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The effect of moist heat treatment on the characteristic of starch-based composite materials coating with chitosan

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ABSTRACT

The starch-based composite material (STM) was prepared with cassava starch and modified cellulose and coated with chitosan to obtain better hydrophobic and heat-resistant properties. The hydrogen bond interactions between chitosan and basic material were proven by FTIR. By the SEM analysis, the blends showed a good compatibility and the cavities in STM was repaired and smoothed after coating. From the results of polarized optical microscope, AFM and positron annihilation lifetime spectroscopy, coating the STM with chitosan decreased the free volume of uncoated STM after moist heat treatment, the amorphous regions of the latter absorbed water more easily than the former. The mechanical properties of uncoated STM were inferior to the coated STM. Furthermore, chitosan coating decreased the gain weight and slowed the dissolution rate of starch. This study shows chitosan coating could enhance the water barrier and heat-resistant properties of STM.

1. Introduction

Biodegradable starch-based composite materials, such as starch/cellulose, starch/PVA (poly-vinyl alcohol), etc., have recently been investigated due to great potential markets in agricultural foils, garbage or composting bags, food packaging, fast food industry as well as biomedical fields (María et al., 2009; Zhai, Zhao, Fumio, & Tamikazu, 2004). Starch is renewable and biodegradable polysaccharides, which is composed of amylose and amylopectin, a linear and a branched polysaccharide chain, respectively. Starch has been used to produce biodegradable material to partially or entirely replace plastic polymers because of its low cost and renewability (Shi et al., 2007).

Since chitosan (CS) is a biodegradable polysaccharide having amine groups, much attention has been put on the utilization of CS as functionalized polysaccharides. Studies on functionalized CS blend films such as cellulose CS, PVA-CS blend film, etc., have been reported (María et al., 2009). The water resistance properties of above functionalized CS blend films could be increased by the dry heat treatment to chitosan acetate film (Garnpimol, Ritthide, Thawatchai, & Tamotsu, 2002). It is an alternative way to make composite material with starch and other hydrophilic or hydrophobic biopolymers.

However, starch-based materials have poor water resistance, poor mechanical properties and instability with moist heat treatment, which limited their wide applications. In most literatures for starch-based film, its properties can be modified by the addition of various chemicals in minor amounts. For example, plasticizers, such as glycerol and sorbitol are often used to modify the mechanical properties of the film (Rodriguez, Oses, Ziani, & Mate, 2006). Jagannath, Nanjappa, Das Gupta, and Bawa (2003) blended starch with different proteins or hydrophobic materials to decrease the water vapor permeability of the films and to increase their tensile strength. Some information is also available concerning the change of physical properties of plasticized films based on starch with storage (Fama’, Flores, Gerschenson, & Goyanes, 2006). Incorporation of these additives may, somehow, cause some positive changes in the barrier properties of the film. Still it cannot meet the standards for practical applications.

In general, the characteristic of starch-based materials is often sensitive and responsive to the changes in the environment such as humidity, temperature and so on. In this paper, an efficient and practical method is used to prepare starch-based composite materials by mixing cassava starch with modified cellulose, and coated

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with CS in order to solve the above problems especially the instability with moist heat treatment. This work is focused on the effect of moist heat treatment on the of uncoated and coated STM in terms of FTIR, morphology and mechanical properties commonly. Moreover the relationship between the properties and the microstructure of STM was studied via positron annihilation lifetime spectroscopy and the dissolution rate of starch for the first time. It provides a new, simple and quantitative method to study microstructure and water resistance of starch-based materials, which also provides an insight to its characteristic response to moist heat treatment.

2. Experimental

2.1. Materials

Starch was supplied by Guangxi Maple Leaf Starch Co. (Nanning, China). The original moisture content was 12 wt%. Chitosan was supplied by Beihai halobios Co. Ltd., (Beihai, China), with a deacetylation degree of 76% and the weight molecular weight of 1.24×10^5 Da.

2.2. Preparation of STM

Cassava, cellulose and glycerol were mixed in the molar ratio of 4:1:1.5. The mixture was sealed and stored for 24 h at room temperature. The melt blending procedure was performed in the plat vulcanizing press (Qingdao Secondly Rubber Machinery Co., Ltd., China) to prepare the basal material with the thickness of 400 μm.

CS solution of 2% (w/v) was coated on the double-sided of the basal material (10 cm × 10 cm) by a casting/solvent evaporation technique to make film with the thickness of one-side about 40 μm. The coated STM was dried in an oven at 50 °C for 2 h prior to further treatment.

2.3. Characterization of STM

FTIR spectra were obtained on a Nexus-470 FTIR spectrophotometer (Nicolet Co., USA) by the method of transmission. The samples were prepared by mixing the fine powder with KBr and pressing.

The upper surface and fracture surface morphologies of the STM were observed by Hitachi S-3400 SEM. Prior to the observation, specimen was immersed into liquid nitrogen, fractured, and then sputter coated with a thin layer of gold.

2.4. The morphology of STM

The non-coating and coated STM were exposed to moist heat saturated steam at 100 °C for 30 min and soaked in 50 °C water for 30 min. The morphology was obtained by polarized optical microscope (XPV-203E, Shanghai Changfang Optical Instrument Co., Ltd., China).

The surface morphology of the films was analyzed by atomic force microscopy (AFM) with a Nanoscope III, Multimode (Digital Instruments) with a 50 nm × 50 nm scan size and a 50 nm vertical range. Measurements were taken from several areas of the film surface using the tapping mode. The resulting data set for each sample was transformed into a 3D image. The average sample roughness was estimated with the Nanoscope 5.30r3sr3 software of the equipment.

2.5. Positron lifetime measurements

The aliquot of the samples with size of 10 mm × 10 mm × 0.6 mm were cut and each of them composed of two replicates. Positron annihilation lifetime spectroscopy (PALS) was performed by using a conventional fast–fast spectrometer. The positron source (^{22}Na) with an activity 3.7×10^5 Bq, sealed in a thin foil of Kapton, was mounted in a sample–source–sample sandwich. PALS with a time resolution of 248 ps full-width at half-maximum (FWHM) were recorded at room temperature (25 °C). Typical three-component analysis was performed using the POSITRONFIT EXTENDED software.

2.6. Mechanical properties

STM was cut into dumbbell (GB/T1040-92), and its tensile strength (TS) and reserved elongation at break (E) were measured at microelectronics testing machine (Model CMT6502, Shenzhen SANS Material Test Instrument Co., Ltd., China) with a crosshead speed 25 mm/min. TS and E tests were replicated five times for each type of film.

The samples were stored in a desiccator at 25 °C with 36% relative humidity for 48 h prior to further treatment, and then they are exposed to moist heat treatment of saturated steam at 100 °C for 30 min and then soaked in 50 °C water for 30 min. The treated STM was dried in an oven at 50 °C prior to measuring its mechanical properties.

2.7. Water sorption (WS) of STM

To determine the amount of water absorbed, STM (2.5 cm × 2.5 cm) were carefully cut, weighed (W_1) and then hang up at 100 °C hot steam. In every 10 min, excess surface water was wiped off using filter paper and the weight of the film was measured (W_2). The water sorption was calculated using the following formula: $\text{WS}(\%) = (W_2 - W_1)/W_1 \times 100\%$.

2.8. The dissolution rate of starch (Tim et al., 2007)

To determine the dissolution rate of starch of STM, STM (2.5 cm × 2.5 cm) was carefully cut, and then immersed in distilled water at 100 °C for 5 min. After cooling at room temperature, iodine reagent ($V = 0.1$ ml, 1 g iodine and 4 g potassium iodide in 100 ml water) was added to the above solution. Subsequently, the absorbance at 600 nm (A_1) was measured at 25 °C. Another piece of STM (2.5 cm × 2.5 cm) was heated in 100 °C water to dissolve completely. The solution was treated the same as above, then the absorbance was measured at the same condition (A_0). The ratio A_1/A_0 can be used as a measure for dissolution rate of starch.

3. Results and discussion

3.1. Structure and morphology characterization

FTIR spectra of CS and STM were showed in Fig. 1. Before coating, the broad band at 3410 cm^{-1} ascribed to the stretching vibration of the –OH group of starch. The band at 1645 cm^{-1} was ascribed to the δ (O–H) bending of water in starch (Xu, Kim, Hanna, & Nag, 2005). When two or more substances are mixed, the physical blends versus chemical interactions are reflected by changes in characteristic adsorption peaks. After CS coating, the broad band at 3410 cm^{-1} of the –OH stretching in basal material shifted to 3432 cm^{-1}, which overlaps the –NH$_2$ stretching of CS coating in the same region. The bands at 1645 cm^{-1} of the δ (O–H) bending of water in basal material shifted to 1637 cm^{-1}. Lower peak wave number means stronger interactions (Pawlak & Mucha, 2003). This result indicated that interactions were present between the hydroxyl groups of starch and the amino groups of CS (Aoi, Takasu, Tsuchiya, & Okada, 1998). It also shows a certain degree of miscibility between the starch in the basal film and the coating CS.

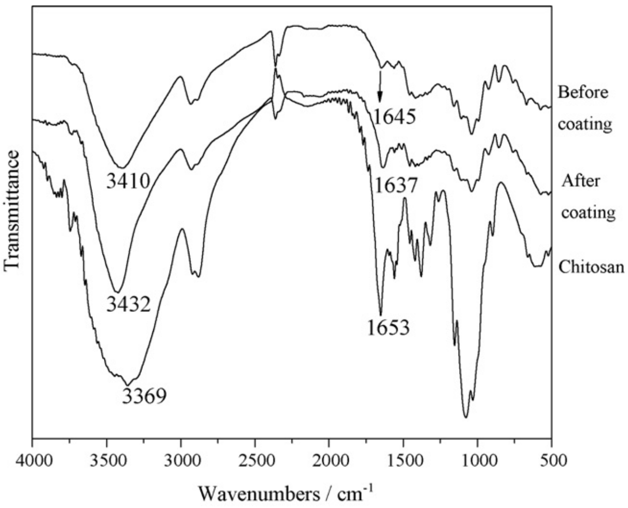

Fig. 1. The IR spectra of CS and STM (before and after coating with CS).

Fig. 2 shows the images of the upper surfaces and the fracture surfaces of starch-based composite film before and after coating. The upper surface of the film with CS coating was very smooth, which was significantly different from the materials without CS coating; obviously, it was due to the coating of CS, which is distributed uniformly on the upper surface. Furthermore, the fracture surface of starch-based composite material before and after coating was similar. It was found that the incorporation of starch and cellulose into the material resulted in a significant change of fracture morphologies. Their cross-sections were rough and some discontinuousness was observed. These surface differences are expected to have great influence on the mechanical properties of the materials.

3.2. Effect of moist heat treatment on the morphology

Both untreated and treated composite materials are shown in Fig. 3. It was obvious that the materials without coating were swelled, softened and eventually dissolved a little when they were steamed or soaked in hot water. It was due to that water was adsorbed on starch by hydrogen bonding with the hydroxyl groups on the starch chains when the material was treated by hot water or steam (Mali, Sakanaka, Yamashita, & Grossmann, 2005). After coating the materials spent slightly longer time to swell when they were treated under the same condition. It meant that CS coating could enhance the water barrier and heat-resistant properties of starch-based composite material.

Fig. 4 shows detailed information of the surface morphology of the CS coating. It was obvious that untreated coating had smooth

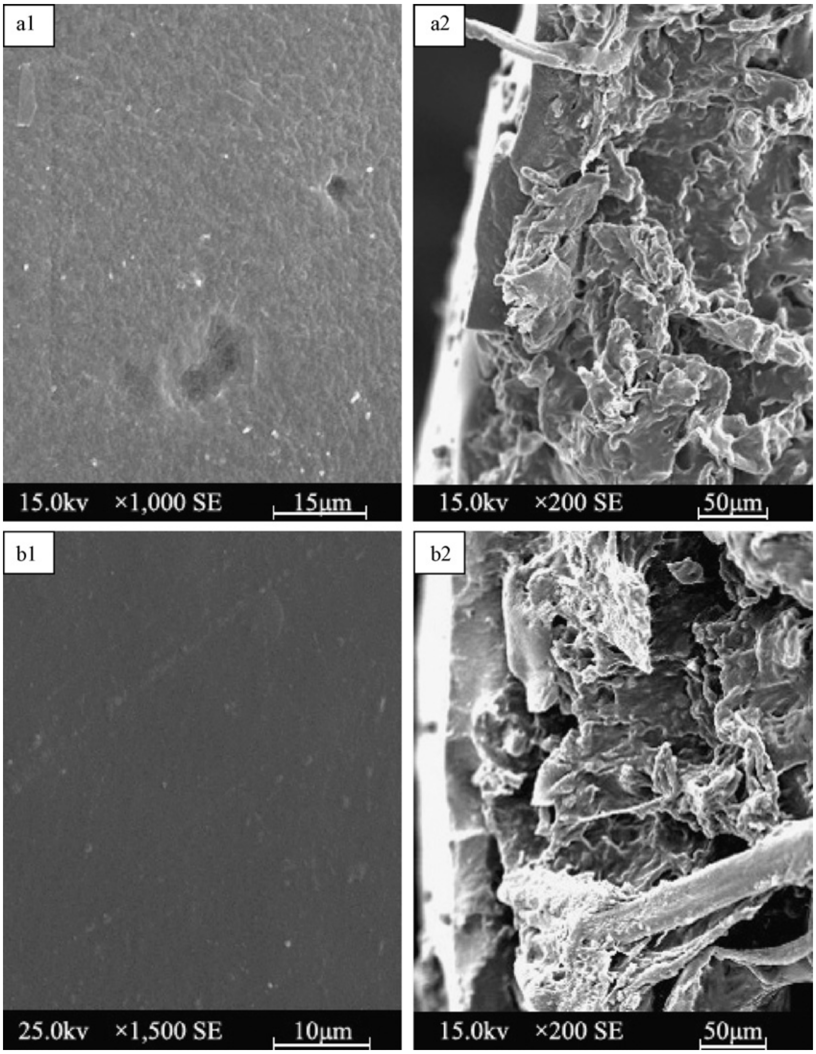

Fig. 2. SEM images of STM before (a1 and a2) and after (b1 and b2) coating with CS: (a1 and b1) upper surface and (a2 and b2) fracture surface.

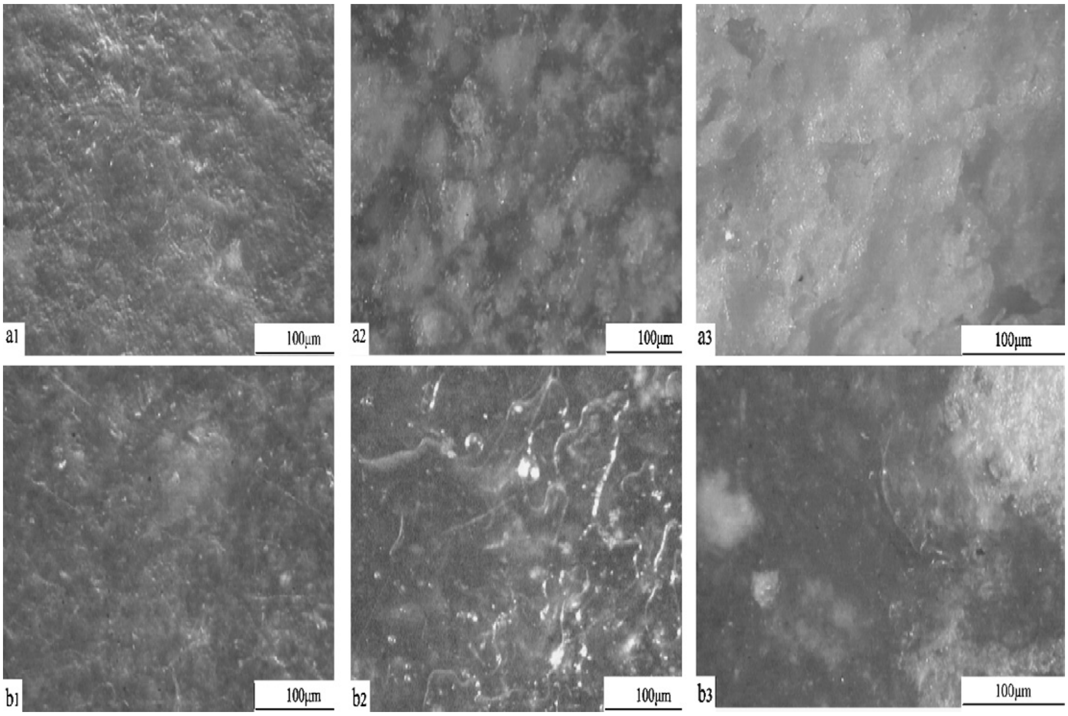

Fig. 3. Optical micrographs of STM before and after moist heat treatment: (a1 and b1) no treatment; (a2 and b2) hot water vapor; (a3 and b3) soak in hot water.

surface and CS molecular chain arranged in order and closely packed. After treated by moisture heat vapor of 100 °C hot steam, the coating had accidented surface but the coating still retain in its integrity. The mean roughness (Ra) is the arithmetic average of the deviations from the center plane. From the results of roughness analysis, Ra of untreated CS film was 7.078 nm while Ra of treated CS film was 23.017 nm. The work of Joseph, Jedediah, and John (2004) pointed out the fact that the permeability is highly affected by how closely the polymer chains are packed. There is a positive correlation between water vapor permeability and roughness (Parris, Coffin, Joubran, & Pessen, 1995). The higher roughness resulted in the higher water vapor permeability.

From the results of AFM, before treated with 100 °C hot steam CS molecular chain had arranged in order and closely packed like a barrier to prevent the passage of water and heat from surrounding into STM. Furthermore untreated STM had lower water vapor permeability because it had lower Ra. More water vapor could steam more heat at the same time and same area of the film (Thomas, Fre'de'ric, & Andre'e, 2007). So untreated CS film could prevent the transfer of water and heat because it was much more uniform and compact molecular chains and lower Ra. By contraries, after treated with 100 °C hot steam CS molecular chain had arranged out of order and the surface was accidented with higher Ra, which meant treated STM would facilitate to the transport of water. The coating was corroded which induced water vapor permeated through the basal material. The water molecular infiltrated through amorphous area of the film. CS molecular chain had twisted one another by a strong hydrogen bonding interaction between CS and water. As a result, water molecular permeated through treated STM more easily. Namely, the hydrophobic and heat-resistant ability of treated STM became weakly.

3.3. PALS analysis

All PALS were resolved into three components using POSITRONFIT EXTENDED software. The first lifetime (τ_1), intensity (I_1)

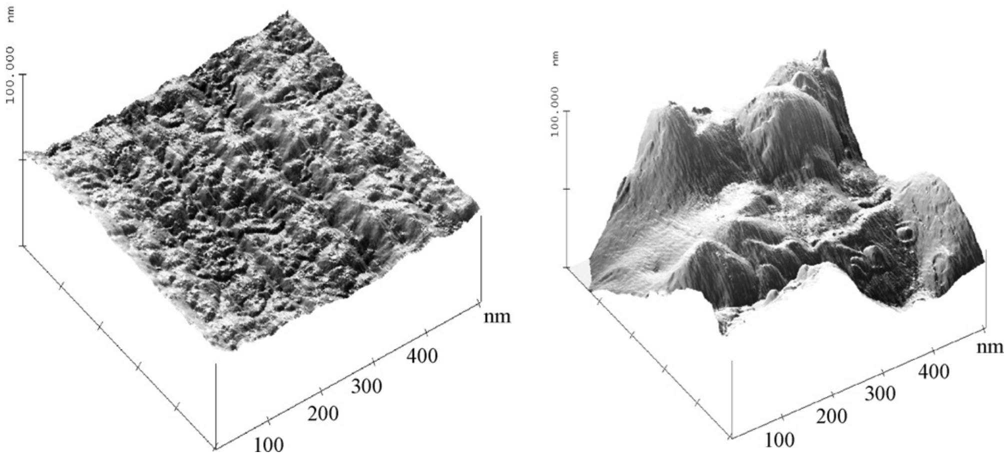

Fig. 4. AFM topographic images (data scale 50 nm) of CS coating of untreated (A) and treated (B) by hot water vapor.

Table 1
Positron annihilation lifetime of STM.

Sample	τ_1/ps	τ_2/ps	τ_3/ps	I_1/%	I_2/%	I_3/%	τ_m/ps
1#	185 ± 2	408 ± 16	1562 ± 29	28.3	51.8	19.8	583.18
2#	189 ± 2	418 ± 15	1686 ± 32	30.4	50.3	19.3	593.63
3#	203 ± 3	449 ± 19	1781 ± 42	35.4	46.3	18.3	605.73
4#	205 ± 3	447 ± 20	1646 ± 41	35.5	48.2	17.3	568.18
5#	199 ± 2	417 ± 18	1614 ± 32	31.7	49.3	19.0	575.42
6#	194 ± 2	417 ± 17	1659 ± 33	30.3	51.0	18.6	580.39

1#, 2# and 3#: starch-based composite material without coating CS; 4#, 5# and6#: starch-based composite material with coating CS; 1# and 4#: no treatment; 2# and 5#: moisture heat treatment; 3# and 6#: soak in hot water.

and the second lifetime (τ_2), intensity (I_2) were attributed to the self-annihilation of para-positronium (p-Ps) and the positron annihilation, respectively. The third lifetime (τ_3), intensity (I_3) results from the pick-off annihilation of o-Ps in the free volume holes. τ_m stand for the average positron lifetime ($\tau_m/\text{ps} = \tau_1 \times I_1 + \tau_2 \times I_2 + \tau_3 \times I_3$). The relationship between the o-Ps lifetime and the radius of the free volume hole R has been established by an empirical equation (Wang et al., 2009) as follows:

$$\tau_3 = \frac{1}{2}\left(1 - \frac{R}{R_0} + \frac{1}{2\pi}\sin 2\pi\frac{R}{R_0}\right)^{-1}$$

where $R = R_0 + \Delta R$ and ($\Delta R = 0.166$ nm) are the fitted empirical electron layer thickness. According to the equation, τ_3 is correlated with the size of the free volume holes. The lifetime is sensitive to the size of the trap: the large the trap, the longer the lifetime (Zs Kajcsos et al., 2009). It was obvious in Table 1 that the value of the o-Ps lifetime τ_3 of STM before coating CS increased with the moist heat treatment of 100 °C hot steam and soaked in 50 °C water. After socked in 50 °C water, the positron annihilation lifetime (τ_3) of non-coating STM had increased 219 ps, but the τ_3 of STM after coating with the same treatment just increased 13 ps. The results indicated that the bigger the free volume, the higher the content of the water absorption and the diffusion coefficient (Wang et al., 2009). Namely the amorphous regions of non-coating STM were easily water swelling and formed loose white spots. The CS coating could enhance its water resistance and stability with moist heat treatment. It was agreed with the results of optical micrographs.

Table 1 shows that the intensity I_3 of different treatment had no significant change. It might be explained as follows: the STM had the larger intermolecular-space holes, even after water molecules permeated into the hole, there was still enough space for o-Ps annihilation, therefore, and the entering water had little effect on the number of the free volume holes (Mohamed & Hamdy, 2003). This meant that the effect of water on the microstructure of STM was mainly related to the size of free volume rather than the numbers of the free volume.

3.4. *Effect of moist heat treatment on the mechanic property*

The change of mechanical properties of STM before and after coating CS with different treatment and relative humidity (R_H) were shown in Fig. 5. It was found that TS values of STM with coating increased from 3.48 to 6.77 MPa. No matter which type treatment was used, the TS values of STM with coating CS were higher than that without coating. It meant that CS coating could enhance the mechanical intensity, which agreed with the results of optical micrographs and PALS.

E-Values of starch-based composite material after coating CS with different treatment were changed slightly. But before coating *E*-values had changed a lot especially when it was soaked in 50 °C water.

With the decrease of R_H, the TS increased. After coating with CS, STM had better TS than that before coating in any cases with different R_H. It meant that CS coating was a barrier of moisture. With the increase of relative humidity, *E*-values of starch-based composite material were increased.

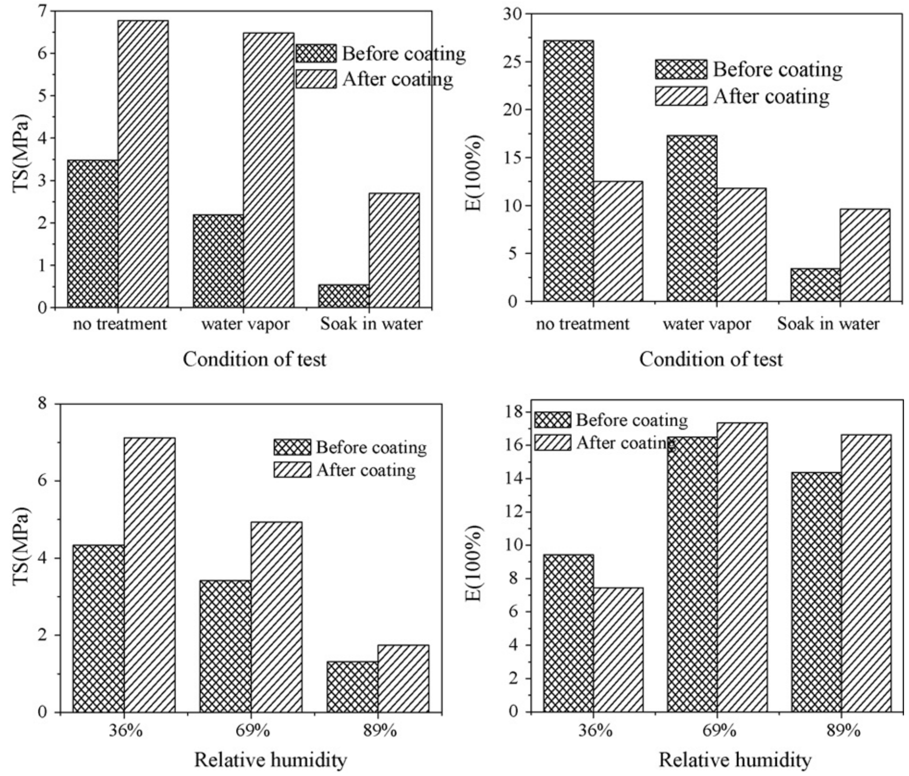

Fig. 5. The change of mechanical properties of STM.

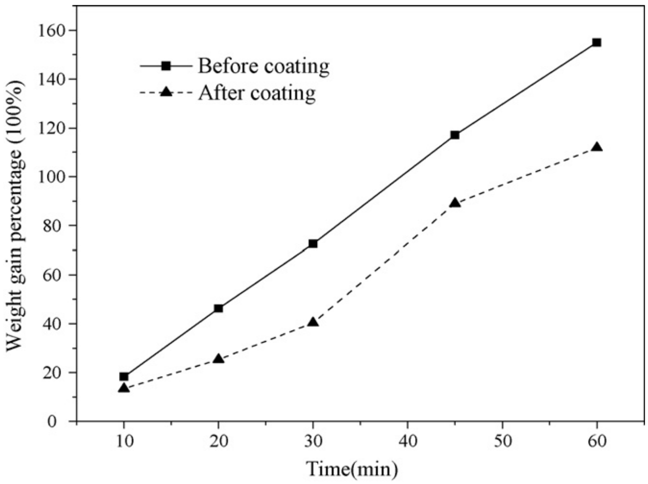

Fig. 6. The effect of heat moisture treatment on weight gain of STM.

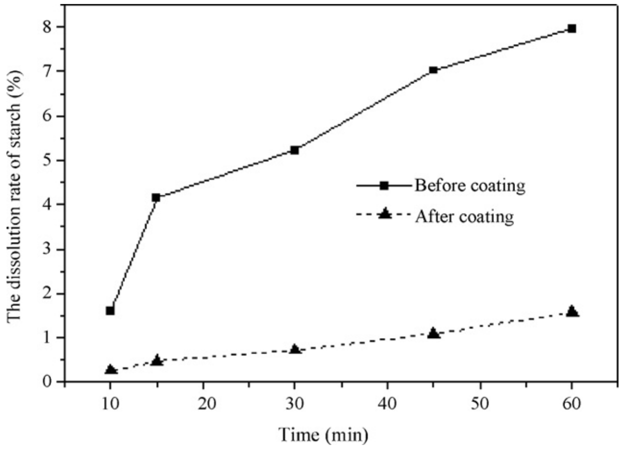

Fig. 7. The dissolution rate of starch after STM soaked in hot water.

3.5. The water resistant property

Fig. 6 shows that the weight gain of STM decreased from 72.5% to 40.3% after coating CS treated in high temperature steam (100 °C) for 30 min. As the weight gain of STM was decreased the water absorption capacity of STM was also decreased. It meant that the hydrophobic and heat-resistant property of STM was increased. It was obvious that the weight gain of STM with coating was lower than that without coating. It meant that CS could prevent STM from absorbing water.

Fig. 7 shows that the dissolution rate of starch of STM without coating increased to 4.15% rapidly especially in the first 15 min. After soaking in water for 30 min, the dissolution rate of starch of STM without coating was 5.22% while the coated one was 0.73% only. The dissolution rate of starch of STM with coating increased relatively slowly and lowered than that of without coating. When STM was soaked in water, water molecular permeated through the material and interacted to starch molecular. The interaction of starch molecular was weak and starch was dissolved. As a result we could see some holes on the surface of optical micrographs of STM. After coating CS could effectively prevent the dissolution of starch because CS molecular chain had arranged in order and formed a compact film.

4. Conclusion

The starch-based composite materials coating with CS were successfully prepared. The mechanical properties of STM were largely improved after CS coating. After coating with CS, STM had better properties of the water barrier and heat-resistant, indicating CS coating had modified the characteristic of STM effectively. FTIR analyses of STM indicated that the hydrogen bond interaction between CS and basic material exists in STM. By the SEM analysis, the blends had a good compatibility and the cavities in STM was repaired and smoothed after coating In addition, the change of STM properties were related to the change of microstructure and morphology of STM during moist heat treatment. The effect of water on the microstructure of STM was mainly related to the size of free volume rather than the numbers of the free volume. So STM could sustain after moist heat environment. Such biodegradable, hydrophobic and heat-resistant starch-based material can be an alternative to some macromolecule polymers and will have substantial applications in moist heat environment.

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References

Aoi, K., Takasu, A., Tsuchiya, M., & Okada, M. (1998). New chitin-based polymer hybrids. 3. Miscibility of chintin-graft-poly(2-ethyl-2-oxazoline) with poly(vinyl alcohol). *Macromolecular Chemistry and Physics*, *199*, 2805–2811.

Fama', L., Flores, S., Gerschenson, L., & Goyanes, S. (2006). Physical characterization of cassava starch biofilms with special reference to dynamic mechanical properties at low temperatures. *Carbohydrate Polymers*, *66*, 8–15.

Garnpimol, C., Ritthide, J., Thawatchai, P., & Tamotsu, K. (2002). Moist heat treatment on physicochemical change of chitosan salt films. *International Journal of Pharmaceutics*, *232*, 11–22.

Jagannath, J. H., Nanjappa, C., Das Gupta, D. K., & Bawa, A. S. (2003). Mechanical and barrier properties of edible starch–protein-based films. *Journal Applied Polymer Science*, *88*, 64–71.

Joseph, S. G., Jedediah, O. W., & John, D. L. (2004). Permeability and durability effects of cellulose polymer variation in polymer inclusion membranes. *Journal of Membrane Science*, *229*, 87–93.

Mali, S., Sakanaka, L. S., Yamashita, F., & Grossmann, M. V. E. (2005). Water sorption and mechanical properties of cassava starch films and their relation to plasticizing effect. *Carbohydrate Polymers*, *60*, 283–289.

María, B., Vásconez, Silvia, K., Flores, Carmen, A., Campos, et al. (2009). Antimicrobial activity and physical properties of chitosan–tapioca starch based edible films and coatings. *Food Research International*, *42*, 762–769.

Mohamed, & Hamdy, F. M. (2003). Study of the effect of electric field on positron annihilation parameters in polymers. *Radiation Physics and Chemistry*, *68*, 449.

Parris, N., Coffin, D. R., Joubran, R. F., & Pessen, H. (1995). Composition factors affecting the water vapor permeability and tensile properties of hydrophilic films. *Journal of Agricultural and Food Chemistry*, *43*, 1432–1435.

Pawlak, A., & Mucha, M. (2003). Thermogravimetric and FTIR studies of chitosan blends. *Thermochimica Acta*, *396*, 153–166.

Rodriguez, M., Oses, J., Ziani, K., & Mate, J. I. (2006). Combined effect of plasticizers and surfactants on the physical properties of starch based edible films. *Food Research International*, *39*, 840–846.

Shi, R., Zhang, Z. Z., Liu, Q. Y., Han, Y. M., Zhang, L. Q., Chen, D. F., et al. (2007). Characterization of citric acid/glycerol co-plasticized thermoplastic starch prepared by melts blending. *Carbohydrate Polymers*, *69*, 748–755.

Thomas, K., Fre'de'ric, D., & Andre'e, V. (2007). Influence of thermal process on structure and functional properties of emulsion-based edible films. *Food Hydrocolloids*, *21*, 879–888.

Tim, B., Ikenna, S., Ngene, Jeroen, J. G., Van, S., Anja, E. M., et al. (2007). Comparison of methods to determine the degree of gelatinisation for both high and low starch concentrations. *Carbohydrate Polymers*, *67*, 481–490.

Wang, J. J., Wang, B., Zhou, W., Gong, J., Gong, Z. L., & Yue, S. J. (2009). Investigation of free volume in epoxy resins studied by PALS. *Material Science Forum*, *607*, 82–84 (Switzerland).

Xu, Y. X., Kim, K. M., Hanna, M. A., & Nag, D. (2005). Chitosan–starch composite film: Preparation and characterization. *Industrial Crops and Products*, *21*, 185–192.

Zhai, M. L., Zhao, L., Fumio, Y., & Tamikazu, K. (2004). Study on antibacterial starch/CS blend film formed under the action of irradiation. *Carbohydrate Polymers*, *57*, 83–88.

Zs Kajcsos, C., Kosanovic, S., Bosnar, B., Subotic, P., Major, L., Liszkay, D., et al. (2009). Monitoring the crystallization stages of silicate by positron lifetime spectroscopy. *Material Science Forum*, *607*, 173–176 (Switzerland).