Front. Agric. China 2011, 5(4): 649–654
DOI 10.1007/s11703-011-1143-x

RESEARCH ARTICLE

Study on filming of oxidized starch/PVA

Zhizhou CHEN (✉), Lin ZHANG, Lin WANG

College of Food Science and Technology, Agricultural University of Hebei; Hebei Agricultural Products Processing Engineering Technology Research Center, Baoding 071001, China

Abstract **In this study, oxidized starch was taken as raw material to prepare filming. Single factor and orthogonal experiments were conducted to investigate its properties. The results showed that the different concentrations of oxidized starch, glycerol, polyvinyl alcohol (PVA) and glutaraldehyde had significant effects on the properties of the oxidized starch/PVA films, among which the most important factor was glycerol, followed by the oxidized starch, PVA and glutaraldehyde. The optimum film-forming conditions were 6.0% oxidized starch, 6.0% PVA, 2.5% glycerol and 0.6% glutaraldehyde.**

Keywords oxidized starch, filming, optimization of processing parameters

Introduction

With the rapid development of modern industrial technology, environmental pollution has drawn increasing attentions worldwide (Judy, 2000). Plastic products from petrochemicals are widely used in packaging, automobile, healthcare application, communication and electronic industries (Song and Wang, 2001; Zhang et al., 2002). As these conventional synthetic polymers are not easily degraded due to their high molecular mass and hydrophobic characteristics, they can accumulate in the environment and become a significant source of environmental pollution. Therefore, finding biodegradable materials has occupied an important position in the field of degradable materials in recent years (Qao, 2002; Wang et al., 2004).

Oxidized starch is a product of starch reaction with oxidants in acid, alkaline or neutral media (Wang and Wang, 2003). Starch is usually obtained from potato, cassava, sweet potato and corn, etc. (Funke et al., 1998; Luis, 2001). Compared to the native starch, the oxidized starch shows high solubility, but low viscosity and expansion of performances. Therefore, the good transparency and permeability lead to the good ability to form a film (Miladinov and Hanna, 2001).

The present study can provide a technical support for the industrialization of the processing technology of oxidized starch films.

Received June 9, 2011; accepted August 30, 2011
Correspondence: Zhizhou CHEN
E-mail: chenzhizhou2003@yahoo.com

Materials and methods

The materials used in this study were oxidized starch, polyvinyl alcohol (PVA), glycerol and glutaraldehyde (50%).

The process of preparing oxidized starch film was as follows: PVA dissolved → PVA filtered → PVA mixed with oxidized starch → gelatinized in water bath for 5 min → pH controlled to 6 → crosslinking adopted for 25 min (Water bath temperature at 100°C) → defoamered with vacuum pump → coated on the glass board → dried in drying oven at 70–90°C → the oxidized starch film uncovered→ stored at room temperature for 24 h → balanced at the dryer for 24 h → film properties tested.

In the preliminary experiment, the test samples were prepared into slivers of 100 mm×15 mm. And then the tensile strength and breaking elongation of the samples were tested by tensile strength determinator at the drawing speed of 400 mm/s, while the maximum tension and length of the film were recorded when the film was broken. The tensile strength was calculated with formulas $TS=F\times10^{-6}/S$, where TS, F and S are the tensile strength of the sample, the maximum tension of the film when it was broken and the cross-sectional area of the sample respectively. The breaking elongation was calculated by $E=(L_1-L_0)/L_0\times100\%$, in which E, L_0 and L_1 are respectively the breaking elongation, the length of the film and the length of the film when it fractured.

The film samples were cut into rectangles and affixed to cuvette surface, then tested by UV-Vis spectrophotometer at the transmission rate of 600 nm, with an empty cuvette used as the control. The value of light transmission was used as film transparency indirectly.

Another piece of sample was cut into squares of 100 mm×100 mm, with its weight measured twice respectively after drying at 100°C for 1 hour and after 12 hours of soaking in 300 mL aqua water following the drying step. The above two weights were then used in the calculation of water absorption rate.

Results and discussion

Effects of oxidized starch concentration on properties of the film

The results showed that oxidized starch was more soluble than native starch in water, and the effects on film properties of oxidized starch concentrations are shown in Figs. 1–3. It can be obtained from those charts that it was hard to remove film when the concentration was higher than 8.0%, while on the other hand, when it was less than 4.5%, the film was thin and had low mechanical strength.

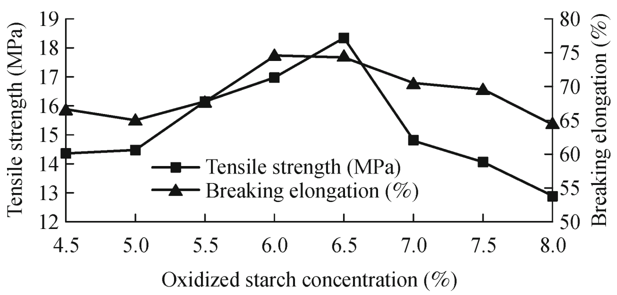

Figure 1 Effects of different oxidized starch concentrations on tensile strength and breaking elongation.

With the increase of oxidized starch concentration, the tensile strength and breaking elongation rate increased initially, however, when the concentration was 6.5%, the two mentioned parameters of the film reached maximum, and then began to decrease with the further increase. The reason might be that the amount of crosslinking agent and the plasticizer were insufficient, while the oxidized starch granules might upset this balance of the rigid mesh structure (Fig. 1).

As shown in Fig. 2, with the increase of oxidized starch concentration, the light transmission rate of the film showed an increasing trend at the beginning and then reduced. When oxidized starch concentration was between 4.5% and 6.5%, the transparency rose along with the concentration elevation, nevertheless, when oxidized starch concentration was higher than 6.5%, the oxidized starch was too much to dissolve,

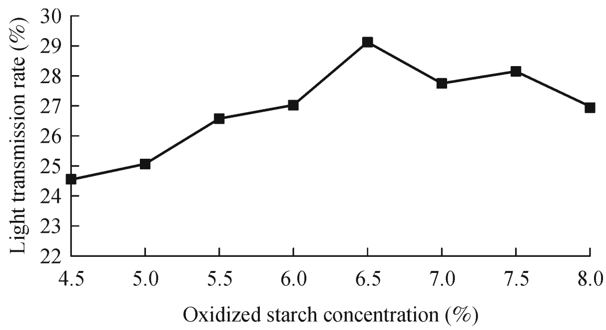

Figure 2 Effects of different oxidized starch concentrations on light transmission rate.

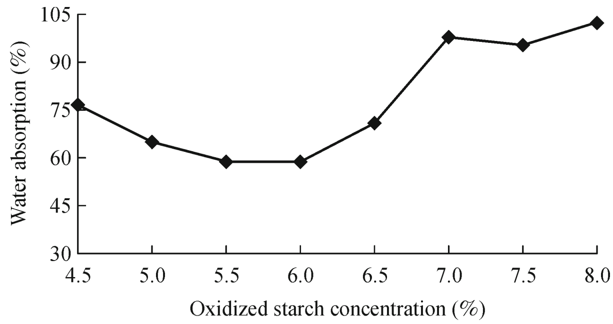

Figure 3 Effects of different oxidized starch concentrations on water absorption.

leading to lower transparency.

Contrarily, with the increase of oxidized starch concentration, the water absorption of the film showed a reducing trend originally and increased later, and the lowest water absorption appeared when oxidized starch concentration was 6.0% (Fig. 3).

The oxidized starch concentration was optimized to 6.5% by comprehensive consideration of the above 3 factors.

Effects of polyvinyl alcohol (PVA) concentration on properties of the film

The effects of PVA concentration on properties of the film are shown in Figs. 4–6. Results showed that the amount of PVA had significant effects on mechanical properties of the film. Accompanied by the action of the crosslinking agent, PVA and oxidized starch could form a rigid mesh structure, and the mechanical properties of the thin films were enhanced. Another test found out that when PVA concentration was less than 2.5%, it would be difficult to uncover the corn starch film.

When the PVA concentration increased, the tensile strength rate elevated consistently within the tested amount, though the breaking elongation rate went up at first and declined subsequently, with its peak appearing at the PVA concentration of 5.5% (Fig. 4).

According to Fig. 5, the light transmission rate of the film tended to ascend initially yet descended at a later time, along

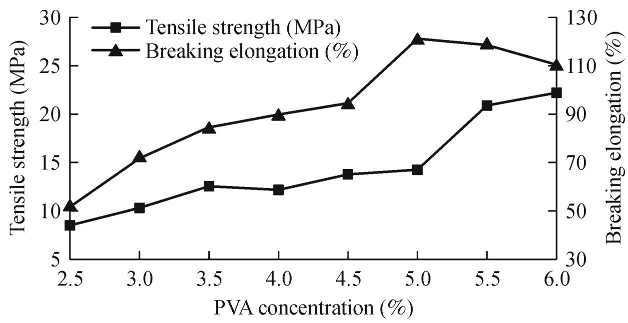

Figure 4 Effects of different polyvinyl alcohol concentrations on tensile strength and breaking elongation.

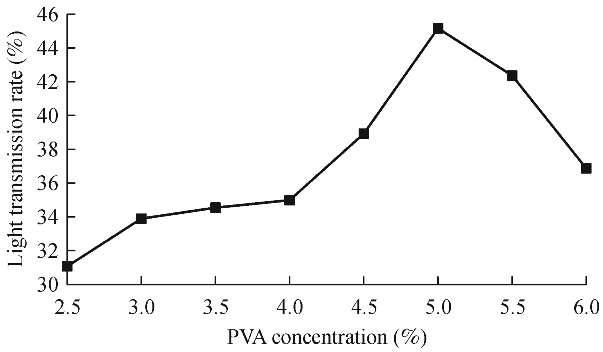

Figure 5 Effects of different polyvinyl alcohol concentrations on light transmission rate.

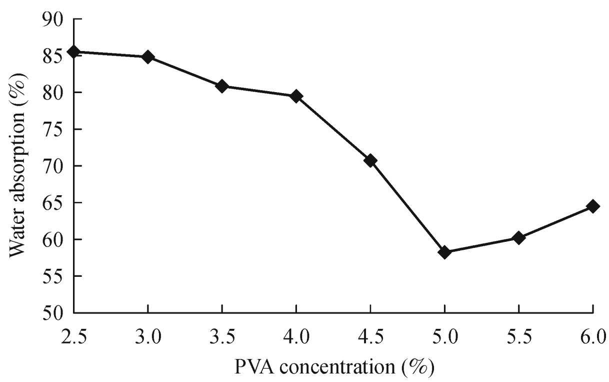

Figure 6 Effects of different polyvinyl alcohol concentration on water absorption.

with the increase of PVA concentration, and the highest transmission rate was reached when the PVA concentration was 5.0%.

At the same time, Fig. 6 indicated that, with the increase of PVA concentration, the water absorption of the film showed a reducing trend at the beginning, with a bottom appearing at the PVA concentration of 5.0%, however, it began to rise after that.

As a conclusion, the optimum PVA concentration was 5.5% based on comprehensive consideration of the mentioned results.

Effects of glycerol concentration on properties of the film

Figs. 7–9 demonstrate a trend of glycerol concentration effect on properties of the film.

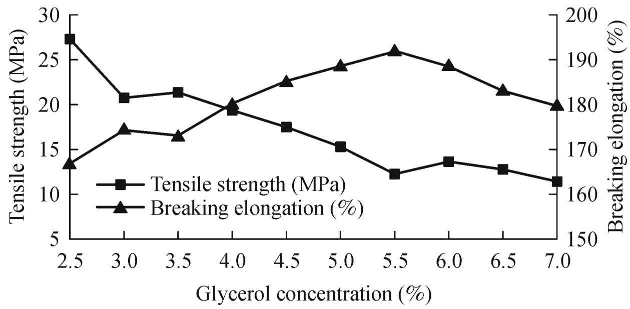

Figure 7 Effects of different glycerol concentrations on tensile strength and breaking elongation.

As shown in Fig. 7, when the glycerol concentration rose, the tensile strength rate decreased while the breaking elongation rate increased originally, but began to decline when glycerol concentration was more than 5.5%, due to the glycerol's small molecular weight. It was proved that low molecular weight of glycerol would make molecular move so easily as to penetrate into the macromolecular chains of oxidized starch and destroy the force between oxidized starch granules, then the tensile strength was decreased. On the other hand, too high glycerol content would make the interaction between molecules replaced by the interaction between glycerol with small molecule and the starch molecule, resulting in frailty of the primal interaction and decline of the breaking elongation.

Furthermore, the light transmission rate of the film fell on the whole with the elevation of glycerol concentration. Certain amount of plasticizer was supposed to reduce the glass transition temperature of the film, avoid cracks or holes in the film, and enhance its transparency. Nevertheless, too high amount of plasticizer could cause the macromolecules to form a dense network structure, consequently the light transmission rate would reduce (Fig. 8).

Besides, it can be seen in Fig.9 that, for higher than 5.5%

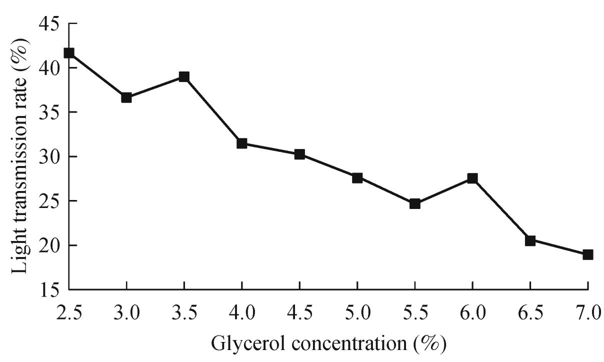

Figure 8 Effects of different glycerol concentration on light transmission rate.

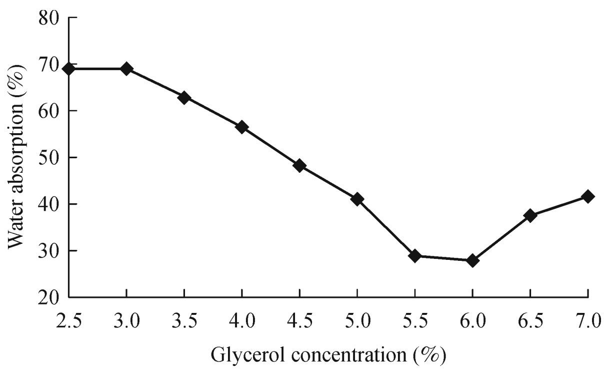

Figure 9 Effects of different glycerol concentration on water absorption.

glycerol concentration, the water absorption advanced, because glycerol is available to penetrate into the starch molecules, promote the oxidized starch and PVA mode in hydrogen to form a dense network structure and cause the gaps between molecules to shrink, resulting in the reduction of the water absorption.

To sum up, the optimum glycerol concentration was 2.5% by comprehensive consideration of the above 3 parameters.

Effects of glutaraldehyde concentration on properties of the film

The following three charts (Figs. 10–12) illustrate the effects of glutaraldehyde concentration on properties of the film.

According to Fig. 10, when glutaraldehyde was used as a crosslinking agent, the tensile strength and breaking elongation increased rapidly accompanied by the increase of the glutaraldehyde concentration(within the upper limitation of 0.55%). When at the 0.55% glutaraldehyde concentration, the tensile strength approached to the top, moreover, it tended to be stable when beyond 0.55%. As the increase of crosslinking agent could improve the crosslinking degree of the oxidized starch/PVA, the crosslinking copolymerization of intermolecular forces could be enhanced, as well as the tensile strength of the film improved. Meanwhile, the interaction force in the oxidized starch/PVA between the two phases increased gradually with the increase in crosslinking degree, and the toughness of the film and the breaking elongation rate were improved. However, a certain amount of crosslinking agent would make the intermolecular slide difficult due to the formation of molecular network structure, leading to reduction of breaking elongation rate.

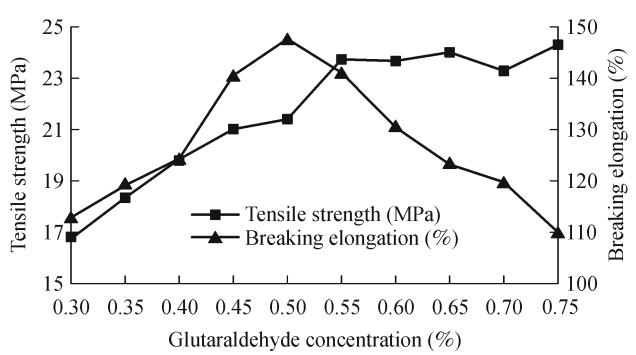

Figure 10 Effects of different glutaraldehyde concentrations on tensile strength and breaking elongation.

Additionally, the light transmission rate of the film was not gained significantly during the increase of glutaraldehyde concentration (Fig. 11) until the glutaraldehyde concentration reached to 0.6% since the increasing speed of light transmission rate of film tended to be slow. The reason was that the compatibility of the blend could be improved when the glutaraldehyde concentration ascended, which led to the increase of the light transmission rate of the film.

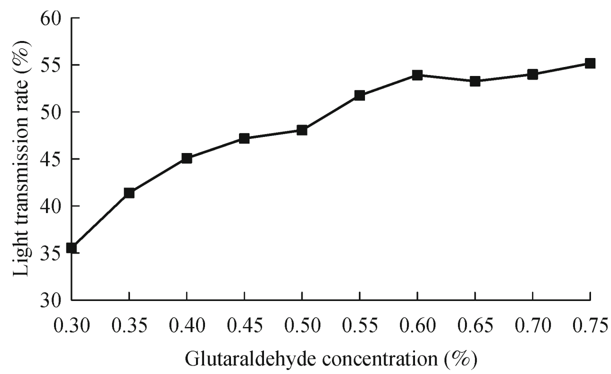

Figure 11 Effects of different glutaraldehyde concentrations on light transmission rate.

In the meantime, the water absorption dropped with the rising of the glutaraldehyde concentration. When the glutaraldehyde concentration was higher than 0.5%, the reduction of the water absorption was not significant. Added by the amount of glutaraldehyde, oxidized starch and PVA crossed with each other through hydrogen would be tightly bonded, shielding the hydroxyl and carboxyl groups, therefore, the water absorption declined. Furthermore, when the blend system formed a good compatibility and then increased

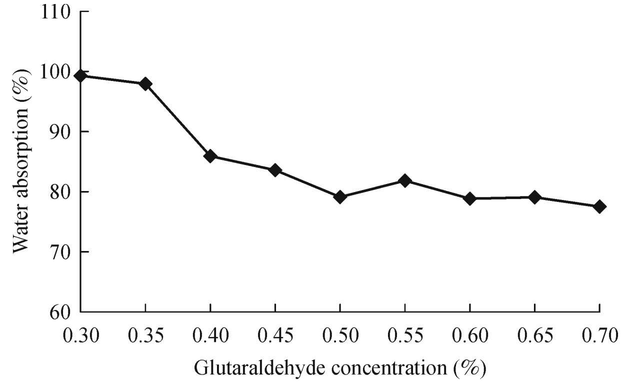

Figure 12 Effects of different glutaraldehyde concentration on water absorption.

Table 1 Result and analysis of the filming orthogonal experiments

Experimental number	Factors				Comprehensive evaluation
	Oxidized starch A (%)	PVA B (%)	Glycerol C (%)	Glutaraldehyde D (%)	
1	1(6.0)	1(5.0)	1(2.5)	1(0.5)	60.80
2	1	2(5.5)	2(3.0)	2(0.55)	64.10
3	1	3(6.0)	3(3.5)	3(0.6)	64.88
4	2(6.5)	1	2	3	46.62
5	2	2	3	1	38.21
6	2	3	1	2	67.57
7	3(7.0)	1	3	2	33.80
8	3	2	1	3	61.75
9	3	3	2	1	44.14
T1	189.78	141.22	190.12	143.15	–
T2	152.40	164.06	154.86	165.47	–
T3	139.69	176.59	136.89	173.25	–
R2	63.26	47.07	63.37	47.72	–
R2	50.80	54.69	51.62	55.16	–
R3	46.56	58.86	45.63	57.75	–
M	16.70	11.79	17.74	10.03	–

Table 2 Test results of the filming parallel experiments

Combination	Tensile strength (MPa)	Elongation rate (%)	Light transmission rate (%)	Water absorption (%)	Comprehensive evaluation
$A_1B_3C_1D_3$	25.36	160.08%	55.45	62.78%	71.56
$A_2B_3C_1D_2$	24.84	158.00%	55.15	72.91%	67.57

the concentration of glutaraldehyde, the change the water absorption of the film was insignificant (Fig. 12).

With comprehensive consideration of above results, the glutaraldehyde concentration was optimized to 0.55%.

Orthogonal experiment

The single factor experiments showed that oxidized starch concentration, glycerol concentration, polyvinyl alcohol (PVA) concentration and glutaraldehyde concentration all affect the filming. Based on these results, a $L_9(3^4)$ orthogonal experiment was conducted to optimize the filming condition, and its results are presented in Table1.

According to Table 1, statistical analysis revealed that the optimum condition consists of A_1 B_3 C_1 and D_3, with 6.0% oxidized starch, 6.0% PVA, 2.5% glycerol and 0.6% glutaraldehyde of film-forming., respectively, of which the most important factor affecting the properties of the film was the glycerol concentration, followed by the oxidized starch, the PVA concentration and the glutaraldehyde concentration.

Verification of the best condition

The experiments were conducted to compare A_1 B_3 C_1 and D_3 (6.0% oxidized starch, 6.0% PVA, 2.5% glycerol, 0.6% glutaraldehyde) and the best evaluated orthogonal experimental condition was the combination of $A_2B_3C_1D_2$ (6.5% oxidized starch, 6.0% PVA, 2.5% glycerol, 0.55% glutaraldehyde), which are consistent with the results from Table 2.

Conclusion

According to the study, different concentrations of oxidized starch, glycerol, polyvinyl alcohol (PVA) and glutaraldehyde had significant effects on the properties of the oxidized starch/PVA films, among which the most important factor was glycerol, followed by the oxidized starch, PVA and glutaraldehyde, respectively. The optimum film-forming conditions were 6.0% oxidized starch, 6.0% PVA, 2.5% glycerol and 0.6% glutaraldehyde.

References

Funke U, Bergthaller W, Lindhauer M G (1998). Processing and characterization of biodegradable products based on starch. Polymer Degradation and Stability, (59):293–296

Judy R (2000). What's new in edible film. Food Processing, (7): 61–62

Miladinov V D, Hanna M A (2001). Temperatures and ethanol effects on the properties of extruded modified starch. Industrial Crops and Products, 13(1): 21–28

Qao S W (2002). Preparation of oxygenated starch by new technology.

Journal of Qingdao University (Natural Science Edition), 13(4): 42–46 (in Chinese)

Luis M R (2001). Development and characterization of biodegradable/edible film. Food Science, (1): 160–163

Song C C, Wang X P (2001). Production of new corn starch adhesive. Chemistry and Adhesion, (4): 181–182 (in Chinese)

Wang X Y, Zhu W C, Wang B (2004). Recent progress on oxidized starch. Adhesion in China, 25(3): 35–38 (in Chinese)

Wang Y J, Wang L F (2003). Physicochemical properties of common and waxy corn starches oxidized by different levels of sodium hypochlorite. Carbohydrate Polymers, (52): 207–217 (in Chinese)

Zhang J W, Zhu Y Y, Zhang Q, Lin X S (2002). Experiment of preparing dialdehyde starch with corn starch. Transactions of the Chinese Society of Agricultural Engineering, 18(3): 135–138 (in Chinese)