

Preparation and Characterization of Corn Starch and Lignosulfonate Blend Film with a High Content of Lignosulfonate

Ruixin Shi and Bin Li *

A degradable starch/lignin blend film was prepared using corn starch and sodium lignosulfonate via a casting and solvent evaporation method. The effect of sorbitol content on the swelling properties of starch/lignosulfonate blend films was investigated. The effect of lignosulfonate content on the swelling and mechanical properties was also studied. The results showed that when the mass ratio of sorbitol to starch changed over a wide range, from 0:9 to 9:9, the water absorption of the blend films increased at first and then decreased. When the mass ratio of lignosulfonate to starch changed in the same range, the ultimate stress of the blend films decreased markedly, while the water absorption and elongation at break did not show any regular pattern. When the mass ratios of sorbitol to starch and lignosulfonate to starch were both 6:9, the resultant film presented good elasticity and improved hydrophobicity compared to those without lignosulfonate.

Keywords: Corn starch; Lignosulfonate; Blend film; Water absorption capacity; Morphology; Mechanical properties; Thermal stability

Contact information: College of Science and Post-doctoral Mobile Research Station of Forestry Engineering, Northeast Forestry University, China, 150040; *Corresponding author: Libinzh62@163.com

INTRODUCTION

Many countries are encouraging the development and use of degradable films made from natural polymers as an alternative to petroleum-based films. This demand for natural polymers is due to a fast depletion of petroleum-based resources, as well as serious environmental pollution associated with them (Chapman 1994; Chiellini and Solaro 1996; Krochta and De Mulder-Johnston 1996). Starch is an ideal raw material for preparing degradable films, due to its good film forming properties, a wide range of resources, low price, renewability, and biodegradability. However, its applications are greatly limited due to its peculiar structural characteristics, which lead to problems like poor water resistance and mechanical properties (Carvalho *et al.* 2001). To overcome these drawbacks, organic or inorganic fillers are added while preparing starch-based biocomposites. For instance, water vapor barrier can be improved by adding microparticles (Carvalho *et al.* 2001) and nanoparticles (Tang *et al.* 2009; Yu *et al.* 2009). Reinforcement agents such as clays (Avella *et al.* 2005) and cellulosic fibers (Müller *et al.* 2009) can also be used to improve the mechanical resistance of starch-based films.

Lignin is the second most abundant terrestrial biopolymer after cellulose (Rastogi and Dwivedi 2008). Around 5×10^6 metric tons of lignin are produced annually in industries (Mai *et al.* 2000). A major portion of industrial lignin is incinerated to produce steam and energy (Mohan *et al.* 2006). However, the utilization of lignin as a fuel is not an economically viable option, and it has been underutilized industrially (El Mansouri and Salvadó 2006; Doherty *et al.* 2011). Lignin is a crosslinked macromolecular material, based

on three kinds of monolignols, and it can be blended with polymers (Lora and Glasser 2002). Due to its aromatic structure and the presence of phenolic residues, lignin has multiple functions and can be used as a compatibilizer (Graupner 2008), plasticizer (Baumberger *et al.* 1998a), hydrophobizing agent (Baumberger *et al.* 1998b; Zheng *et al.* 2008), flame retardant (Reti *et al.* 2008), optical modifier (Toh *et al.* 2005), or stabilizer (Pucciariello *et al.* 2010). Furthermore, it has interesting properties, such as antimicrobial activity (Cruz *et al.* 2001) and cytotoxicity (Ugartondo *et al.* 2008) that render it potentially useful in high-value applications. The incorporation of lignin into starch matrix has a positive effect on its mechanical, thermal, and water and gas barrier properties (Lepifre *et al.* 2004a; Lepifre *et al.* 2004b; Calgeris *et al.* 2012; Privas *et al.* 2013; Kaewtatip and Thongmee 2013).

In this work, corn starch and sodium lignosulfonate were used to prepare blend films. The structure, morphology, and thermal properties of the blend films were characterized by Fourier transform infrared (FTIR) spectroscopy, thermogravimetry (TG), X-ray diffraction (XRD), and scanning electron microscopy (SEM). Furthermore, the effects of sorbitol and lignosulfonate content on the swelling and mechanical properties of the blend films were investigated. The mechanism by which lignosulfonate influenced the properties of starch-based composite films was also discussed.

EXPERIMENTAL

Materials

Corn starch (0.05% protein, 0.17% lipid, 0.12% ash, and 26.94% amylose (dry basis)) was purchased from Daqing Jialiang Development Co. Ltd., Daqing, China. Sodium lignosulfonate, technically pure grade (refined before use by alcohol precipitation; average $M_w = 12240$ g/mol, 8% sulfur), was obtained from Xinya Chemical Technology Co. Ltd., Liaocheng, China. Sorbitol, analytically pure grade, was purchased from Zhiyuan Chemical Reagent Co. Ltd., Tianjin, China.

Preparation of Films

The solutions used for film casting were prepared by adding a known percentage of corn starch to distilled water (9 g corn starch/ 100 g water) at room temperature. Sorbitol was added as the plasticizer at different concentrations (1, 2, 3, 4, 5, 6, 7, 8, or 9 g sorbitol/ 9 g corn starch). Sodium lignosulfonate in different concentrations (0, 1, 2, 3, 4, 5, 6, 7, 8, 9 g lignosulfonate/ 9 g corn starch) was then introduced into the above solution. Furthermore, when the effect of sorbitol content on the film properties was to be studied, the mass ratio of lignosulfonate to starch was constant at 1:9. When the effect of lignosulfonate content on the film properties was to be studied, the mass ratio of sorbitol to starch was constant at 6:9. The mixture was stirred at 500 rpm for 2 h at 75 °C. The solution was then transferred to a suction bottle, and air bubbles in the solution were removed using a vacuum pump.

A 70 g portion of each dispersion was poured onto a stainless plate to yield a film having dimensions of 10×10 cm². Plates were left for 2 h at 70 °C in an oven, followed by 20 °C overnight. Films were peeled manually and stored in desiccators, maintained at 25 °C and 57% relative humidity (RH) (saturated sodium bromide solution). The blend films prepared were brown in color and the thickness of each film was measured with a hand-held micrometer (Mitutoyo, Tokyo Japan).

FTIR Analysis

The FTIR spectra of blend films were recorded on a Nicolet Avatar 360 spectrophotometer (ThermoScientific, Waltham, MA, USA). The spectra were recorded in transmittance mode over a spectral range of 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} .

TG Analysis

Thermogravimetric analysis of blend films was conducted using a Perkin-Elmer TGA-6 thermal analyzer (Fremont, CA, USA). Samples were heated from 40 to 700 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ in nitrogen atmosphere.

X-ray Diffraction Studies

The X-ray diffraction patterns were recorded using Cu $K\alpha$ radiation at 40 kV and 30 mA, in the 2θ range of 5 to 80 $^{\circ}$ using a D/MAX-RB X-ray diffractometer (Rigaku, Tokyo, Japan).

Scanning Electron Microscopy Analysis

The morphologies of blend films were examined by SEM, using a Quanta 200 scanning electron microscope (FEI, Hillsboro, OR, USA). Results of four representative samples have been presented, which include the neat starch film, the blend films with minimum and maximum lignosulfonate contents (the mass ratios of lignosulfonate to starch of 1:9 and 9:9), and the blend film with the lowest water absorption (mass ratio of lignosulfonate to starch of 6:9).

To analyze cross-sections of the samples, the films were cryofractured by immersion them in liquid nitrogen. The film specimens were mounted on bronze stubs using double-sided tape and coated with a layer of gold (40 to 50 nm), which provided a good cross-sectional view.

Water Absorption

Water absorptions of the films were measured according to the national standard, GB/T 1034-2008 (2008). Samples were cut into square pieces of 30 mm \times 30 mm and dried to a constant weight at 50 $^{\circ}\text{C}$ in a vacuum oven. The weight of each specimen was recorded as the initial weight (M_0). The film was then soaked in 50 mL of distilled water for 24 h at room temperature. The water on the surfaces was then wiped off using filter paper. Finally, the sample was weighed again (M).

Tests were conducted in triplicate, and water absorption was calculated using the following formula,

$$\text{Water absorption (\%)} = 100 \times (M - M_0) / M_0 \quad (1)$$

where, M_0 and M are the initial weight and the weight of the sample after swelling.

Mechanical Properties

Films were cut into strips of 100 mm \times 10 mm, and an XD-T-20A tensile tester (Ruiger, Shenzhen, China) was employed to test the ultimate stress and elongation at break with an extension speed of 5 mm/min, according to the national standard GB/T 13022-91 (1991). Each test was repeated five times, and the average and standard deviations were calculated. The tests were carried out at 25 $^{\circ}\text{C}$ and a constant relative humidity of 45%.

RESULTS AND DISCUSSION

FTIR Spectroscopy of the Films

FTIR spectra of the components and blend films are presented in Fig. 1. Spectra of all the samples showed a strong and broad peak between 3000 cm^{-1} and 3500 cm^{-1} , which could be assigned to hydrogen-bonded O-H stretching vibration. Besides this, all the spectra also displayed two peaks: the first one between 2800 cm^{-1} and 3000 cm^{-1} , due to C-H stretching vibrations and the second one at $\sim 1455\text{ cm}^{-1}$, due to C-H bending vibrations of methylene groups. The absorption peaks between 1000 cm^{-1} and 1200 cm^{-1} were characteristic of the C-O stretching vibrations of C-OH and C-O-C (Wang *et al.* 2008).

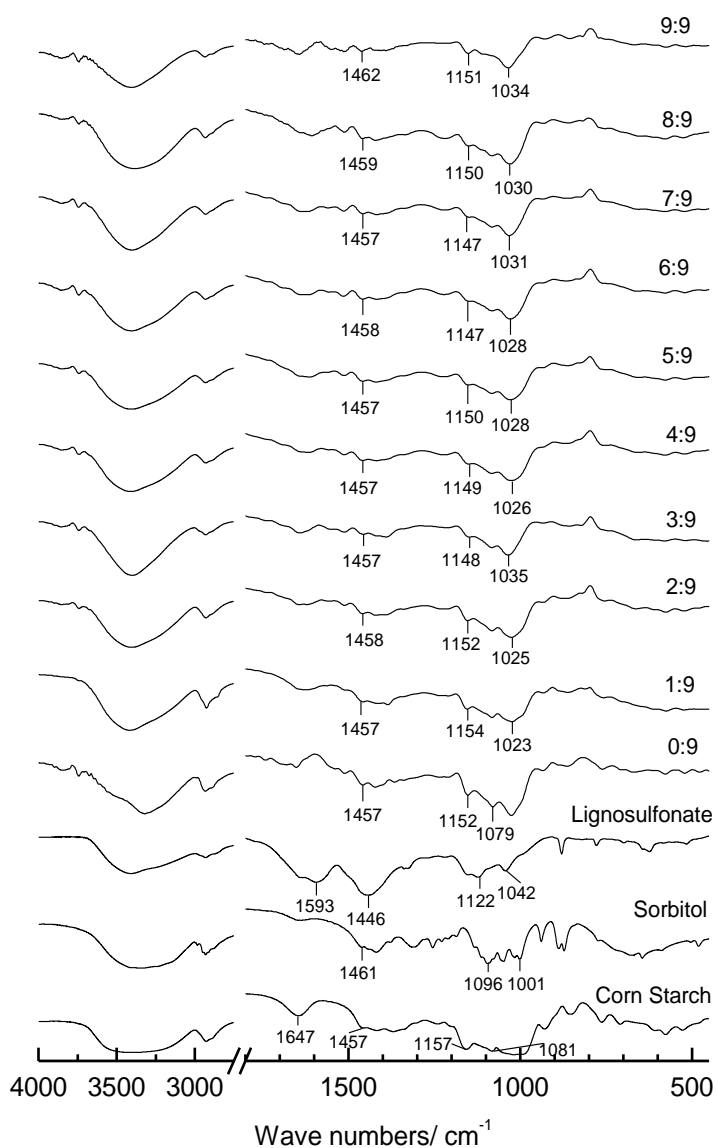


Fig. 1. FTIR spectra of corn starch, sorbitol, lignosulfonate, and starch/lignosulfonate blend films with lignosulfonate-to-starch mass ratios ranging from 0:9 to 9:9

In the spectrum of corn starch powder, the characteristic peak that appeared at 1647 cm^{-1} was believed by Fang *et al.* (2002) to be a feature of the tightly bound water molecules present in starch. Peaks at 1157 cm^{-1} and 1081 cm^{-1} were attributed to the stretching vibrations of C-O in C-O-H groups (Wu *et al.* 2009). In the spectrum of neat starch film, which was marked as 0:9 in Fig. 1, both the peaks were shifted to lower wave numbers, that is, 1152 cm^{-1} and 1078 cm^{-1} , respectively. This suggested the formation of new hydrogen bonds by addition of sorbitol, which was used as the plasticizer in the film.

In case of sodium lignosulfonate powder, peaks at 1593 and 1446 cm^{-1} corresponded to the aromatic ring vibrations of the phenylpropane skeleton. The peak at 1122 cm^{-1} was characteristic of the syringyl unit. The peak at 1042 cm^{-1} could be attributed to the stretching vibration of S=O of sulfonic group. It was clear that the starch/lignosulfonate blend films, having different lignosulfonate contents, exhibited similar peaks in FTIR spectra, which included the characteristic absorption peaks of both lignosulfonate and starch. By comparing the spectra of the starch/lignosulfonate blend films with that of lignosulfonate and corn starch powder, it was evident that the peaks at 1157 cm^{-1} and 1042 cm^{-1} , due to stretching vibrations of C-O and S=O, respectively, were shifted to lower wave numbers in the blend film. This may be the result of interactions, such as hydrogen bonding between the components in the blend films.

Thermogravimetric Analyses of Films

The results of thermogravimetric analyses of lignosulfonate and blend films are shown in Fig. 2. As is shown in the figure, the pyrolysis of lignosulfonate occurred in three stages. The first stage between 100 and $200\text{ }^{\circ}\text{C}$ represented the loss of absorbed and bound water. Between 200 and $400\text{ }^{\circ}\text{C}$, chemical bonds (ether linkages and carbon-carbon linkages) in lignosulfonate were cleaved. The last stage, from 500 to $700\text{ }^{\circ}\text{C}$, was due to decomposition and carbonization of lignosulfonate or its pyrolysis products. In the starch film, the slow weight loss that occurred prior to $200\text{ }^{\circ}\text{C}$ was also due to evaporation of water.

The maximum weight loss between 280 and $360\text{ }^{\circ}\text{C}$ was ascribed to the decomposition of starch and volatilization of sorbitol, as previously reported (Muhammed *et al.* 2015). For the blend films, the temperature corresponding to the maximum rate of weight loss was lower than that of the starch film. Moreover, the TG curves of blend films showed an additional weight loss stage in the range of 400 to $500\text{ }^{\circ}\text{C}$, which could be attributed to further pyrolysis of lignosulfonate. This stage was more prominent in the curves of the samples made with 1:9, 6:9, and 7:9 lignosulfonate-to-starch mass ratios. The thermal behaviors of starch/lignosulfonate blend films were similar to those reported previously (Calgeris *et al.* 2012).

The TG analysis data are presented in Table 1, where T_{10} and T_{50} represent the temperatures at which the weight loss of a sample reached 10% and 50%, respectively. W_{600} and W_{700} represent the amount of residual char at $600\text{ }^{\circ}\text{C}$ and $700\text{ }^{\circ}\text{C}$, respectively. The T_{10} values for all of the blend films were lower than that of the neat starch film. The W_{700} value for blend films was much higher than that of the neat starch film, except for the samples made with lignosulfonate-to-starch mass ratios of 1:9 and 7:9. The higher char residues of blend films were the result of thermally stable aromatic structures in the lignosulfonate backbone (Bartkowiak and Zakrzewski 2004; Brebu and Vasile 2010).

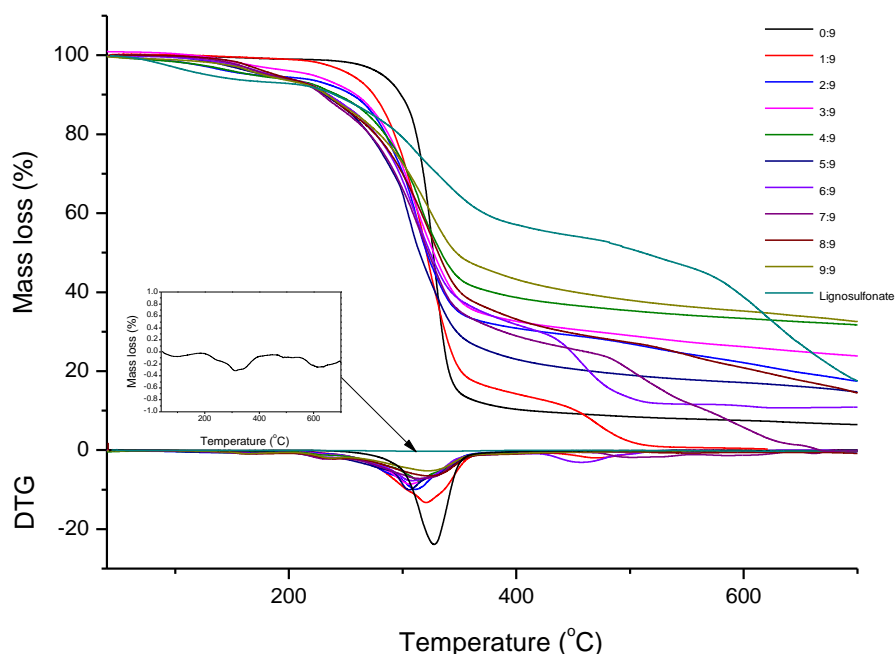


Fig. 2. TG and DTG curves of lignosulfonate and starch/lignosulfonate blend films with lignosulfonate-to-starch mass ratios ranging from 0:9 to 9:9

Table 1. Thermal Parameters of Lignosulfonate Powder and Starch/Lignosulfonate Films with Lignosulfonate-to-Starch Mass Ratios Ranging from 0:9 to 9:9

	Lignosulfonate-to-Starch Ratio										Ligno-sulfonate
	0:9	1:9	2:9	3:9	4:9	5:9	6:9	7:9	8:9	9:9	
T_{10} (°C)	298.5	274.6	255.3	259.0	242.4	231.2	234.9	229.5	233.5	233.3	240.4
T_{50} (°C)	326.8	320.9	321.2	327.4	334.0	314.9	324.2	322.8	331.3	347.3	511.1
W_{600} (%)	7.51	0.44	22.14	26.19	33.34	17.09	11.19	5.74	20.82	35.22	38.74
W_{700} (%)	6.46	0	17.45	23.84	31.70	14.71	10.91	0	14.46	32.53	17.52

XRD Analyses of Films

Evolution of the crystalline structure of starch in the starch/lignosulfonate films was investigated by XRD (Fig. 3). The XRD pattern of starch granules showed three diffraction peaks at 15.2° , 17.0° , and 23.0° , which was consistent with an earlier study (Spiridon *et al.* 2011). As to the pattern of starch film (marked as 0:9 in Fig. 3), since starch was gelatinized and sorbitol was used as the plasticizer, the diffraction peaks of starch disappeared. This implied that the crystalline structure of B-type starch was destroyed. Additionally, the presence of a weak broad peak at 20° suggested the formation of a V-type crystal structure, due to recrystallization of some amylose (Ma *et al.* 2008). When lignosulfonate was added to the starch matrix in a mass ratio of 1:9, the pattern changed. More specifically, comparison with the starch granules showed that the peak at 15.2° disappeared, whereas

the peak at 23.0° remained. Moreover, comparison to the plasticized starch film showed that the peak intensity around 20° increased. By increasing the lignosulfonate content in the blend films, all of the peaks gradually decreased. When the lignosulfonate-to-starch mass ratio was 9:9, there was no obvious peak seen in the XRD pattern. Hence, the addition of lignosulfonate influenced the microstructures of the films. It had especially influenced the structure of starch by preventing recrystallization *via* interactions, such as hydrogen bonding interactions between starch, lignosulfonate, and sorbitol molecules.

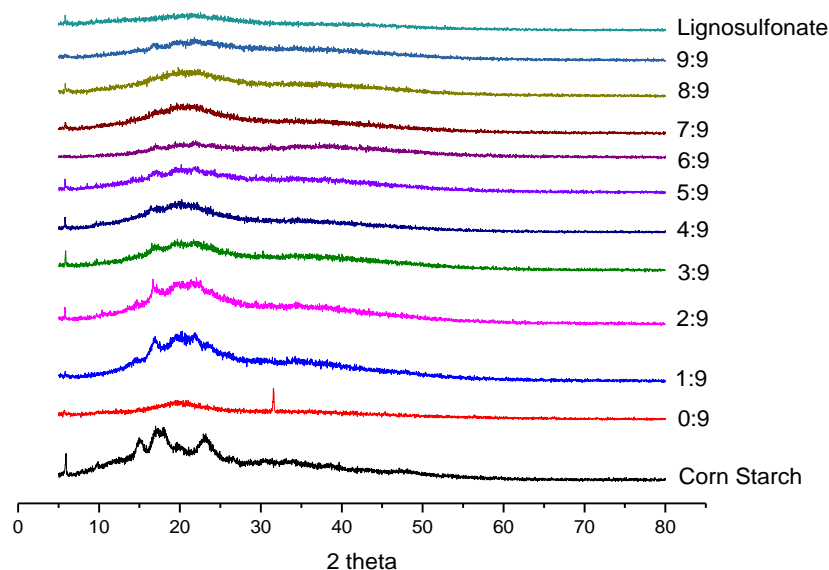


Fig. 3. XRD patterns of starch, lignosulfonate, and starch/lignosulfonate blend films with lignosulfonate-to-starch mass ratios ranging from 0:9 to 9:9

Morphological Study of Films

SEM images of the fractured surfaces of starch/lignosulfonate blend films are presented in Fig. 4. Since sodium lignosulfonate is a water-soluble polymer and the blend films were prepared by solution casting, similar to the neat starch film, the fractured surface of the blend films was smooth and there was no evidence of insoluble lignosulfonate powder appearing on the fractured surface. Both the neat starch film and blend films appeared homogeneous macroscopically. On the other hand, with an increase in the lignosulfonate content, greater numbers of microvoids were present on the fractured surfaces of the blend films. This may be ascribed to the fact that with an increase in the lignosulfonate content, the film-forming solution became more viscous and the degassing operation became difficult. Thus there were more bubbles left in the film-forming solution which formed microvoids in the films.

Effect of Sorbitol on Swelling Properties of Films

Corn starch used in this study was semi-crystalline in nature. When dissolved in hot water, the crystalline structures of amylose and amylopectin were lost, and the polymers became hydrated. During formation of the film, the starch molecules rearranged themselves by hydrogen bonds, causing embrittlement of the film, which was undesired (Vázquez and Álvarez 2009; Rindlav *et al.* 1997; Arvanitoyannis *et al.* 1997; Arvanitoyannis and Biliaderis 1998; Sothornvit and Krochta 2001; Talja *et al.* 2008).

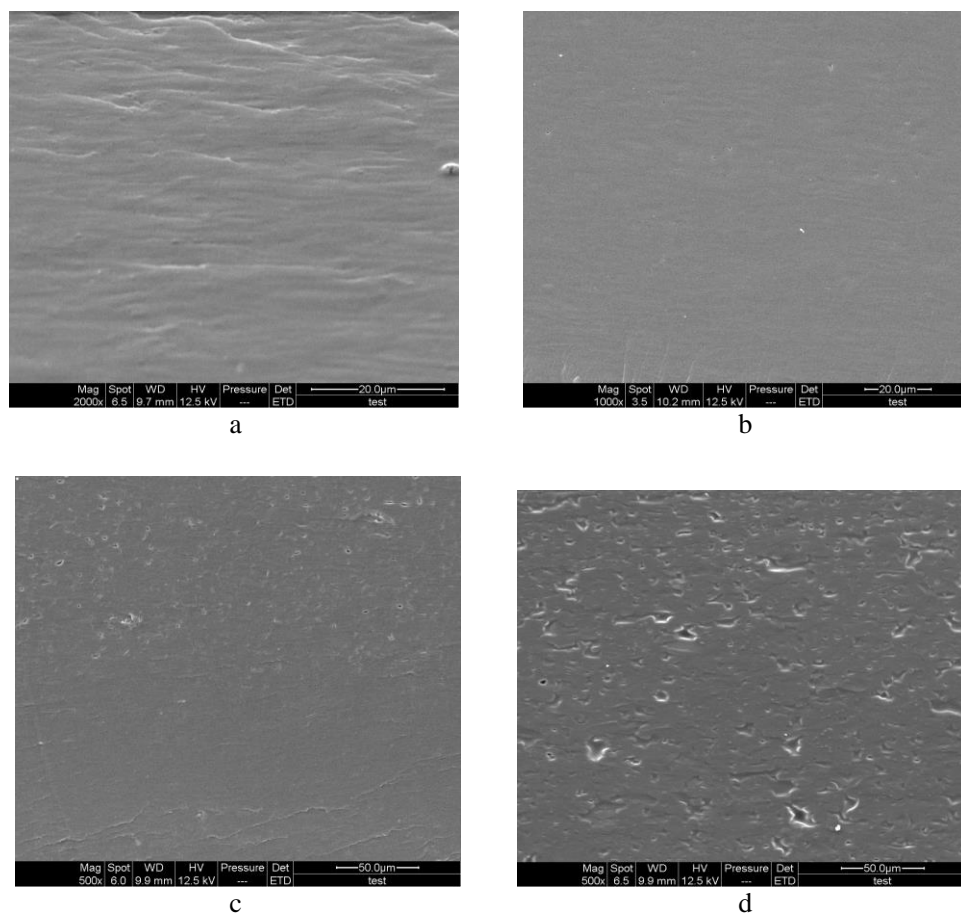


Fig. 4. SEM images of starch/lignosulfonate films with lignosulfonate-to-starch mass ratios of (a) 0:9, (b) 1:9, (c) 6:9 and (d) 9:9

Similar to earlier reports, the unplasticized starch film prepared in this study was very brittle and difficult to peel from the casting surface. A plasticizer, which could affect the intra- and intermolecular interactions in starch, was needed to overcome this problem (Laohakunjit and Noomhorm 2004; Wypych 2004; Galdeano *et al.* 2009).

Sugar alcohols are plasticizers commonly used for preparing films. Pre-experimental results showed that starch film plasticized with sorbitol was more hydrophobic than that plasticized with glycerol. This can be explained by the fact that glycerol is more hydrophilic in nature than sorbitol (García *et al.* 2000; Müller *et al.* 2008; Fakhouri *et al.* 2009; Abdorreza *et al.* 2011). As reported earlier (Galdeano *et al.* 2009) sorbitol is homogeneously incorporated within a network of hydrogen bonds between the starch molecular chains, which makes the film more flexible, soft, and transparent. So sorbitol was chosen as the plasticizer for this study.

As is shown in Fig. 5, by increasing the sorbitol content, the absorption of water by the film increased initially and later decreased. In the blend films, sorbitol molecules were small and could easily gain access to the spaces between the polymeric chains and form hydrogen bonds. This reduced the intermolecular interactions and increased the intermolecular distances (Galdeano *et al.*, 2009). Hence, in comparison to the unplasticized film, there could be a greater number of free hydroxyl groups in the polymer, which could absorb more water molecules. Compared to the unplasticized film (marked as 0:9 in Fig. 5), the water absorbed by the blend film, prepared with the mass ratio of sorbitol to starch of 1:9, increased. When more sorbitol was added, that is, when the mass ratio was increased

from 1:9 to 2:9, the water absorption increased further. However, when the mass ratio was increased to 3:9, there was a decrease in water absorption. This could be attributed to the fact that with further addition of sorbitol, some of sorbitol molecules could penetrate into the blend system of starch and ligninosulfonate. These sorbitol molecules could combine with the free hydroxyl groups, leading to the decrease in water absorption. Hence, the subsequent increase of mass ratio was accompanied by a decrease in water absorption. When the mass ratio increased to 6:9, the water absorption decreased to 59.35%. This was the minimum value obtained in this series, and did not change appreciably with further increase in the sorbitol content. Hence, in the follow-up experiments, films were prepared using a 6:9 mass ratio of sorbitol to starch.

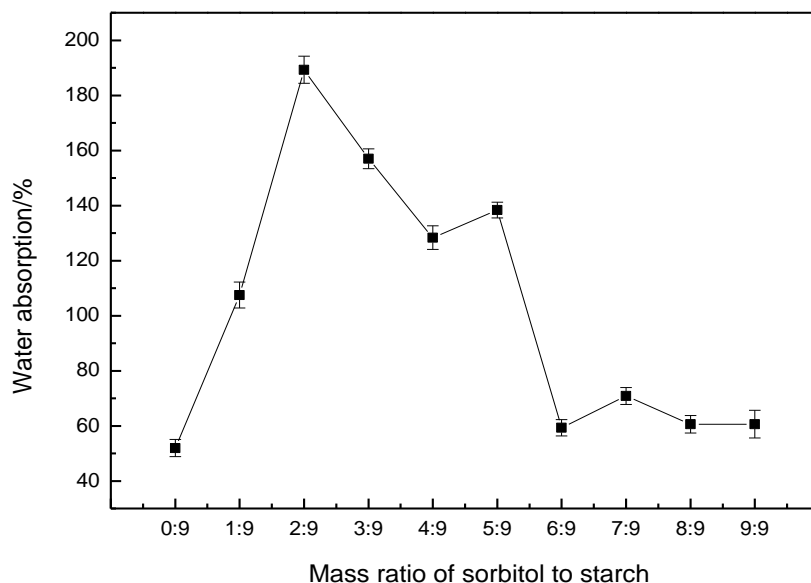


Fig. 5. Water absorptions of starch/lignosulfonate films with varying sorbitol contents

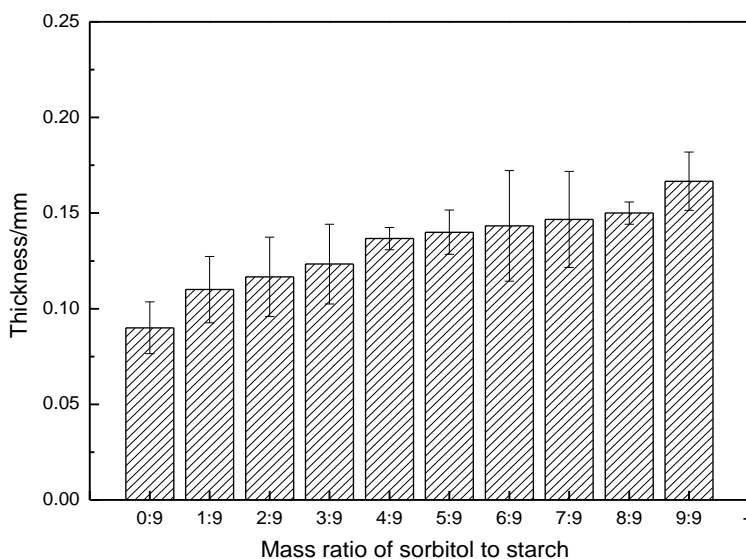


Fig. 6. Thicknesses of starch/lignosulfonate films with varying sorbitol contents

Figure 6 shows the effect of sorbitol content on thickness of the films. It was clear that higher sorbitol content resulted in a thicker blend film. This result is consistent with a previous study on the effects of plasticizer on starch films (Mohammadi *et al.* 2011).

Effect of Lignosulfonate Content on Mechanical and Swelling Properties of Starch/Lignosulfonate Films

The effect of lignosulfonate content on Young's modulus, ultimate stress, and elongation at break of the starch/lignosulfonate films is shown in Fig. 7. The starch/lignosulfonate films were prepared with sorbitol as the plasticizer and 6:9 mass ratio of sorbitol to starch. It can be seen in Fig. 7 that films with added lignosulfonate exhibited matrix reinforcement, which was expressed by markedly increased Young's moduli. On the other hand, with an increase in the lignosulfonate content, the ultimate stress decreased. When the mass ratio of lignosulfonate to starch increased from 1:9 to 2:9, the ultimate stress decreased from 5.11 MPa to 2.26 MPa. Thereafter, with a further increase in the lignosulfonate content from 2:9 to 8:9, the values of ultimate stress fluctuated in the range of 1.61 MPa to 2.32 MPa. Finally, when the mass ratio was increased to 9:9, the ultimate stress decreased to a minimum of 0.92 MPa, and the film became very hard and brittle. In a similar manner, the ultimate stress of polypropylene was found to decrease after the addition of 20% lignosulfonate (Kharade and Kale 1999).

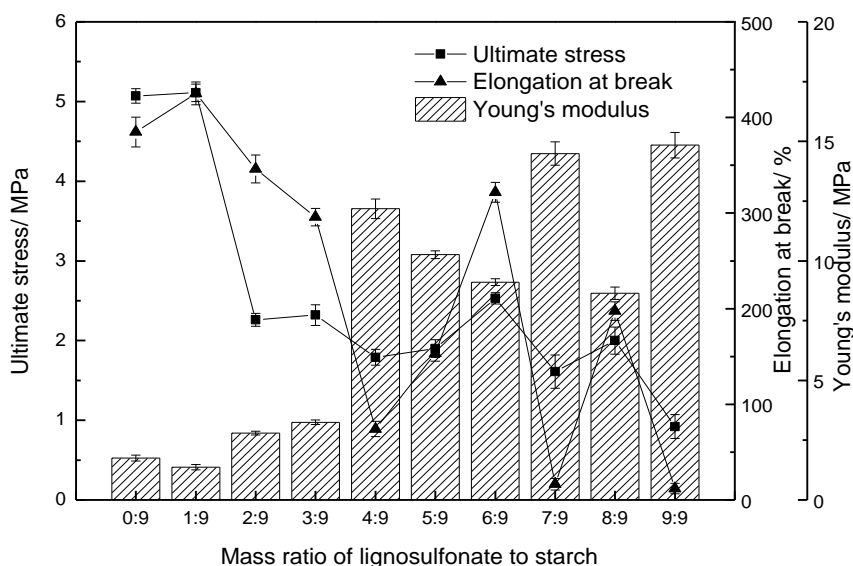


Fig. 7. Mechanical properties of films with different lignosulfonate content

The elongation at break was also found to be highly dependent on the lignosulfonate content. It showed a trend similar to that of the ultimate stress. Except for films prepared with the mass ratios of 4:9, 7:9, and 9:9, the elongation at break was higher than 100%, which implied that they had good elasticity. When the mass ratio was 9:9, the film showed a minimum elongation of 11.9%. Compared to an earlier report (Baumberger *et al.* 1997), a wider range of lignosulfonate content was tested in this study. The decrease in the mechanical properties of the blend films may be attributed to the phase separation phenomenon. Phase separation phenomenon in starch/polymer blends was noticed in many studies (Vikman *et al.* 1999; Schwach and Averous 2004; Belard *et al.* 2009). The microscopic observations revealed a heterogeneous structure in the starch/lignin blend

films (Baumberger *et al.* 1997). Furthermore the agglomeration of lignosulfonate could be another cause (Vengal and Srikumar 2005). Finally the existence of microvoids in the blend films could have been the main cause of deterioration of mechanical properties of the films.

The water absorptions of blend films made using different lignosulfonate contents are presented in Fig. 8. Increase in the lignosulfonate content did not show any regular trend of water absorption. In order to make a composite film with relatively high ultimate stress, good elasticity, and low water absorption, lignosulfonate and starch in a mass ratio of 6:9 would be preferred.

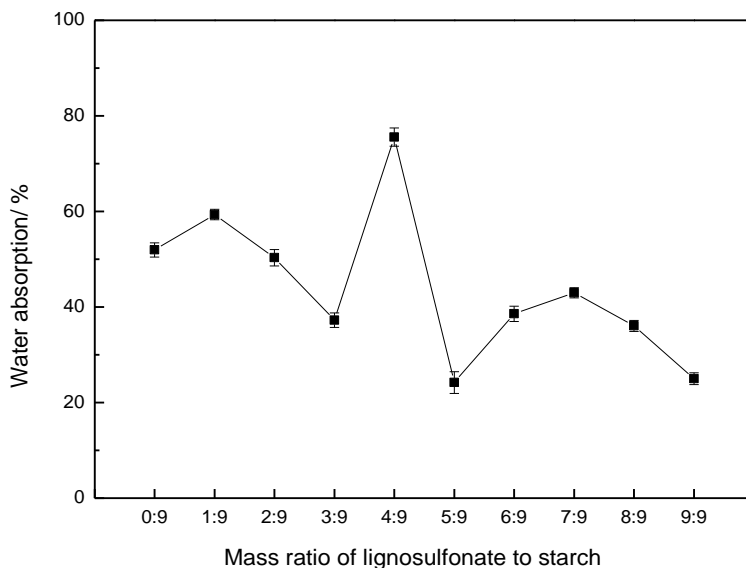


Fig. 8. Swelling behaviors of films with different lignosulfonate content

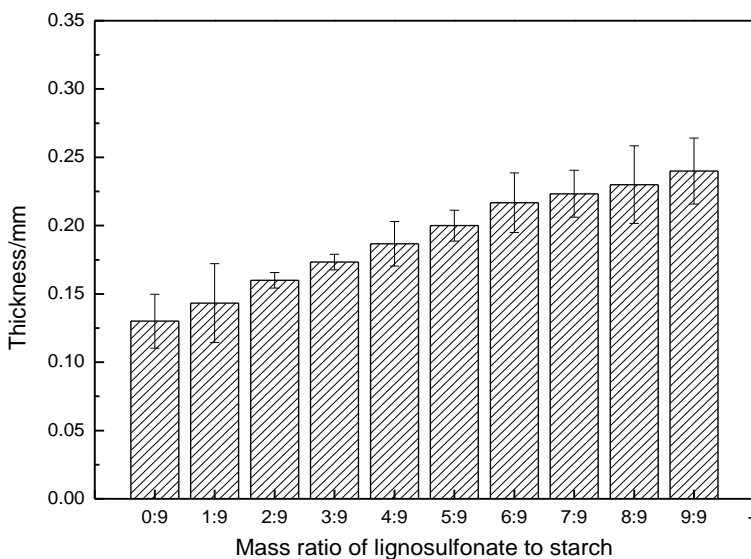


Fig. 9. Thickness of starch/lignosulfonate films with varying lignosulfonate contents

Figure 9 shows that with an increase in the lignosulfonate content of the blend films, the film thickness increased, which was similar to the effect of sorbitol on film thickness.

This could be attributed to the increase in the lignosulfonate content in the blend films on a dry weight basis.

CONCLUSIONS

1. The effect of lignosulfonate stoichiometry on the mechanical properties and hydrophobicity of starch/lignosulfonate blend films was studied. As the lignosulfonate-to-starch mass ratio was increased from 1:9 to 9:9, the hydrophobicity of films improved and the ultimate stress was reduced. With a lignosulfonate-to-starch mass ratio of 6:9, the swelling and mechanical properties of blend films were optimal, with an ultimate stress of 2.53 MPa, elongation rate of 321.76%, and water absorption of 38.57%.
2. Analyses of the films by SEM, FT-IR, and XRD showed that the compatibility between lignosulfonate, starch, and sorbitol was good and that multiple interactions between the components of the film, including hydrogen bonds and dipole-dipole forces could limit recrystallization. The TG results showed that the char residue of starch/lignosulfonate films was markedly higher than that of the starch film.
3. The upper limit of the lignosulfonate-to-starch mass ratio was 9:9. Any further addition of lignosulfonate destroyed the film-forming property of the mixture.

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