

## Effect of the Carbonyl Content on the Properties of Composite Films Based on Oxidized Starch and Gelatin

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**ABSTRACT:** To improve the properties of gelatin, oxidized starch (OS) with different carbonyl content was introduced into the gelatin. In this study, we researched the influence of the carbonyl content of OS on the rheological characteristics, swelling behavior, thermal properties, and wettability of the modified gelatin film (MGF). The MGF samples were prepared by the casting of a 10% w/w solution of gelatin and OS with 18.9, 38.7, and 49.3% carbonyl content, respectively. The results of the dynamic viscosity demonstrated that the influence of the temperature on the rheological characteristics of native gelatin film (NGF) was more obvious than that of MGF. Meanwhile, the viscosity of the samples decreased with increasing carbonyl content in OS. Both the differential scanning calorimetry and thermogravimetry curves indicated that the denaturation and pyrogenic decomposition temperatures of the MGF samples were higher than those of NGF; this meant that the crosslinking between NGF and OS improved the physicochemical properties of gelatin. Compared with the NGF sample, MGF was less hydrophilic because the hydrophilic groups of gelatin could be shielded by OS. Meanwhile, the acid–base and salt sensitivity of the MGF samples were very obvious; therefore, the MGF samples could potentially be used as biomedical materials. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 3809–3815, 2013

**KEYWORDS:** crosslinking; differential scanning calorimetry (DSC); rheology; swelling; thermogravimetric analysis (TGA)

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### INTRODUCTION

The increasing use of plastics and their nonbiodegradability have raised environmental awareness, and hence, there is a need for the development of environmentally friendly degradable materials, especially green materials derived from natural polymer materials. Gelatin is a measurable hydrolysate and thermally denatured product of the collagen existing in the connective tissue of all mammals. The elementary construction unit of collagen was  $(\text{Gly}-X-Y)_n$ ; the elements were glycine, proline, and hydroxyproline or hydroxyl-lysine, respectively. Because of the special structure of collagen in different animals, the composite materials rooted in gelatin are widely applied in the medical field as capsule shell and *in vivo* implantation materials.<sup>1,2</sup> However, the native gelatin membranes have many insufficiencies, including fragility in the dry state, a low percentage of elongation, an easy ability to crack and swell, and a low strength and elastic modulus. Therefore, gelatin material needs to be modified before its actual application.<sup>3</sup> The reported research on modified methods include crosslinking, graft reaction, plasticization, and blending.<sup>4–6</sup> During these methods, with modification by physical or chemical crosslinking, not only

can the mechanical performance of gelatin materials be improved obviously, but also the loss rate caused by swelling can be reduced; this provides wide application prospects as sustained medicine-release agents.<sup>7,8</sup> Therefore, more and more researchers have begun to study the crosslinking modification of gelatin.

Formaldehyde and glutaraldehyde are the most familiar crosslinking agents for gelatin modification; for example, the research of Mariana et al.<sup>9</sup> showed that glutaraldehyde could improve the thermal and mechanical strengths of caseinate protein. The carbonyl groups can react with the  $\epsilon$ -amino in the lysine of the protein molecules to attain effective crosslinking. Meanwhile, this kind of crosslinking agent also has inevitable and fatal flaws, including its volatile, biological toxicity and its insolubility due to its autohemagglutination; this will not only reduce the crosslinking strength but also bring about yellow staining in modified gelatin.<sup>10</sup> Thus, the development and exploitation of the nontoxic biological crosslinking agent has become a hot research direction.<sup>11,12</sup> Marshall and Rabinowitz<sup>13</sup> found that dextran treated with cyanogen bromide could react with zymoprotein (this is called the Maillard reaction) and then

overcome its thermal instability. The further study of Kato et al.<sup>14</sup> confirmed the excellent emulsifying properties of this zymoprotein–dextran complex. The derivative from dextran also can enhance the antioxidation of ovalbumin and broaden the lysozyme antimicrobial spectrum.<sup>15,16</sup> Then, Schacht et al.<sup>17</sup> verified that the aldehyde dextran could improve the performance of gelatin.

The hydroxyl groups in polysaccharide can be oxidized to carbonyl groups, and this give a broad potentiality to the polysaccharide derivative. For example, Mu et al.<sup>18</sup> researched a glycerol-plasticized gelatin edible film with dialdehyde carboxymethylcellulose as a crosslinking agent. Their results show that the aldehyde group in dialdehyde carboxymethylcellulose could effectively crosslink with the free amino groups in gelatin, and the gained composite film could be used as an excellent edible film. With poly(ethylene glycol) taken as a plasticizer, gelatin with 50% hydroxypropylated high amylase corn starch could be used as capsule materials.<sup>19</sup> Hassan et al.<sup>20</sup> reported the influence of oxidized starch (OS) on the microstructure and rheology of gelatin gels; they found that the OS content could lower the elastic modulus and increase the degree of microscopic phase separation. However, reports on the mechanism of the crosslinking reaction between gelatin and oxidized polysaccharide are few. Moreover, the effect of the carbonyl content in OS on the thermal stability and swelling behavior of modified gelatin film (MGF) should also be considered. Therefore, in this study, we took the OS as the crosslinking agent to investigate the influence of carbonyl groups on the rheological properties, swelling behavior, and thermal stability of gelatin.

## EXPERIMENTAL

### Materials

The OS sample was prepared with hydroxyl peroxide as the oxidizing agent according to ref. 21, and the carbonyl contents of the samples were determined according to this reference. In this study, the OS sample with carbonyl contents of 18.9, 38.7, and 49.3% were prepared. Gelatin and sodium bicarbonate were purchased from Sinopharm Chemical Reagent Co., Ltd. (China).

### Preparation of the Samples

Gelatin (5.00 g) was suspended in water (100 mL) containing OS (0.50 g) for smooth stirring with a magnetic stirrer at pH 6.0. About 6 h later, the pH of solution was adjusted to 7.5 with sodium bicarbonate, with the reactions kept at 45°C for 2 h with sealed conditions. The MGF crosslinked by OS with an 18.9% carbonyl content was tagged as MGF18.9. MGF38.7 and MGF49.3 were the composite films based on the gelatin and OS with 38.7 and 49.3% carbonyl contents, respectively.

### Viscosity Analysis

The viscosity measurements of the native gelatin and the aforementioned three composite film samples were performed with a dynamic viscometer (Dalian Ruigao Co., Ltd., China). The viscometer was preheated to 30, 35, 40, 45, 50, and 55°C for 5 min before every testing. At a certain temperature, the time of the 10-mL sample solution required to flow through a capillary tube viscometer could be determined. The product of the time and the constant of the capillary viscometer was the viscosity at

the tested temperature. The concentration of every tested sample was fixed at 5 wt %.

### Thermal Analysis

The thermal stability of a polypeptide were used to evaluate the crosslinking degree between gelatin and OS in this experiment. The peak of the differential scanning calorimetry (DSC) curve was the direct reflection of the phase change of the sample, and the onset temperature of the first sharp peak was regarded as the denaturation temperature ( $T_d$ ) of the sample. The dry sample (3–5 mg) was sealed into an aluminum pan. Their DSC thermograms were recorded on a DSC calorimeter (Netzsch DSC 200F3, Germany) with a temperature increment of 5°C/min.

Thermogravimetry (TG) analysis of the native gelatin film (NGF) and composite gelatin samples were carried out by means of a PerkinElmer TG analyzer (Pyris I) with a nitrogen flow rate of 60 mL/min and at a heating rate of 10°C/min. Approximately 3 mg of the sample was set into a platinum pan for the TG analysis. In this study, the thermal decomposition temperatures were defined as those at the most obvious weight decrease in the TG curves.

### Swelling Behavior

A certain weight of NGF and the aforementioned three samples (ca. 2.0 g) were put into the solution, and then, the samples were weighed every 2 min. The swelling ratio (SR) of each film sample was calculated by eq. (1), in which  $W_s$  is the weight of film in swelling conditions and  $W_d$  is the weight of dry film. The equilibrium swelling ratio ( $SR_e$ ) was calculated by eq. (2), in which  $W_e$  is the weight of the film in complete swelling conditions. The  $SR_e$  values of the four aforementioned sample films with different acid–base properties and ionic strength were then recorded:

$$SR = \frac{W_s - W_d}{W_d} \quad (1)$$

$$SR_e = \frac{W_e - W_d}{W_d} \quad (2)$$

### Water Contact Angle ( $\theta$ )

The NGF and all of the MGF samples were sized at 1 and 3 cm and were placed on the test slide. The water  $\theta$  of every sample was tested with a JYSP-180 surface  $\theta$  meter (Jinshengxin Instrument Plant, China).

## RESULTS AND DISCUSSION

### Rheology Properties

To evaluate the influence of the carbonyl content on the rheological properties of the gelatin, the dynamic viscosity of NGF, MGF18.9, MGF38.7, and MGF49.3 at different temperatures was measured, and the results are listed in Table I.

From the data listed in Table I, we found that the dynamic viscosity of all of the samples decreased with increasing testing temperature; for example, the dynamic viscosity of the NGF and MGF18.9 samples were 35.78 and 26.63 mm<sup>2</sup>/s, respectively, at 30°C, and these values decreased to 20.78 and 14.88 mm<sup>2</sup>/s, respectively, when the testing temperature was increased to 45°C. Bogdanov et al.<sup>22</sup> found that the melting point of gelatin

**Table I.** Dynamic Viscosity versus the Temperature of the Samples

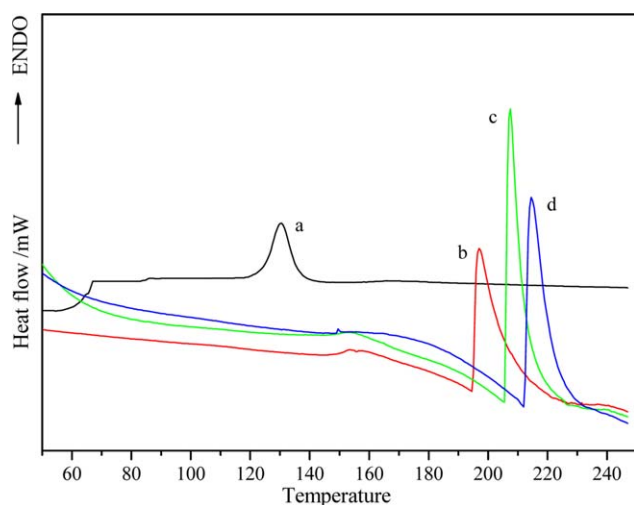
Sample <sup>a</sup>	Dynamic viscosity (mm <sup>2</sup> /s)							
	30°C	35°C	40°C	45°C	50°C	55°C	60°C	65°C
NGF	35.78	28.46	24.17	20.78	18.65	16.21	14.79	12.72
MGF18.9	26.63	22.22	18.44	14.88	12.85	11.43	10.49	9.10
MGF38.7	18.83	14.74	12.44	10.45	9.39	8.10	7.36	6.53
MGF49.3	15.68	11.87	10.34	9.04	8.13	7.07	6.51	6.02

<sup>a</sup>The concentration of all of the samples was 5%

materials depended on the storage conditions, and because of the chemical interaction between gelatin and aldehyde dextran, the rheological temperature of the native gelatin was higher than that of the gelatin–dextran composite gels. The reaction between gelatin and OS in this experiment also decreased the rheological behavior of the gelatin materials. We also found that the influence of the temperature on the dynamic viscosity of the NGF sample was the most obvious in our experiment; this indicated that OS could reduce the sensitivity of gelatin to heat. The difference between the viscosity of the NGF sample and those of the MGF samples was very obvious when the temperature was low; the differences in viscosity among the four samples became smaller with increasing temperature, and the dynamic viscosity of MGF49.3 was always the smallest at each testing temperature.

### Thermal Denaturation

Figure 1 shows the DSC spectra of the NGF and MGF samples. The onset temperature of the first sharp peak in every curve could be regarded as the sample's  $T_d$ . As a matter of fact, the denaturation behavior of gelatin was a dynamic and endothermic dissociation process. The enthalpy change could be reflected by the area of the peak.

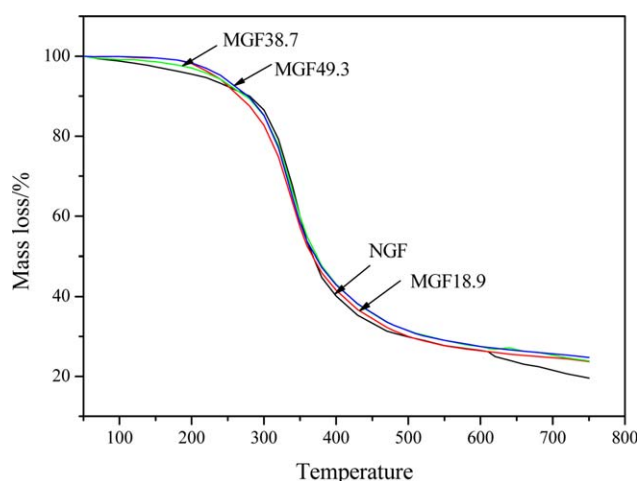


**Figure 1.** DSC curves of the NGF and OS–gelatin composite films. All samples were tested by DSC (Netzsch DSC 200F3). The heating rate was 5°C/min in this experiment. (a) NGF, (b) MGF18.9, (c) MGF38.7, and (d) MGF49.3. The onset temperature point in the DSC curve was the sample's thermal  $T_d$ . [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

From the thermal denatured behavior of the four tested samples, we found that OS obviously improved the thermal stability of the gelatin, and  $T_d$  of the MGF sample increased with the carbonyl content in OS. This was confirmed by the  $T_d$  values of NGF and MGF18.9, which were 120.9 and 195.2°C, respectively, and the  $T_d$  values of MGF38.7 and MGF49.3, which were 206.4 and 211.6°C. The curves in Figure 1 also confirmed the fact that the thermal denaturation process of the samples was an endothermic reaction, and the area of every peak was the enthalpy assimilated in the transformation to the molten state from the solid state. The energy needed for denaturation was smaller for NGF than for the MGF sample, and the enthalpies of transition were 9.03, 31.84, 44.98, and 38.97 J/g for NGF, MGF18.9, MGF38.7, and MGF49.3, respectively. Therefore, according to these data, we concluded that the thermal stabilities of the MGF samples were better than that of the NGF sample. However, it also was obvious that the carbonyl content of OS had little impact on the area of the peak in the DSC curves.

### Pyrolysis Behavior

Figure 2 shows the TG curves of the NGF and MGF samples. According to the differential curves of the four TG curves, the main temperatures reflecting the thermal decomposition could be obtained, and these are listed in Table II.



**Figure 2.** TG curves of the NGF and OS–gelatin composite film. TG analysis was carried out with a PerkinElmer TG analyzer (Pyris I) with a nitrogen flow and heating rates of 60 mL/min and 10°C/min, respectively. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

**Table II.** Decomposition Temperatures of Each Sample

Sample	Onset (°C)	Maximum (°C)	50% mass loss (°C)
NGF	273.7	340.0	368.6
MGF18.9	279.9	340.0	367.7
MGF38.7	281.9	340.0	373.3
MGF49.3	282.0	340.3	371.4

From the TG curves and the data in Table II, we found that the onset decomposition temperature of NGF was 273.7°C; MGF18.9, MGF38.7, and MGF49.3 began to decompose when the temperatures reached 279.9, 281.9, and 282.0°C, respectively. The disparity in the decomposition temperature for the four samples was very small; this indicated that the contribution of OS to the pyrolysis behavior of gelatin was negligible. From this figure, we also drew the conclusion that the remaining mass was lower for the NGF sample than for the MGF samples; these values were 19.58% for NGF and about 23.81% for the three MGF samples. The reason was easy to understand; the amount of burning remnants of OS was higher than that of the commensurable native gelatin. There was only one weight loss stage in the TG curves for all of the samples; this indicated that the MGF sample was not a simple mixture between OS and gelatin. The two chemicals reacted to form a uniform and stable material in these experimental conditions.

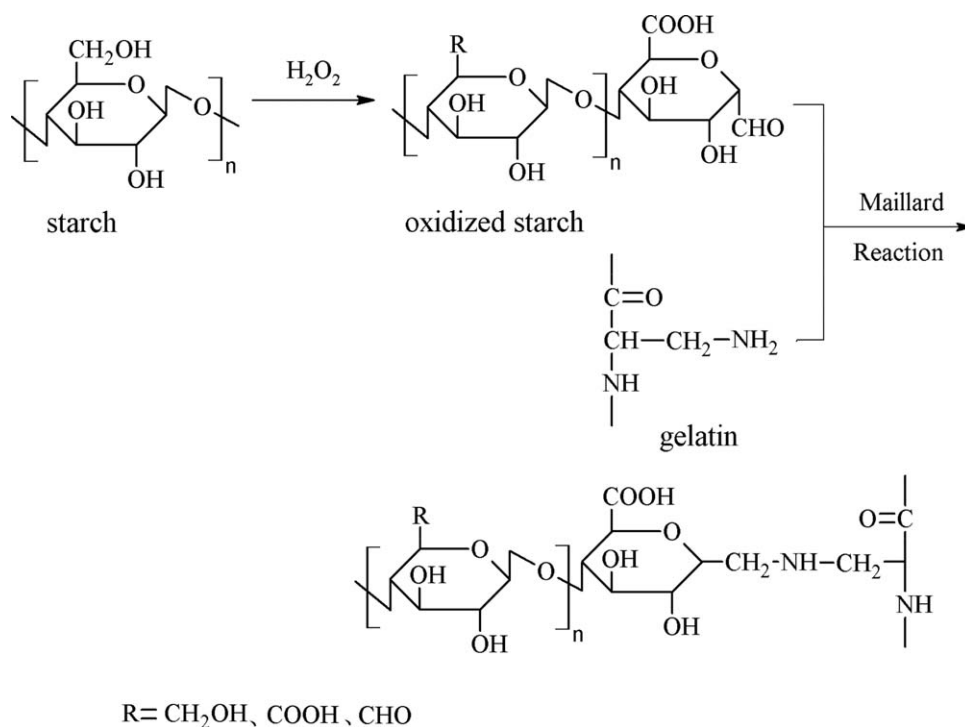
A kind of nonenzymatic reaction can occur between amino compounds and polysaccharides with carbonyl groups; this is called the *Maillard reaction*. Therefore, a Maillard reaction can also occur between protein polypeptides and polysaccharide derivatives

with carbonyl groups. Then, the emulsification of the modified protein will be improved; for example, the solubility of insoluble gluten protein and the resistance to oxidation of ovalbumin can be obviously increased.<sup>15,16</sup> As a common oxidant, hydroxyl peroxide can oxidize the hydroxyl groups existing in glucose units into carbonyl groups, and the product is carboxylic starch when the carbonyl content exceeds 54%.<sup>21</sup> Therefore, the OS sample in this study included ketone starch and aldehyde starch. The cross-linking between OS and gelatin was due to the reaction of the carbonyl groups in OS and the free amino groups in gelatin; this could also be defined as a Maillard reaction. The connection model is simulated in Figure 3, in which —R could be —CH<sub>2</sub>OH, —COOH, or —CHO with variations in the oxidation degree of OS. The cross density increased with increasing carbonyl content in OS; thus, the formed grid was more intensive, and the thermal stability of the composite films was excellent.

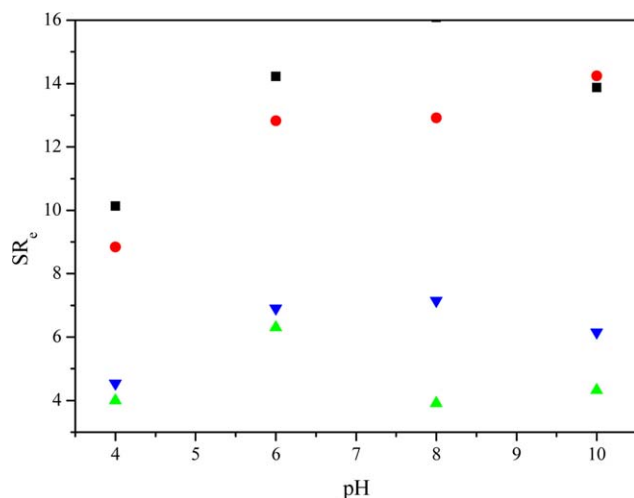
#### Acid–Base Sensitivity

The swelling behavior can reflect the water-resisting properties of materials. The swelling process for the gelatin in cold water is limited, but it can become an infinite swelling state when the temperature exceeds 70°C. Therefore, the storage temperature was an important factor for the gelatin materials' swelling; in addition, the acidity–basicity of solution also affected its swelling behavior. Figure 4 demonstrates the change trend of SR<sub>c</sub> for the four samples in different pH solutions.

The swelling behavior of all of the materials included the following three sections. The first stage was the spreading of the solvent molecule into the material lattice; the second stage was the relaxation of the polymer chain segment, which resulted



**Figure 3.** Connection model between OS and gelatin. The hydroxyl groups in the starch at the C-2, C-3, and C-6 positions could be oxidized to carbonyl or carboxyl groups. Therefore, the —R group could be —CH<sub>2</sub>OH, —COOH, and —CHO depends on the oxidation degree. This figure only lists a schematic structure of OS to imitate the crosslinking model.



**Figure 4.**  $SR_e$  values of the NGF and MGF at pH 4.0, 6.0, 8.0, and 10.0: (■) NGF, (●) MGF18.9, (▲) MGF38.7, and (▼) MGF49.3. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

from the solvent effects. The third stage was the space stretching of the polymer materials chains.<sup>23</sup> The dimensional size of the sample did not change when the swelling degree achieved the equilibrium state, and therefore, the moisture content in the samples did not change with increasing time.

As shown in Figure 4, the  $SR_e$  values of all of the samples showed a good response to the solution's pH value in this experiment. The influence of the solution's acid–base properties on the swelling behavior of the samples were different; for example,  $SR_e$  of the NGF sample increased with increasing pH when the pH was lower than 8.0, and it decreased when the pH exceeded 8.0. Meanwhile, the change tendency of the four samples were obviously different; for example, the maximum  $SR_e$  appeared when the pH was 8.0 for the NGF sample and when the pH was 10.0 for the MGF18.9 sample. However,  $SR_e$  of the NGF sample was always larger than those of the MGF samples; this indicated that the OS could reduce the swelling degree of the gelatin film material. This phenomenon also verified the conclusion that “the reaction between gelatin and crosslinker can reduce the degree of aqueous swelling of gelatin film.”<sup>24,25</sup> We guessed the reason to be the structure of the macromolecular matrix product of the reaction between the gelatin and OS and that both the electric charge density of ionizable groups existed in the side chain of gelatin and the degree of ionization changed with the solution's pH value.<sup>26</sup> The change in the film's ionization degree caused a fracture in the matrix chain segment. Large numbers of free amino groups ( $-NH_2$ ) existed as ammonium ion ( $-NH_3^+$ ) when the pH was low; this meant the gelatin existed as polycations. Therefore, the hydrogen bond formed between the gelatin and OS was weakened because of the electrostatic repulsion, and then, the hydrophilic groups were masked, and this resulted in the decrease of  $SR_e$ . As shown in Figure 4, the  $SR_e$  values of all of the samples were larger in alkaline solution than in acidic solution. The free amino groups ( $-NH_2$ ) were exposed generally with increasing pH value, and the carboxyl group in gelatin existed in the form of  $-COO^-$ .

**Table III.** Time of Complete Swelling versus pH of the Solution

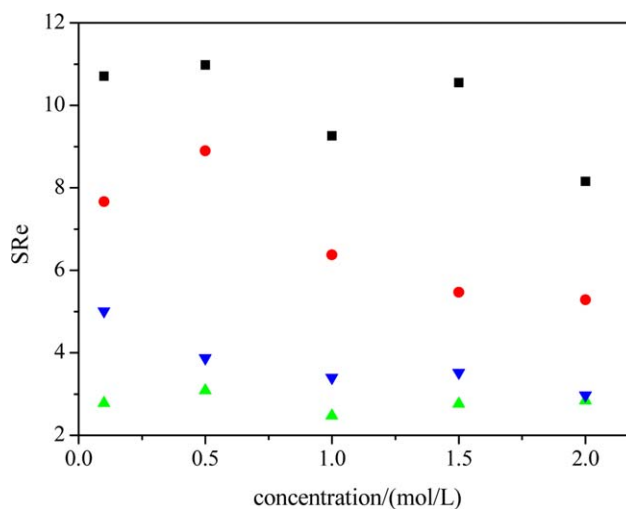
Sample	Time/min			
	pH4.0	pH6.0	pH8.0	pH10.0
NGF	20	20	18	16
MGF18.9	34	32	30	30
MGF38.7	32	32	32	32
MGF49.3	38	36	36	30

Meanwhile, the solubility of the gelatin materials was at a minimum when the pH value of the solution was near its isoelectric point (pI). The  $SR_e$  values of all of the tested samples were the smallest when the pH was 4.0 in this experiment, and the pI of native gelatin was 4.1. Therefore, we concluded that OS almost had no effect on the pI of the gelatin materials. The  $SR_e$  values of all of the MGF samples were smaller than that of NGF sample; this also indicated that the hydrophobic grouping was introduced into the chain of gelatin by crosslinking with OS.

However, in addition to the swelling capacity, the swelling rate also is an important factor during the application of gelatin film materials. From the data listed in Table III, we found that the NGF sample was the first one to reach the equilibrium swelling state, the sample in basic solution needed less time to achieve complete swelling, and the MGF samples also showed similar swelling behavior. The reason could be hypothesized that a compact matrix was formed during the NGF-forming process, and the added OS crosslinked with the active groups of gelatin and caused a smaller mesh. Therefore, the water molecules' inward permeability became difficult. The observed consequence was the longer time to complete swelling for the MGF samples.

#### Salt Sensitivity of the Films

Figure 5 shows the relationship between the  $SR_e$  values of the four tested samples and the ionic strengths of the solution.



**Figure 5.**  $SR_e$  values of the samples versus the ionic strength of the solution at 30°C, including the  $SR_e$  values of NGF and MGF at sodium chloride consistence of 0.1, 0.5, 1.0, 1.5, and 2.0 mol/L: (■) NGF, (●) MGF18.9, (▲) MGF38.7, and (▼) MGF49.3. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

**Table IV.** Time of Complete Swelling versus Concentration of Sodium Chloride

Sample	Time (min)				
	0.1 mol/L	0.5 mol/L	1.0 mol/L	1.5 mol/L	2.0 mol/L
NGF	16	16	16	16	16
MGF18.9	34	30	26	24	20
MGF38.7	34	30	26	24	22
MGF49.3	28	26	26	26	22

Table IV lists the required time for every testing sample to reach equilibrium swelling.

As shown in Figure 5, we found that  $SR_e$  of the NGF sample increased with increasing ionic strength of the solution when the salt concentrations were in the ranges 0.1–0.5 and 1.0–1.5 mol/L, and the  $SR_e$  decreased when the concentrations of sodium chloride were in the ranges 0.5–1.0 and 1.5–2.0 mol/L. The nonmonotonic change in the relationship between  $SR_e$  and the ionic strength indicated that the ionizable group existing in the gelatin film required more contra-ions in solution to migrate into the inside of the film, and these contra-ions were very few when the ionic strength was low; this resulted in an infirm extent of ionization. The increasing ionic strength led to an increase in the ionization degree of the gelatin film, and the water absorption was also enhanced. Meanwhile, the sodium ion also shielded and damaged the intramolecular and intermolecular association in the gelatin membrane and resulted in the stretching of the molecular chain. However, when the concentration of sodium chloride in the solution was higher than that of the membrane, the water reversed osmosis from the membrane sample. This resulted in a decrease in  $SR_e$ .

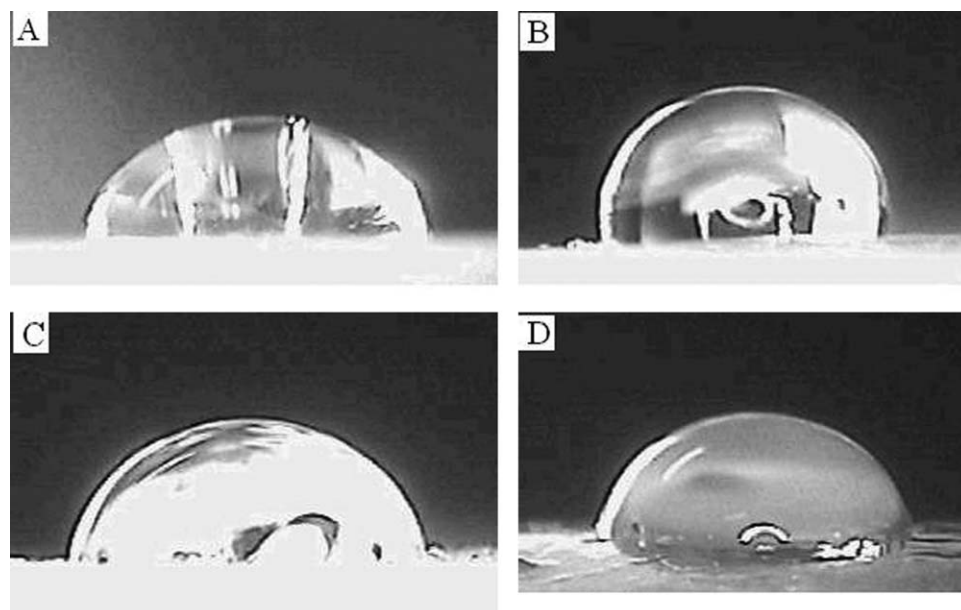
$SR_e$  of the MGF18.9 sample increased with increasing ionic strength in the range 0.1–0.5 mol/L, and it decreased when the concentration exceeded 0.5 mol/L. The reason for this was attributed to the shielding effect of the charge in the solution. The electrolyte shielded the interaction between the samples and the water molecules, and this increased the hydrophobicity of the samples. Therefore, the electrostatic repulsion effect was weakened, and this eventually led to a decrease in  $SR_e$ .

The swelling rates of all of the samples in NaCl solution with different concentrations are listed in Table IV. The data indicated that the NGF sample needed a shorter time to achieve the complete swelling state than the MGF samples, and there was no influence of the sodium chloride on its swelling rate. For all of the MGF samples, the rate increased with increasing concentration of sodium chloride. Also, the swelling rate of the composite gelatin material was always smaller than that of the native gelatin; this indicated that the OS improved the stability of the gelatin materials in the NaCl solution.

#### Water $\theta$ of Film

The wettability between solid materials and liquid can be reflected by  $\theta$ . When  $\theta$  is less than  $90^\circ$ , the solid material is hydrophilic; this means that the liquid can moisturize the solid material. The smaller the angle is, the easier it is to wet. The solid material is hydrophobic when  $\theta$  is greater  $90^\circ$ , and in this condition, the liquid can move on the surface of the solid material rather than penetrate into the pores among the surface of materials. Figure 6 shows the  $\theta$ s of the NGF and MGF samples.

Compared with that of the NGF sample, the  $\theta$ s of the composite gelatin material were larger. The  $\theta$  values were  $67.6^\circ$  for the NGF sample and  $72.7^\circ$ ,  $90.0^\circ$ , and  $85.6^\circ$  for the MGF18.9, MGF38.7, and MGF49.3 samples, respectively. Therefore, we concluded that the OS reduced the hydrophilicity of the gelatin,



**Figure 6.** Water  $\theta$  of the film. The water  $\theta$  of every sample was tested with a JYSP-180 surface  $\theta$  meter (Jinshengxin Instrument Plant, China): (A) NGF, (B) MGF18.9, (C) MGF38.7, and (D) MGF49.3.

and the reason was that the crosslinking reaction between OS and gelatin downgraded the content of hydrophilic groups in the gelatin membranes, which led to a reduced hydrophilicity. We also observed that  $\theta$  of MGF49.3 was smaller than that of MGF38.7; this indicated that excessive carbonyl groups with a certain hydrophilicity could also decrease  $\theta$  of the gelatin material slightly.

## CONCLUSIONS

The Maillard reaction occurred between the gelatin and OS in this experiment because of the Schiff base in the amino group of lysine or hydroxylysine side groups of the gelatin and the carbonyl group of OS. The contribution of the chemical crosslinking reaction to the viscoelastic properties of the OS–gelatin composite films increased with increasing storage temperature. The heat sensitivity of the gelatin material was improved by OS, and the range depended on the content of carbonyl groups in OS. The gelatin film crosslinked with OS also had a better thermal stability. As a drug carrier and adsorption material, the swelling process in the gelatin film is an important factor in controlling the drug-release behavior. The results in this study show that because of its excellent surface densification, the OS–gelatin composite film needed more time to achieve a complete swelling state. In addition, the water  $\theta$  of this kind of composite film was bigger than that of native gelatin; this was because the hydrophilic groups in the side chain of gelatin were shielded after crosslinking by OS. All of the results indicated that the OS–gelatin composite film had good properties and have potential applications as packing and biomedical materials.

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