrophilicity of the as-prepared films was evaluated using an OCA40 contact angle system apparatus (Dataphysics, Filderstadt, Germany) by measuring contact angles of a water droplet at 5 s after landing of the water droplet on the films. Contact angles were determined at seven different positions on each film.

RESULTS AND DISCUSSION

DS and FT-IR Spectra. In this work, grafting of xylan with 2-OSA and 2-DSA was carried out in DMSO, and the derivatives (2-OSA-xylan and 2-DSA-xylan) contain C8 (2-OSA-xylan) and C12 (2-DSA-xylan) hydrocarbon chains, respectively, as shown in Figure 1. An overview of the derivatives is shown in Table 1.

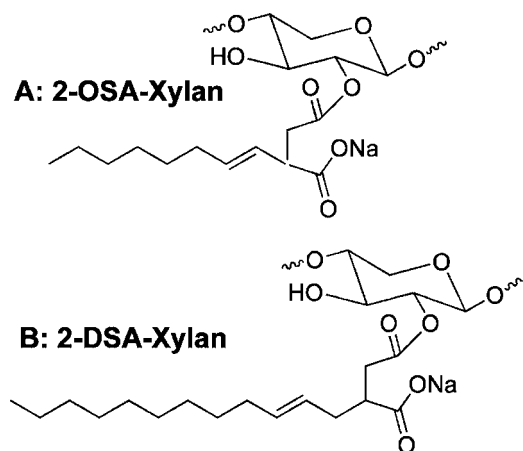


Figure 1. Structures of 2-OSA-xylan and 2-DSA-xylan (substitution may take place at C2 and C3).

The DS of 2-OSA-xylan at low 2-OSA ratio (1:12, 2-OSA-0.067) was small (0.067), and then it increased to 0.29 at the reactant ratio of 1:1 (2-OSA-0.29). The DS of 2-DSA-xylan increased from 0.081 to 0.27 as the reactant ratio increased from 1:8 to 1:1. The results indicate that the reaction between xylan and 2-OSA can be carried out more easily than that between xylan and 2-DSA, which may be due to the stronger steric hindrance or more difficult diffusion of 2-DSA with longer carbon chains.

FT-IR spectra (Figure 2, 2-OSA-xylan is shown here as an example) of xylan show peaks associated with native hemicelluloses

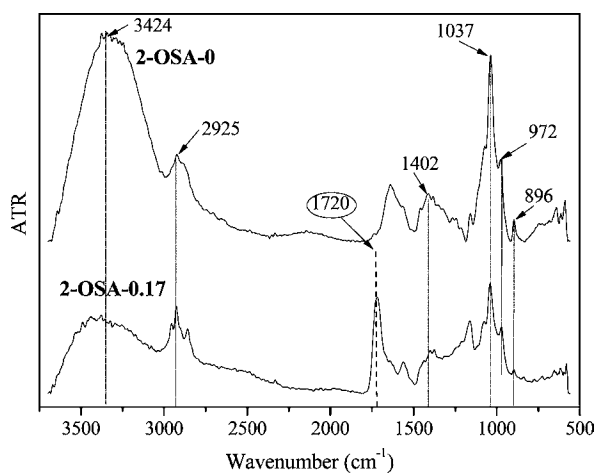


Figure 2. FT-IR spectra of xylan film (2-OSA-0) and 2-OSA-xylan films (2-OSA-0.17).

celluloses at 3424, 2925, 1402, 1037, 972, and 896 cm^{-1} . The formation of a new ester bond in the xylan derivatives is indicated by the peak at 1720 cm^{-1} ,¹⁸ which confirms the reaction of xylan with long-chain anhydrides.

Film-Forming Properties of Xylan and Its Derivatives. It is well-known that xylan films prepared from xylan alone are

rather brittle, and cracks easily occur during the drying process due to the strong intermolecular and intramolecular hydrogen bonds, high glass transition temperature, or rigid chains.^{5,8,14} Extensive works have been focused on improving the film-forming performance of various hemicelluloses by adding secondary components such as plasticizers or cocomponents to hemicelluloses.^{5,7-9} A selective choice of hemicelluloses was also carried out to determine the favorable component for preparing films with better properties.^{7,10} Addition of plasticizers such as xylitol, sorbitol, and glycerol can modify the molecular three-dimensional organization and therefore improves the mechanical properties of film. However, in many cases, cracks still occur in the transparent films even in the presence of plasticizers as a result of serious molecular aggregation caused by numerous hydroxyls and the lack of side chains in hemicelluloses backbones. Obviously, plasticizers cannot significantly decrease this aggregation.^{5,6,11,22}

In this study, 20% sorbitol (based on the total dry weight of xylan and plasticizer) was used to externally plasticize xylan for forming self-supporting hemicelluloses film. Continuous 2-OSA-xylan and 2-DSA-xylan (2-DSA-0.19 and 2-DSA-0.27) films, however, could be formed without addition of any plasticizers, as indicated in Figure 3 and Table 1. It was found that the externally



Figure 3. Optical images of films: 2-OSA-0 and 2-OSA-0.17.

plasticized xylan film (2-OSA-0) was stiff and showed some cracks, which indicates that external plasticization is not effective in preparing xylan films. Furthermore, the externally plasticized xylan film was cohesive because of its high hydrophilicity, which is indicated by the high moisture content (13.92 wt %). The high hydrophilicity will result in poor mechanical properties in high-humidity conditions.²³

The modified samples (2-OSA-0.067, 2-OSA-0.098, 2-OSA-0.17, and 2-OSA-0.22) could not be dissolved in water but could form semivitreous suspension in hot water (80 °C) due to the amphiphilicity of long carbon chain anhydride modified xylan (possessing carboxyl groups and long carbon chains), whereas 2-OSA-0.29 formed a white suspension in hot water because the modified xylan has more hydrophobic long carbon chains. Casting was carried out in an oven at 80 °C to avoid the serious sedimentation of 2-OSA xylan at room temperature. For the unmodified xylan, casting at room temperature could produce continuous xylan film, whereas casting at elevated temperature (80 °C) resulted in discontinuous film as a result of the rapid aggregation of xylan molecules. Therefore, externally plasticized xylan film could be prepared at room temperature only after extended periods of time (4–7 days) by slowly evaporating water. However, continuous, smooth, and flexible 2-OSA-xylan films could be rapidly obtained by casting at 80 °C for 4–8 h. This indicates that serious aggregation of xylan molecules can be effectively avoided in the drying process at elevated temperature.

As compared with 2-OSA-xylan, 2-DSA-xylan showed relatively poor film-forming performance (Table 1). 2-DSA-xylan with a moderate DS (2-DSA-0.15) could not form a

continuous film, whereas 2-OSA-xylan with a low DS (2-OSA-0.064) could form a free-standing film. Furthermore, 2-OSA-xylan films were less smooth than 2-OSA-xylan films. These results indicate that 2-OSA-xylan has better film-forming properties, but the reason is still unknown. Therefore, our interest was focused on 2-OSA-xylan films in the following studies.

Sorbitol plasticized xylan film was stiff and could be easily fractured when the film was folded, whereas 2-OSA-xylan film was flexible and difficult to be folded to fracture. Furthermore, 2-OSA-xylan film with a higher DS was more flexible. Plasticization, a replacement of hydrogen bonds, will increase the free volume and the molecular mobility of a polymer chain, making polymeric material less stiff.²⁴ The xylan chains are supposed to be rigid due to the lack of side chains or substituents,^{17,22} and thus, deformability is usually small. In this work, 2-OSA xylan film was more flexible than the externally plasticized xylan film, which indicates that the pendent 2-OSA half-ester groups act as built-in internal plasticizers for xylan film.

Hydrophilicity. Table 1 shows the equilibrium moisture content of films. The externally plasticized xylan film exhibited high moisture content (13.92 wt %), whereas 2-OSA-xylan and 2-OSA-xylan films had lower moisture contents (5.90–11.67 wt %), showing lower sensitivity toward moisture. The moisture content was significantly decreased as the DS of 2-OSA or 2-OSA half-ester groups increased. The contact angle of water on the film surface as a function of DS is illustrated in Figure 4. The

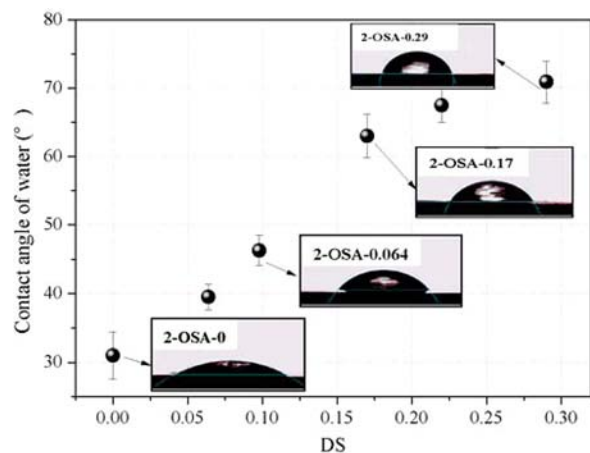


Figure 4. Contact angle of water on xylan and 2-OSA-xylan film surface.

contact angle of xylan film was 31.0°, indicating a high hydrophilicity of xylan chains. Chemical modification with 2-OSA resulted in films with higher contact angles (39.5–71.9°). The grafting of hydrophobic alkenyl chains in xylan backbone yields low moisture sensitive film that can be used in moisture-rich conditions. The contact angles of 2-OSA xylan films with DS of 0.17–0.29 are comparable to the fluorinated xylan films²⁵ and the benzyl chloride modified *O*-acetylgalactoglucosaminan film, which had a DS of approximately 1.3.²³

XRD. Figure 5 shows that the xylan film with external plasticizer (2-OSA-0) displayed a distinct crystalline peak at around $2\theta = 18^\circ$, indicating the crystalline structure in the film. It is known that some hemicellulose films obtained by water casting method are semicrystalline.^{14,15,22} Our previous work also showed that the air-dried xylan powder and xylan films were semicrystalline, whereas the freeze-dried xylan was amorphous.¹¹ Interestingly, films obtained from xylan with high arabinose

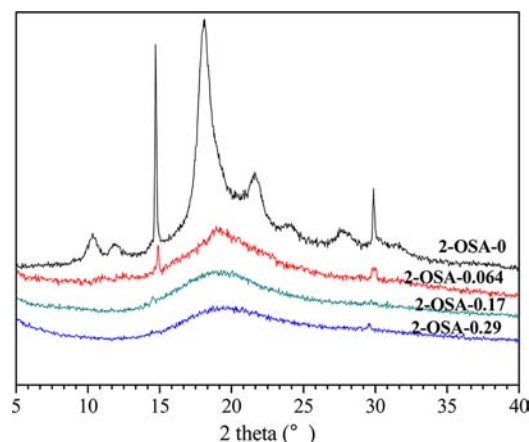


Figure 5. X-ray diffractions of films (from top to bottom): externally plasticized xylan film (2-OSA-0), 2-OSA-xylan films (2-OSA-0.064, 2-OSA-0.17 and 2-OSA-0.29).

content (arabinose/xylose ratio of 0.5) were found to be amorphous, whereas the film with relatively low arabinose content (arabinose/xylose ratio of 0.20–0.37) showed distinct crystallinity.^{17,22,26} It is likely that the unsubstituted regions of the xylan backbone more easily approach each other and form stable interchain associations (strong hydrogen bonds) or crystalline regions, which is supposed to contribute to the brittleness of xylan films. In this study, the arabinose/xylose ratio is 0.084; the lack of side chains (arabinose substituents) in xylan backbone leads to easy association or aggregation of xylan chains in the film-forming process. The presence of plasticizer (sorbitol) did not significantly change and decrease the crystalline structure, which suggests that external plasticization may increase the crystallinity of the xylan film by increasing the polymer chain mobility.^{14,27}

In contrast, 2-OSA-xylan films (2-OSA-0.064, 2-OSA-0.17, and 2-OSA-0.29 in Figure 5) were amorphous; even small amounts of 2-OSA half-ester groups (2-OSA-0.064) could significantly reduce the crystalline structure. This indicates that 2-OSA half-ester groups can significantly hinder the crystallization. It can be explained because the hydrophobic long carbon chains in the xylan backbone can effectively prevent xylan chains from aggregating by disrupting the intramolecular and intermolecular hydrogen bonds during solvent evaporation as a result of the steric hindrance of long side chains. Therefore, internal plasticization is a more effective method to decrease hydrogen bonds than external plasticization, and thus 2-OSA-xylan has better film-forming performance and the film is more flexible than the externally plasticized xylan film.

TG Analysis. Figure 6 shows the typical TGA/DTA curves of the externally plasticized xylan film and 2-OSA-xylan films. The peak degradation temperatures (T_{peak}) were 296, 246, 242, and 230 °C for the externally plasticized 2-OSA-0 and 2-OSA-xylan films, suggesting that externally plasticized film has higher thermal stability. 2-OSA-xylan film with lower DS generally had higher thermal stability than that with higher DS. It is very likely that the decrease of hydrogen bonds is responsible for the decreasing thermal stability of films, because the rupture of hydrogen bonds during thermal degradation requires more energy.

Topography of Film Surface. AFM images with high resolution were recorded to determine the surface structural information of the films, and representative images are shown in

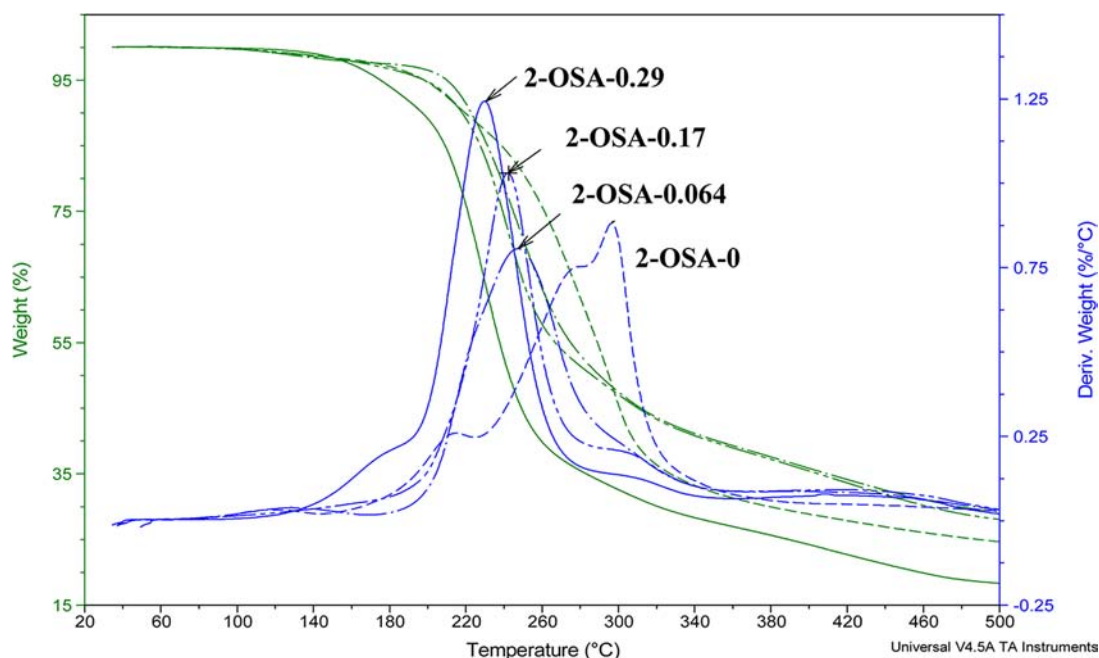


Figure 6. TGA/DTA curves of the externally plasticized xylan film (2-OSA-0) and 2-OSA-xylan films (2-OSA-0.064, 2-OSA-0.17, and 2-OSA-0.29).

Figure 7. Furthermore, AFM, in combination with XRD data, can reveal more interesting details about the molecular aggregation

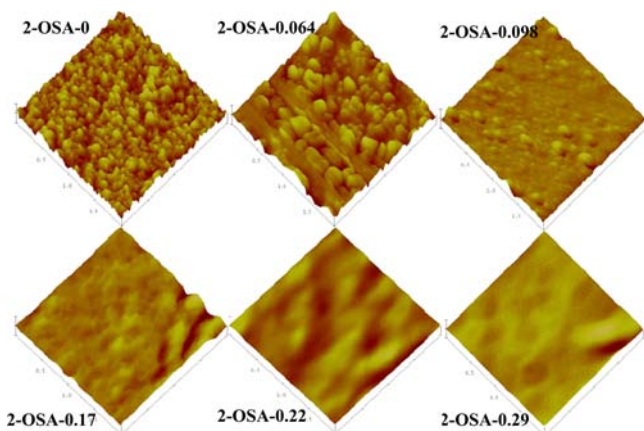


Figure 7. AFM images of films. The scanning scale is $2 \times 2 \mu\text{m}$.

of xylan and the nanostructure of the film surface. It was found that the externally plasticized xylan film surface (2-OSA-0) was composed of large amounts of nanonodules with diameters of 20–100 nm. These nodules tightly connected with each other, forming a rough surface, which is in agreement with our previous work in which the diameters of nodules ranged from 10 to 70 nm,¹¹ and a similar result was also reported for cellulose whisker reinforced xylan films.²⁸ Interestingly, the surface of 2-OSA-xylan film with a DS of 0.064 (2-OSA-0.064) showed fewer, but larger, nodules with diameters of 60–350 nm. With the increase of DS the number of nodules further reduced (2-OSA-0.098), and finally nodules completely disappeared. The 2-OSA-xylan film surface was smooth, which was in sharp contrast with the externally plasticized xylan film surface. This is the first time we have observed a smooth surface of hemicelluloses film at nanoscale.

These results, in combination with the XRD data, demonstrate that the nodules on the film surface result from strong hydrogen

bonds. The reduction of hydrogen bonds is responsible for the decrease and disappearance of nodules. The long alkane chains in xylan act as steric hindrance to disturb the hydrogen bonds and thus inhibit xylan chain aggregation, as shown in Figure 8. The

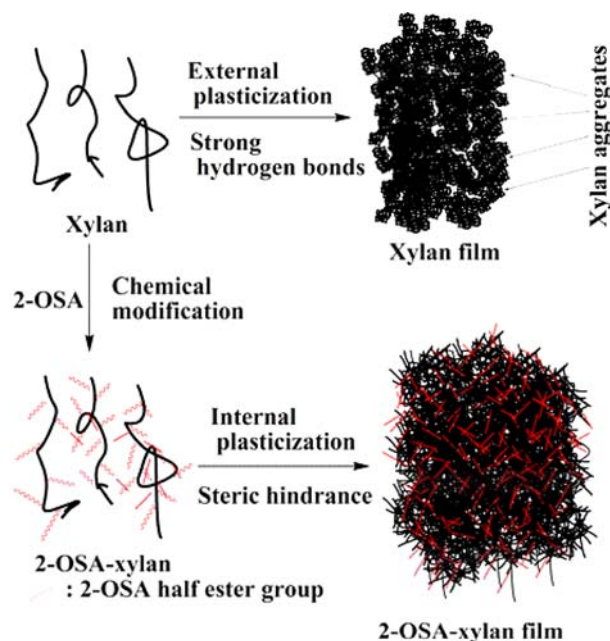


Figure 8. 2-OSA modified xylan film and internally plasticized xylan film.

large nodules on the surface of 2-OSA-0.064 may be due to the incompact aggregation of xylan chains. Xylan chain aggregation also occurred in the interior of the externally plasticized xylan film, but it is difficult to observe these aggregates because of the continuous structure of the interior matrix. The nodules observed on the xylan film surface represent the special molecular aggregates occurring at the solid–gas interface and

can be considered as an index of the degree of hydrogen bonds for hemicelluloses with and without modification.

Mechanical Performance. The tensile stress, Young's modulus, and tensile strain at break of films are shown in Table 2, and the typical stress–strain curves are shown in Figure

Table 2. Tensile Testing Results of the Films Produced

sample	tensile strength (MPa)	tensile strain at break (%)	Young's modulus (MPa)
2-OSA-0	20.8 ± 3.2	3.4 ± 1.1	717 ± 45
2-OSA-0.064	44.0 ± 4.1	7.9 ± 1.8	638 ± 46
2-OSA-0.098	28.5 ± 4.4	9.2 ± 2.5	401 ± 31
2-OSA-0.17	23.2 ± 4.8	18.2 ± 2.5	209 ± 22
2-OSA-0.22	7.3 ± 2.0	23.0 ± 3.1	87 ± 14
2-OSA-0.29	6.9 ± 2.5	35.1 ± 4.4	81 ± 17

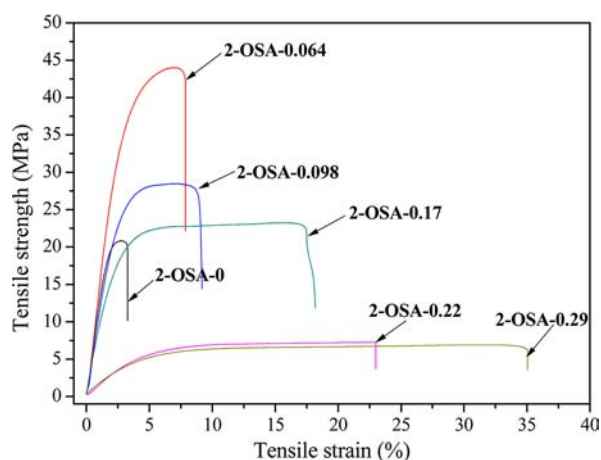


Figure 9. Tensile strain curves of films. The samples listed in Table 1 are indicated in the figure.

9. The externally plasticized xylan film (2-OSA-0) had low tensile strength, which is indicated by the stress strength of 20.8 MPa and tensile strain of 3.4%. 2-OSA-xylan film with a DS of 0.064 exhibited the highest tensile strength (44.0 MPa) and a moderate tensile strain (7.9%), improved by 111 and 132%, respectively. The further increase of DS caused a decrease in tensile strength but a significant increase in tensile strain. The tensile strength of 2-OSA-xylan film with a DS of 0.29 was low (6.9 MPa), whereas the strain was high, up to 35.1%, showing an increase of 932%. These results reveal that even a very small substitution of 2-OSA half-ester groups can produce xylan film with high tensile strength.

For biomacromolecule (e.g., cellulose, starch) films with or without external plasticizers, mechanical strength mainly depends on the hydrogen bonds. External plasticization (a replacement of hydrogen bridges acting among the chains by the interaction of the plasticizer and the groups forming those bridges) leads to a considerable decrease of strength because of the decreasing hydrogen bonds.^{6,14,29} In other words, external plasticization can improve the film-forming performance of biopolymers at the cost of decreasing their tensile strength. In this work, continuous xylan film without external plasticizer cannot be formed because strong hydrogen bonds caused strong internal stress, resulting in cracks and defects within the film.³⁰

Although the presence of external plasticizer can produce a continuous film by replacing hydrogen bonds, some cracks and defects still occurred (Figure 3, 2-OSA-0), and thus the tensile strength and strain are low. This suggests that external plasticization is insufficient to produce high-strength xylan film.

With the introduction of long alkane chains into the xylan backbone, xylan films (2-OSA-0.064, 2-OSA-0.098, and 2-OSA-0.17) become flexible and show higher tensile strength than 2-OSA-0. This indicates that properly inhibiting the aggregation of xylan chains by long alkane chains (Figure 7, 2-OSA-0.064, 2-OSA-0.098, and 2-OSA-0.17) is very beneficial for improving the tensile strength of xylan films. Interestingly, a low substitution of 2-OSA half-ester groups (2-OSA-0.064) can produce a significant increase in tensile strength for xylan film, whereas films with relatively high substitutions (DS = 0.098–0.29) show low tensile strength. This result, in combination with XRD and AFM data, demonstrates that small amounts of long alkane chains (DS = 0.064, for instance) can significantly disturb the arrangement of xylan chains and properly decrease the hydrogen bonds, resulting in film with amorphous structure, fewer molecule aggregates, and fewer internal defects or less stress. This is responsible for the higher tensile strength of 2-OSA-0.064. The increase of 2-OSA half-ester groups (higher DS), however, further increases the distance of xylan moieties and thus will significantly decrease hydrogen bonds and increase the mobility of xylan chains,^{29,31} producing xylan film with low tensile stress and high strain. It should be noted that, besides the hydrogen bonds, there will be interactions between the hydrophobic chains themselves. This kind of interaction, however, is relatively weak as compared with hydrogen bonds, as indicated by the lower tensile strength of films with higher long alkane chain contents (2-OSA-0.22 and 2-OSA-0.29, for instance). Therefore, the tensile stress and strain can reflect the strength of hydrogen bonds in xylan matrix.

This is in sharp contrast with externally plasticized hemicellulose films^{6,14,29,31} and benzyl chloride modified *O*-acetylgalactoglucosaminan films.²⁴ In these cases, the tensile strength of the externally plasticized or benzyl chloride modified films was significantly reduced. Addition of enhancements such as cellulose whiskers and cellulose microfibrils can produce hemicellulose films with higher tensile strength, but low tensile strain, stiffness, and high hydroscopicity are still pendent problems in producing high-strength hemicellulose films.^{11,16,17} In this work, a low substitution of 2-OSA half-ester groups could significantly improve the mechanical strength and decrease the stiffness and hydroscopicity of xylan film. Furthermore, 2-OSA-xylan films can be rapidly formed (4–8 h) at elevated temperature, which is also in contrast with 4–7 days for the preparation of the externally plasticized films at room temperature. Therefore, long-chain anhydride modification can produce internally plasticized film with high performances (flexible, hydrophobic, high tensile strength, and stress) that have never before been achieved by other methods (e.g., external plasticization by xylitol, sorbitol, or glycerol or external enhancement by cellulose microcrystal and nanofiber).^{6,14,29,31} The combination of flexibility, hydrophobicity, and high tensile strength, along with low substitution degree, makes these materials ideal candidates for further investigation of producing high-strength hemicellulose films for food packaging.

In summary, this is the first attempt to prepare internally plasticized hemicellulose films by grafting of hemicelluloses with long alkenyl chains. The pendent 2-OSA half-ester groups act as internal plasticizer by interfering with the association of

hydroxyls and disturbing the regular arrangement of xylan chains in the film-forming process due to the steric hindrance of 2-OSA half-ester groups. For this reason, the internally plasticized films have amorphous structure and better film-forming performance than the externally plasticized film. The hydrophobic alkenyl chains also can yield low moisture sensitive films that can be used in moisture-rich conditions. Furthermore, internal plasticization is a more effective method to improve the tensile strength of hemicellulose films. A low substitution of 2-OSA half-ester groups can produce xylan film with high tensile strength, whereas a high substitution will lead to high tensile strain.

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Notes

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