

The Contrastive Study on the Influence of Different Cellulose Derivatives on Properties of Chitosan –Starch Complex Films

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Abstract: Cellulose derivatives sodium carboxymethyl cellulose (CMCNa) and methyl cellulose (MC) were added into the chitosan –starch complex films separately. And the new complex films were obtained by cast line. Some properties of the complex films such as tensile strength, tensile elongation, water vapor transmission rate (WVTR), transparency, water absorption and the resistance to acids and bases were investigated. Through contrasting these properties with those of the films without cellulose derivatives, the influence of different cellulose derivatives on properties of chitosan –starch complex films was studied. The results showed that the ensile strength of complex films decreased slowly and tensile elongation increased greatly as the CMCNa content increased. When the mass ratio of chitosan to CMCNa was 3:1, the tensile elongation was highest. As MC was blended into the complex films, the ensile strength of complex films increased greatly and tensile elongation changed very little. When the mass ratio of chitosan to MC was 2:1, the ensile strength was highest. The WVTR of complex films with CMCNa or MC was larger than that of the films without cellulose derivatives. The influence of CMCNa on WVTR was more significant than that of CM. The WVTR of complex film was highest as the mass ratio of chitosan to CMCNa was 4:1. The transparency and water absorption of complex films were decreased gradually while CMCNa or MC was added. And the change of the complex films with MC was more obvious than that of the films with CMCNa. Both of the complex films hydrolyzed slowly when they were dipped into diluted acid and they didn't hydrolyze when the solution was strong acid. When the complex films were immersed into alkali, they curled and didn't dissolve.

Keywords: Cellulose Derivatives; Chitosan; Starch; Complex Film

1. Introduction

Starch and chitosan are abundant renewable natural resources and both of them have biocompatibility and biodegradability. In recent years, starch and chitosan have been used to prepare environmentally friendly materials in many studies. By blending, the interaction of the polymer components makes complex films better property. These materials have an extremely wide range of applications. For example, they may be used in a variety of packaging materials and provide protection to foods. With concerns about limited natural resources and the environment, the use of starch and chitosan to produce biodegradable packaging materials that can improve product quality and reduce waste disposal problems is significant. But the use of chitosan –starch complex films are limited because of their high moisture permeability and brittleness. The properties of chitosan –starch complex films can be modified to improve barrier and mechanical properties by the addition of third component.

The main objective of the present study was to prepare chitosan–starch complex films using different cellulose derivatives, and to investigate their effects on some properties of the films such as tensile strength, tensile

elongation, water vapor transmission rate(WVTR), transparency, water absorption and the resistance to acids and bases.

2. Materials and methods

2.1. Materials

Chitosan with degree of deacetylation above 90% and methyl cellulose (MC), were obtained from Sinopharm Chemical Reagent Co.,Ltd. (Shanghai, China). Potato starch was purchased from Beijing Aoboxing Biotech Company Ltd. (Beijing, China). Acetic acid, glycerol and hydrochloric acid were purchased from Beijing Chemical Works (Beijing, China). Glycol was purchased from Shantou Xilong Chemical Co., Ltd. (Shantou, China). Sodium carboxymethyl cellulose (CMCNa) and sodium hydroxide were purchased from Tianjin Jinke Fine Chemicals Institute (Tianjin, China). All reagents and chemicals were of analytical grade or better.

2.2. Preparation of films

2.2.1. CMCNa solution preparation

One gram of CMCNa was dissolved in a constantly stirred liquid of 600ml distilled water by heating at 65°C using a water bath (Guangming medical instrument factory, Beijing, China) until completely dissolved.

2.2.2. MC solution preparation

Three grams of MC were dissolved in a constantly stirred liquid of 100ml distilled water by heating for 3 hours at 65°C using a water bath. The solution was standing for 12 hours and then was strained through standard sieve with 80 meshes to remove undissolved debris. 0.03g/ml MC solution was prepared.

2.2.3. Preparation of complex films

2% chitosan solution was prepared by dissolving chitosan in 6% acetic acid solution. 5% starch solution was prepared by dissolving potato starch in constantly stirred distilled water at 80 °C. The starch solution and the chitosan solution were fully mixed by solid content ratio of 1:1. And a certain amount of plasticizer was added into the mixture. The mixture was homogenized using a homogenizer (Guangming medical instrument factory, Beijing, China) at 80°C. After cooling, the mixture was fixed into a vacuum deaerator (Beijing Orient Sun-Tec Co.,Ltd., Beijing, China) to remove foam. And then the mixture was cast onto a level silicon-coated polyester film (30 cm×30 cm). The cast film was dried overnight at ambient conditions (23°C and 50%RH). Ambient temperature and relative humidity varied with the season. After the solvent evaporated, films were removed and labeled. The drying films without cellulose derivatives were stored at ambient conditions until used. In addition, five types of chitosan–starch-CMCNa complex films were prepared by reinforcement with CMCNa. The mass ratios of chitosan and CMCNa were 9:1, 6:1, 4:1, 3:1, 2:1, respectively. Four types of chitosan–starch-MC complex films were prepared by reinforcement with MC. The mass ratios of chitosan and MC were 2:1, 1:1, 1:2, 1:3, respectively.

2.3. Tensile strength and elongation

XLW(PC) auto tensile tester (Labthink Instruments Co.,Ltd.,Jinan, China) was used to measure tensile strength(TS) at break and percent elongation(%E) at break. TS samples were cut and film thickness was measured with a thickness gage (model 7327, mitutoyo corporation, Japan). TS was calculated by dividing the maximum (peak) load by the cross-sectional area. Percent elongation at break was calculated by dividing the elongation at the moment of rupture by the initial length of specimen and multiplying by 100. For each TS and %E value, five samples were tested.

2.4. Water vapor transmission rate (WVTR)

WVTR(g/m²·24h) was tested according to ASTM E96 using TSY-T1 water vapor permeability tester (Labthink Instruments Co.,Ltd.,Jinan, China). Saturated water vapor transmitted through specimen in a unit time under specified conditions of temperature and humidity (23°C and 90%RH). The transmitted mass was determined by testing the decreasing weight of distilled water with time

going. Test samples (Φ100mm) were cut from the cast films and the test area was 63.58cm².

2.5 Transparency

S22PC visible spectrophotometer (Lengguang Technology Co., Ltd., Shanghai, China) was used to measure light transmittance which represented transparency. Test samples (10mm×60mm) were affixed to the cuvette surface by transparent tape. Light transmittance of complex films was measured. Four wavelength were used, 460nm, 480nm, 540nm and 600nm. For each type of film, light transmittance measurements were replicated four times.

2.6 Water absorption

Test samples (40mm×40mm) were cut from the cast films. The weights of films were measured before soaking. They were designated as W₁. The films were immersed in the beaker containing distilled water. After 24 hours, the films were removed carefully and water on the surface of films was absorbed with a filter paper. Then the weights of films were measured and designated as W₂. Water absorption (Q) was calculated as

$$Q\%=(W_2-W_1)/W_1\times 100\%。$$

For each type of film, water absorption measurements were replicated five times.

2.7. Resistance to acids and bases

Test samples (20mm×20mm) were cut from the cast films. Then they were immersed in different acids and bases, and the phenomenon of dissolution was observed and recorded. Five types of solutions were used, 2% acetic acid, 0.1mol/l hydrochloric acid, 6mol/l hydrochloric acid, 1% sodium hydroxide and 4% sodium hydroxide.

3 Results and discussion

3.1 Effect of CMCNa

3.1.1 Tensile strength

chitosan –starch- CMCNa complex films were prepared and then immersed in distilled water, 1% sodium hydroxide and 4% sodium hydroxide, respectively. After drying, TS was measured.

TS values of chitosan –starch- CMCNa complex films processed with distilled water, 1% sodium hydroxide and 4% sodium hydroxide are shown in Fig.1. If the complex films were not processed with sodium hydroxide, TS decreased with an increase in CMCNa slightly. The main reason for the decrease in tensile strength is that the interaction between CMCNa with negative charge and chitosan with positive charge reduces the role of hydrogen bonds. Among the complex films processed with 1% sodium hydroxide, the highest TS value was 43.10MPa when the mass ratio of chitosan to CMCNa was 9:1, whereas the lowest TS value was 29.11MPa

when the mass ratio of chitosan to CMCNa was 4:1. Among the complex films processed with 4% sodium hydroxide, TS values ranged from 25.03 to 35.50 MPa. TS of the films that the mass ratio of chitosan to CMCNa was 3:1 was highest, and the films that the mass ratio was 6:1 had the lowest TS. Fig. 1 shows that TS values of the films processed with sodium hydroxide were higher than those of without sodium hydroxide significantly. The reason for the difference is films with sodium hydroxide have more compact structure than those without sodium hydroxide. Comparing the three types of films, TS value of films with 1% sodium hydroxide can be best.

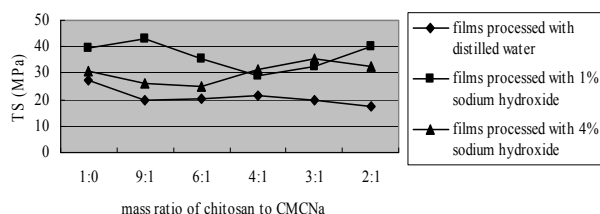


Fig. 1 Tensile strength of different chitosan-starch- CMCNa complex films

3.1.2 Elongation at break

E (a measure of a film's ability to stretch) of complex films also varied according to the mass ratio of chitosan to CMCNa and the different soaking solutions (Fig. 2). If the complex films were not processed with sodium hydroxide, E increased significantly with an increase in CMCNa. The highest E value was 43.3% when the mass ratio of chitosan to CMCNa was 3:1. As CMCNa increased continuously, chitosan and CMCNa cannot be fully mixed, resulting in decreased elongation. Films processed with sodium hydroxide were the tougher (lower E values) and films processed without sodium hydroxide were the more resilient (greater E values) among the films tested. E values of the films processed with sodium hydroxide are roughly equal to those of the films without CMCNa. The reason for the decrease in elongation is that the films processed with sodium hydroxide have more compact structure so that extensibility of films reduced as strength of films increased.

3.1.3 Water vapor transmission rate (WVTR)

Fig.3 shows the results of WVTR that ranged from 169.09 to 270.06 g/m²·24h. WVTR of complex films first increased and then decreased with the addition of CMCNa. WVTR value was highest when the mass ratio of chitosan to CMCNa was 4:1. Generally, the addition of CMCNa increased WVTR of complex films.

3.1.4 Transparency

Transparency was represented by light transmittance. Light transmittance values of films under different light

wavelength conditions were shown in Fig.4. Light transmittance value was lowest at 460nm, that is to say, 460nm was the maximum absorption wavelength. Light transmittance values of films decreased constantly as CMCNa increased because the greater the proportion of CMCNa, the worse the compatibility of polymer components.

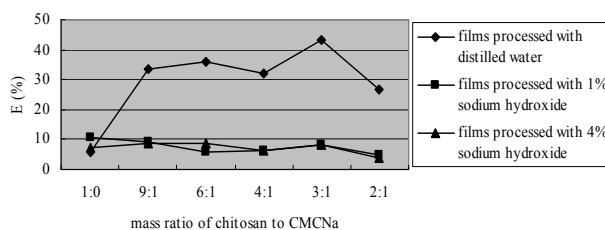


Fig. 2 Elongation of different chitosan-starch- CMCNa complex films

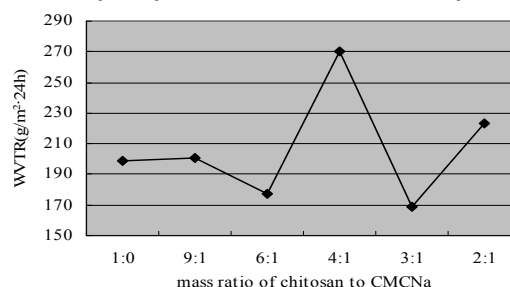


Fig. 3 WVTR of different chitosan-starch- CMCNa complex films

3.1.5 Water absorption

Experiment results show the relationship between the mass ratio of chitosan to CMCNa and water absorption. From the results, it is clear that there was a sharp decline in water absorption with the addition of CMCNa, and the lowest water absorption occurred when the mass ratio of chitosan to CMCNa was 2:1. But the lowest absorption was not significantly different from that of chitosan –starch films.

3.1.6 Resistance to acids and bases

There was no significant difference among different types of complex films. The samples evidently expanded

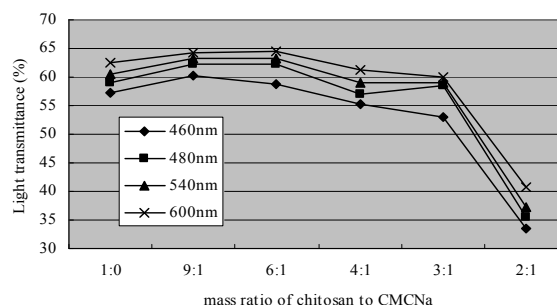


Fig. 4 Light transmittance of different chitosan-starch- CMCNa complex films

in dilute acid because of slow hydrolysis of chitosan. But

the samples curled slowly and didn't expand in alkali liquor. The main reason is that hydrophilic properties of chitosan and starch result in moisture absorption and curling of complex films.

3.2 Effect of MC

3.2.1. Tensile strength

TS values of chitosan–starch–MC complex films processed with distilled water, 1% sodium hydroxide and 4% sodium hydroxide are given in Fig.5. If the complex films were not processed with sodium hydroxide, TS values of complex films increased sharply when MC was added. This is probably due to the fact that there are many hydrophilic groups such as hydroxyl, methyl in MC. During drying, intermolecular hydrogen bonding is more and more strong with the continuous loss of water. But TS values decreased slightly as the addition of MC increased. Among the complex films processed with 1% sodium hydroxide, TS decreased with an increase in MC, whereas there was no significant difference in TS among the complex films processed with 4% sodium hydroxide. Generally, TS values of chitosan–starch–MC complex films processed with sodium hydroxide were lower than those of films without sodium hydroxide.

3.2.2. Elongation at break

Fig.6 shows E values of chitosan–starch–MC complex films processed with distilled water, 1% sodium hydroxide and 4% sodium hydroxide. The percentage of MC did not have an evident effect on E properties of complex films. Generally, it is known that there is an inverse relationship between TS and E of biopolymer films. It is proved in this test. E values of chitosan–starch–MC complex films processed with sodium hydroxide were higher than those of films without sodium hydroxide.

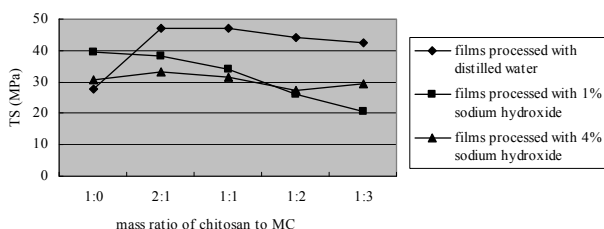


Fig. 5 Tensile strength of different chitosan-starch- MC complex films

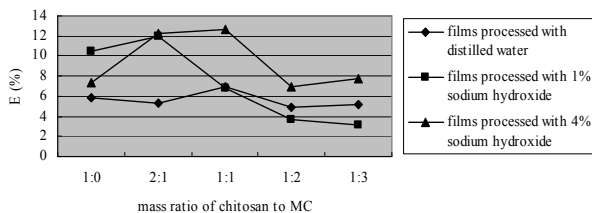


Fig. 6 Elongation of different chitosan-starch- MC complex films

3.2.3. Water vapor transmission rate (WVTR)

Fig.7 shows WVTR values of chitosan–starch–MC complex films ranged from 195.70 to 213.25 g/m²·24h. Overall, the addition of MC slightly increased WVTR of complex films. The change may be attributed to the less compact structure of chitosan–starch–MC complex films.

3.2.4. Transparency

Light transmittance values of films under different light wavelength conditions are shown in Fig.8. 460nm was also the maximum absorption wavelength. Light transmittance values of films were lowest as the mass ratio of chitosan to MC was 1:1. The addition of MC significantly decreased transparency of complex films. This was probably due to the fact that MC had poor compatibility with chitosan and starch which led to low light transmittance.

3.2.5. Water absorption

Experiment results show the relationship between the mass ratio of chitosan to MC and water absorption. Water absorption values decreased slightly with an increase in MC. Water absorption of complex films is related with the amount of hydrophilic groups and structure of films. Chitosan, starch and MC are hydrophilic high polymers so that complex films easily absorb water.

3.2.6. Resistance to acids and bases

There was no significant difference between chitosan–starch- CMCNa films and chitosan –starch- MC films when both of them were immersed into acid or alkali.

3.3. Properties comparison

3.3.1. Different cellulose derivatives

The ensile strength of complex films decreased slowly

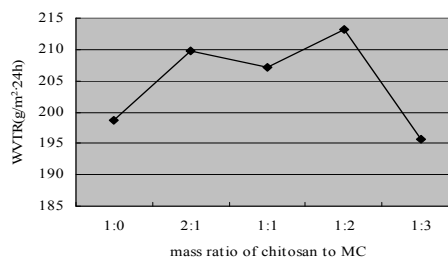


Fig. 7 WVTR of different chitosan-starch- MC complex films

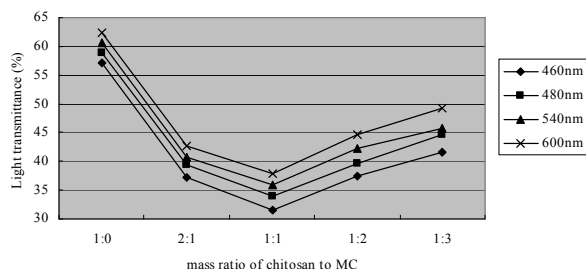


Fig. 8 Light transmittance of different chitosan-starch- MC complex films

and tensile elongation increased greatly as the CMCNa content increased. When the mass ratio of chitosan to CMCNa was 3:1, the tensile elongation was highest. As MC was blended into the complex films, the tensile strength of complex films increased greatly and tensile elongation changed very little. When the mass ratio of chitosan to MC was 2:1, the tensile strength was highest. The WVTR of complex films with CMCNa or MC was larger than that of the films without cellulose derivatives. The influence of CMCNa on WVTR was more significant than that of MC. The WVTR of complex film was highest as the mass ratio of chitosan to CMCNa was 4:1. The transparency and water absorption of complex films were decreased gradually while CMCNa or MC was added. And the change of the complex films with MC was more obvious than that of the films with CMCNa. Both of the complex films hydrolyzed slowly when they were dipped into diluted acid and they didn't hydrolyze when the solution was strong acid. When the complex films were immersed into alkali, they curled and didn't dissolve.

3.3.2. Commercial food packaging materials

Table 1 shows mechanical properties and WVTR of commercial food packaging materials. It is clear that TS values of plastic films were low, but E values were high especially because of large elastic deformation of plastic materials. On the contrary, TS values of packaging paper were much higher than those of commercial plastic films. However, properties of paper result in low E values. Both of two types of materials can be used in packaging and other applications. Mechanical properties of chitosan–starch complex films in the present study were between those of plastic and paper materials. If chitosan–starch complex films can be modified to further improve barrier, there will be a high potential for complex films to be used in packaging.

4. Conclusions

Properties of chitosan-starch complex films can be

Table 1. Mechanical properties and WVTR of commercial food packaging materials

Food packaging materials	Direction	Thickness/mm	TS /MPa	E /%	WVTR / (g/m ² ·24h)
Plastic 1	CD	0.031	18.31	226.7	5.66
	MD		10.85	164.1	
Plastic 2	CD	0.031	19.91	282	4.71
	MD		15.29	218.4	
Plastic 3	MD	0.024	26.25	178.3	5.66
	CD		14.95	157.1	
Paper		0.093	68.17	2.7	

changed through adding different cellulose derivatives. In the present study, oxygen transmission rates of complex film samples have been tested to evaluate oxygen permeability of films. Primarily test results indicated that chitosan-starch complex films processed with CMCNa or MC had a barrier for oxygen. So it further suggests that the complex films may be exploited for food packaging applications.

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