Preparation and Characterization of Nano-Ag/Chitosan Composites

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Abstract. In this paper, the optimum synthesis conditions of nano-Ag/chitosan composites were studied, and the effects of silver nitrate dosage on the shape memory effect and mechanical properties of the composites were further characterized. The present study shows that the optimum conditions for the synthesis of Ag nanoparticles (Ag NPs) are: 1 % silver nitrate, 1 g chitosan, a synthesis temperature of 90 °C, and a reaction time of 5 h. The Ag NPs not only improve the shape memory efficiency of the composite material, but also improve the mechanical properties. The pristine sample of chitosan material did not restore its original shape after 41 s, however, the shape recovery rate of Ag/chitosan composites reached more than 90 % after 21 s. Moreover, the tensile strength of the composite material was as high as 88.9 MPa after adding Ag NPs, increasing by 82.17 % compared to pristine samples.

1. Introduction

The scientific name of chitosan is polyaminoglucose, which is a natural biopolymer linear polysaccharide[1]. Scientists hailed chitosan as the sixth essential element of life after protein, vitamins, fats, carbohydrates and minerals[2]. Chitosan is widely used in many fields such as food nutrition, chemical industry, medicine, industry, agriculture, environmental protection and biology[3]. The Ag NPs material has the advantages of physical and chemical stability. The surface plasmon resonance of Ag NPs is due to the cooperative vibration of the electron cloud on the surface of the particle, and its characteristic absorption peak is usually between 400~450 nm[4]. Among the many heavy metals with bactericidal capabilities, Ag NPs has the advantages of strong bactericidal ability, long lasting effect, small amount and high safety, thus it is favored by researchers[5]. The higher biocompatibility of Ag NPs enables it to be better used in biology and medicine[6].

In this paper, chitosan is used as a stabilizer and reducing agent to reduce Ag+, Ag nanoparticle-chitosan composite is prepared. In the reaction process, Ag+ is chelated with amino or hydroxyl in chitosan, and Ag NPs are prepared by in situ reduction. In this way, the Ag NPs will not aggregate and will be dispersed uniformly, and the composite material will also have good biocompatibility. This paper mainly studied the optimum synthesis conditions of nano-Ag/chitosan composites and the effect of Ag NPs on the shape memory effect and physical and mechanical properties of Ag/chitosan composites.
2. Experimental

2.1. Materials and Instruments
Silver nitrate (AR) and chitosan (AR) were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China) and Acetic Acid (AR) were obtained from Laiyang Economic and Technological Development Zone Fine Chemical Factory (Shandong, China).

721 spectrometer was purchased from Shanghai Precision Scientific Instrument Co. Ltd (Shanghai, China), Laser dust particle sizing analyzer of JMGO78 were supplied by Britain Malvern company, Electro-mechanical Universal Testing Machines of UTM2502 was bought from Shenzhen Sansilan Technology Co. Ltd. (Shenzhen, China), Transmission Electron Microscope of JEM-1200EX were supplied by Japan JEOL company.

2.2. Synthesis method
The calculated amount of chitosan was dissolved in glacial acetic acid, an appropriate amount of silver nitrate was added, and the reaction was carried out at a certain temperature and time to synthesize a uniformly dispersed silver nanosol. The synthesized silver nanosol was injected into a mold, the silver nano/chitosan composite was synthesized after drying in an oven at 65 °C.

In the pristine experiment, chitosan was dissolved in glacial acetic acid, injected directly into a mold and dried in an oven at 65 °C.

2.3. Characterization
The synthesis of silver nanosols was confirmed by 721 spectrophotometer and quantitative analysis was performed. In this paper, the detection wavelength range is 300~550 nm, and the step length is 5 nm. Distilled water is used as a blank control. The shape memory performance test first requires that the sample be bent into a "U" shape, and then continue to stress the sample to ensure that the sample deformation, wait until the shape of the sample is fixed, you can remove the external force, and finally heat the sample to the deformation temperature, and record Shape recovery time and calculated shape recovery rate, Using a U-shaped edge as a reference, the recovery angle θ' is the angle between the side tangent to the sample movement and the X-axis, and the shape recovery rate RR=θ'×180°/180°×100 %[7]. The static mechanical performance test of this article is performed at room temperature.

3. Results and Discussion

3.1 Determination of the optimum reaction conditions of the synthesis of Ag NPs

3.1.1 Temperature

| Sequence number | Reaction temperature (°C) | Wavelength (nm) |
|-----------------|---------------------------|-----------------|
| 1               | 60                        | 415             |
| 2               | 70                        | 410             |
| 3               | 80                        | 395             |
| 4               | 90                        | 405             |
The characteristic absorption peak of surface plasmon resonance of nanosilver particles is generally between 400–450 nm, and is a single peak. Table 1 explores the effect of different reaction temperatures on the reaction under conditions of a silver nitrate molar ratio of 1 %, chitosan of 1 g, and a reaction time of 5 h. In Figure 1, all the absorption peaks appear between 400–450 nm, indicating that silver nanoparticles have been successfully prepared. When the temperature is 60 °C, 70 °C, 80 °C, 90 °C, the absorption peaks appear at 415 nm, 410 nm, 395 nm and 405 nm, respectively, and the absorption peaks gradually change from weak to stronger. It shows that with the increase of temperature, more silver nanoparticles are generated in the reaction system. Moreover, as the temperature increases, Ag⁺ in the reaction system intensifies the movement, which is favorable for the reduction and nucleation of Ag⁺. The faster the rate of reduction of Ag⁺, the greater the number of silver nanoparticles produced in the reaction system, thus illustrating that high temperatures accelerate the reaction process. In order to make the reaction more thorough, 90 °C was finally selected as the reaction temperature in the production of composite materials.

3.1.2 Chitosan weight

Table 2. Effect of CS weight on synthesis of Ag NPs

| Sequence number | Chitosan (g) | wavelength (nm) |
|-----------------|--------------|-----------------|
| 1               | 0.1          | 395             |
| 2               | 0.25         | 420             |
| 3               | 0.4          | 400             |
| 4               | 1.0          | 405             |
Table 2 shows the effect of the addition amount of chitosan on the reaction under the condition that the molar ratio of silver nitrate is 1 %, the reaction temperature is 90 °C, and the reaction time is 5 h. It can be seen from Figure 2 that when the amount of chitosan is 0.1 g, 0.25 g, 0.4 g and 1.0 g, the absorption peaks appear at 395 nm, 420 nm, 400 nm and 405 nm, respectively, and the absorption peaks gradually change from weak to strong. It shows that with the increase of chitosan addition, more silver nanoparticles are generated in the reaction system. Since chitosan is simultaneously used as a reducing agent and a fixing agent in the process of preparing the silver sol, when the amount of chitosan increases, the concentration of the reactants increases, resulting in an increase in the reaction rate. Therefore, we chose 1 g of chitosan in the reaction of making composite materials.

### 3.1.3 AgNO₃ concentration

Table 3. Effect of AgNO₃ concentration on synthesis of Ag NPs

| Sequence number | AgNO₃ (%) | Wavelength (nm) |
|-----------------|-----------|-----------------|
| 1               | 1         | 400             |
| 2               | 2         | 420             |
| 3               | 3         | 440             |

Figure 3. UV–vis spectra of Ag NPs under different concentrations of AgNO₃
In Table 3, the effect of the addition of silver nitrate on the reaction was investigated, under the conditions of chitosan 1 g, reaction temperature 90 °C, and reaction time 5 h. It can be seen from Figure 3 that when the amount of silver nitrate is 1 %, 2 % and 3 %, the samples show strong absorption peaks at 400 nm, 420 nm and 440 nm, respectively, indicating that the addition of AgNO₃ can promote the reaction. However, the absorption peak was red-shifted with the increase in the amount of AgNO₃, indicating that increasing the amount of AgNO₃ increased the particle size of the resulting nanosilver particles. So we chose to absorb the peak at 400 nm, which is 1 % for silver nitrate.

3.1.4 Reaction time

| Sequence number | reaction time (h) | wavelength (nm) |
|-----------------|------------------|----------------|
| 1               | 1                | 395            |
| 2               | 2.5              | 400            |
| 3               | 4                | 403            |
| 4               | 5                | 405            |

Figure 4. UV–vis spectra of Ag NPs under different reaction time

Table 4 shows the effect of reaction time on the reaction under the conditions of a silver nitrate molar ratio of 1 %, chitosan of 1 g, and a reaction temperature of 90 °C. After the reaction was carried out for 1 h, the solution was light yellow. After 2.5 h, the solution appeared light red. After 4 h, the solution appeared burgundy. And after 5 h, the solution was red-brown and no longer changed. In addition, it can be seen from Figure 4 that the absorption peaks were detected at 395 nm, 400 nm, 403 nm and 405 nm, respectively, and the absorption peaks gradually changed from weak to strong. This shows that as the reaction time increases, more silver nanoparticles are formed in the reaction system. It is indicated that the reaction time determines the extent of the reaction, and the basic reaction is complete when the reaction is performed for 5 h. And the peak value is around 405 nm, so when preparing silver nanoparticles and preparing composites, we chose 5 h as the final reaction time.

3.2 Characterization

3.2.1. Particle size and TEM
Figure 5 shows the particle size distribution of Ag NPs-chitosan synthesized under optimal reaction conditions. Figure 6 shows the scanning electron micrograph of Ag NPs. It can be seen that the particle size of the ion is mainly focused on around 10-100 nm, and the dispersion effect is good, there is no aggregation phenomenon.

3.2.2 Shape memory test
From Figure 7, it can be seen that the film of pristine sample material does not continue to recover after 41 s in 37 °C water, and finally appears in a rolled shape, and the shape memory property is not good. From Figure 8, it can be clearly seen that the nano-Ag/chitosan composite recovers its original shape, and it only takes 21 s, and the shape recovery rate reaches more than 90 % . This shows that the addition of silver nanoparticles gives the composite a strong shape memory.

3.2.3 Tensile test
Figure 9 shows that with the increase of silver nitrate content, the maximum stress of nano-Ag/chitosan composites gradually increases, the stress of pristine samples is 48.8 MPa, and the stress becomes 68.1 MPa after adding 1% of AgNO₃, the stress becomes 84.0 MPa when 2% of AgNO₃ is added, and the stress becomes 88.9 MPa when 3% of AgNO₃ is added, and the strength of the sample is much higher than that of the pristine sample.

4. Conclusion
The optimum conditions for the synthesis of nano-Ag/chitosan composites were as follows: the amount of silver nitrate was 1%, the amount of chitosan was 1 g, the reaction temperature was 90 °C, and the reaction time was 5 h. Finally, the silver nanosol was left in an oven at 65 °C for 6 h to prepare a composite membrane. The synthesis of silver nanoparticles was confirmed by UV spectroscopy. The particle size distribution proved that the generated silver nanoparticles were uniformly dispersed. Experiments show that the composite material has strong shape memory performance and physical and mechanical properties.

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