

Study on In Situ Synthesis of Konjac Glucomannan/Silver Nanocomposites via Photochemical Reduction

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ABSTRACT: Konjac glucomannan (KGM)/Silver nanocomposites have been prepared directly in the dilute hydrosol of KGM using photochemical reduction of Ag⁺. The KGM/Ag nanocomposites have been characterized by means of Fourier transform infrared (FTIR) spectra, transmission electron microscopy (TEM), and thermalgravimetry (TG). The results of FTIR showed that the wavenumbers and the strengths of some characteristic peaks of KGM treated by silver nanoparticles were changed obviously, the characteristic peaks of the O—H stretching and the C—O—(H) stretching became wider with increasing concentrations of the reactants, and the characteristic peaks of the O—H stretching and the C—O—(H) stretching shifted to high wavenumbers with increasing time of photochemical reduction. The images of TEM indicated that Ag nanoparticles

were finely dispersed inside the KGM films with different shapes, such as sphere-like (average diameters of 9 ± 4 nm) and star-like (edge lengths of about 20 nm), respectively. These suggested that the morphology and the agglomerated state of Ag nanoparticles in the composites changed with the conditions of the preparation, especially with the concentrations of Ag⁺ and KGM as well as the time of photochemical reduction. The KGM and KGM/Ag films had remarkably different thermal properties from the TG curves. The mechanism of interaction between the polysaccharide and the silver nanoparticles has also been generally discussed. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1323–1327, 2006

Key words: photochemistry; nanocomposites; polysaccharides; konjac glucomannan (KGM); silver nanoparticles

INTRODUCTION

Nanocomposites of inorganic nanoparticles embedded within a polymer matrix have attracted much interest, particularly over the past decade, for they can combine the virtue of two types of materials. They are not usual composites that were traditionally discussed but are hybrids with nanometer-sized particles. Because of large specific surface areas of the nanoscale dispersed phase and strong interfacial effects between inorganic phase and organic phase, some unique properties emerge, such as quantum size effect and synergistic effect, which have broad range of potential applications in optics, electronics, magnetism, catalysis, biotechnology, etc. The study of nanocomposites becomes a hot spot of chemistry, physics, and materials during the 21st century.^{1–4}

Using synthetic polymers as matrices of nanocomposites is very common, whereas using natural polymers is relatively rare: only chitosan, modified starch, and cellulose^{5–9} have been reported. The konjac glucomannan (KGM) is a type of polysaccharide consist-

ing of β -1,4 linked β -D-glucose and β -D-mannose in a molar ratio of approximately 2 : 3. It has many potential applications in medicine, textile, food, chemical engineering, water treatment, and so forth. Although there have been many reports about chemical and physical modifications of KGM (i.e., graft copolymerization, etherification, esterification, crosslinking, interpenetrating polymer networks, etc.),^{10–14} there is no report on the preparation of nanocomposites using KGM as matrix.

This article deals with the *in situ* synthesis of KGM/Ag nanocomposites via photochemical reduction of silver ions and the characterization of nanocomposites using Fourier transform spectra (FTIR), transmission electron microscopy (TEM), and thermalgravimetry (TG), as well as discussion of the mechanism of interaction between the polysaccharide and Ag nanoparticles.

EXPERIMENTAL

Materials

Konjac glucomannan (KGM), supplied by Hongye KGM Company, Hubei, People's Republic of China, was purified with ethanol and then dried under reduced pressure until it reached constant weight.

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AgNO₃, analytical grade, made by No.9509 Factory of PLA, People's Republic of China, was used as obtained.

Methods of synthesis of KGM/Ag nanocomposites

To a dilute hydrosol containing a certain mass fraction of KGM, a proper amount of aqueous solution of AgNO₃ was added and mixed thoroughly. The mixed solution was irradiated using a 500w halogen lamp as light source for an appropriate time to get a solution of the KGM/Ag nanocomposite, which was then decanted onto a clean glass slide and dried naturally in the absence of light to make a thin film. It was further dried under reduced pressure for 24 h, and the KGM/Ag complex film was then removed from the glass slide to obtain the target products.

Characterization

Fourier transform infrared spectra

FTIR spectra of KGM films and KGM/Ag complex films were taken by Avatar 370 of Thermo Nicolet, USA, at wavenumbers from 4000 to 400 cm⁻¹.

Transmission electron microscopy

The TEM micrographs of KGM/Ag nanocomposites were carried out by (Tecnai G2 20 TEM made by FET company) slow evaporation of one drop of a dilute aqueous solution of KGM/Ag nanocomposite on a carbon-coated copper mesh grid operating at an accelerating voltage of 200 kV.

Thermalgravimetry

The TG analysis of KGM film and KGM/Ag complex film were performed by WRT-2P thermobalance made by Shanghai Fine Scientific Instrument Company, People's Republic of China, with a heating rate of 1°C min⁻¹ from 50 to 650°C under air.

RESULTS AND DISCUSSIONS

Analyses of FTIR

Effect of concentrations of Ag⁺ on the FTIR spectra of composites

Figure 1 shows the FTIR spectra of KGM/Ag complex films at five different concentrations of Ag⁺: 0, 0.025, 0.05, 0.075, and 0.10 mol L⁻¹, respectively. The mass fraction of KGM and the photochemical reduction time are fixed at 0.50% and 60 min, respectively. As well known, KGM exhibits associative O—H groups stretching absorption band of polysaccharide at 3380 cm⁻¹, and a characteristic absorption peak of β-1,4-

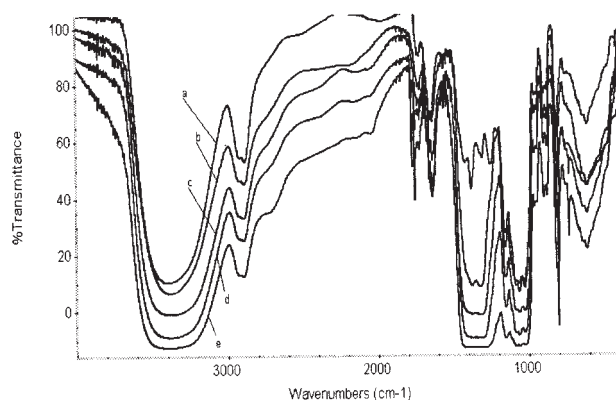


Figure 1 Effect of concentrations of Ag⁺ on the FTIR spectra of composites (concentrations of Ag⁺: (a) 0 mol L⁻¹; (b) 0.025 mol L⁻¹; (c) 0.05 mol L⁻¹; (d) 0.075 mol L⁻¹; (e) 0.1 mol L⁻¹. Mass fraction of KGM: 0.50%. Photochemical reduction time: 60 min).

linked glycosidic bond at 890 cm⁻¹, and a characteristic peak of the enlargement of pyranoid rings at 800 cm⁻¹. In addition, KGM gives rise to a sharp peak at 1150 cm⁻¹, which belongs to C—O stretching absorption of C—O—H, and two peaks for C—O—C ether linkage at 1050 cm⁻¹, as well as a strong bending absorption at 1350 cm⁻¹ for C—O—H bonding.^{15,16} Figure 1 indicates the O—H stretching absorption peak at about 3380 cm⁻¹ and the C—O—H bending absorption peak at 1350 cm⁻¹. The C—O stretching absorption peak of C—O—H at 1150 cm⁻¹ becomes wider with increasing concentration of Ag⁺. However, the KGM is a type of polysaccharide consisting of β-1,4-linked β-D-glycose and β-D-mannose in a molar ratio of 1 to 1.5–1.6. The polar groups —O—H of polysaccharide have good ability of coordination reaction with metal ions (e.g., with silver ions). When OH groups and silver ions form coordination bonds, the interactions between the resultant Ag particles and oxygen atoms of O—H groups become stronger with increasing amount of Ag ions (see the interaction mechanisms in detail in later section). This can lead to corresponding changes both in the positions and in the strengths of IR spectra of KGM. Thus, the stretching peaks of both O—H and C—O become wider gradually. And so does the bending absorption peak of C—O—H at 1350 cm⁻¹ influenced by the Ag particles.

Effect of photochemical reduction time on the FTIR spectra of composites

The FTIR spectra of nanocomposites are shown in Figure 2 with photochemical reduction time at 15, 30, 45, and 60 min, respectively. It can be seen that the O—H stretching peaks at about 3380 cm⁻¹ move to high wavenumbers from 3382.63 cm⁻¹, to 3384.74

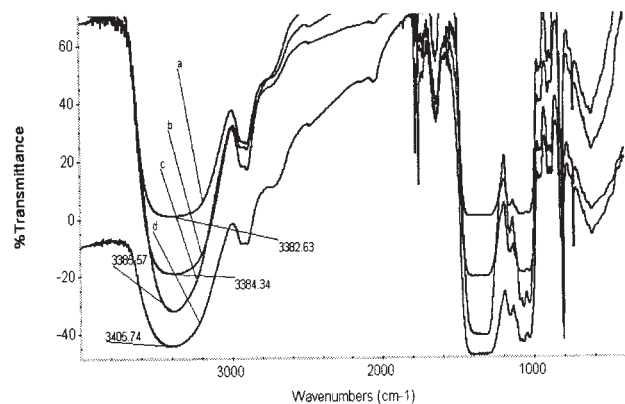


Figure 2 Effect of photochemical reduction time on the FTIR spectra of composites (photochemical reduction time: (a) 15 min; (b) 30 min; (c) 45 min; and (d) 60 min. Mass fraction of KGM: 0.50%. Concentrations of Ag^+ : 0.05 mol L^{-1}).

cm^{-1} , to 3385.53 cm^{-1} , and to 3405.74 cm^{-1} , correspondingly. Moreover, the C—O stretching peaks of C—O—H at about 1150 cm^{-1} indicate the same changing tendency. These may be explained as follows: with the increase of photochemical reduction time, the numbers of silver nanoparticles increase gradually, thus increasing the interaction between OH groups and silver nanoparticles and increasing the wavenumbers of OH stretching peaks. Furthermore, the blue shifts of C—O stretching peak of C—O—H at 1150 cm^{-1} also have something to do with the increase of silver nanoparticles in the system.

Effect of mass fractions of KGM on the FTIR spectra of composites

Figure 3 shows the FTIR spectra of nanocomposites, in which the mass fractions of KGM were used as 0.50,

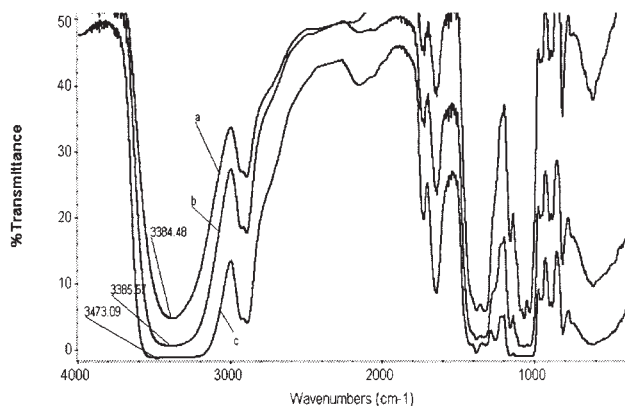


Figure 3 Effect of mass fractions of KGM on the FTIR spectra of composites (mass fraction of KGM: (a) 0.50%; (b) 0.75%; (c) 1.00%. Concentrations of Ag^+ : 0.025 mol L^{-1} . Photochemical reduction time: 60 min).

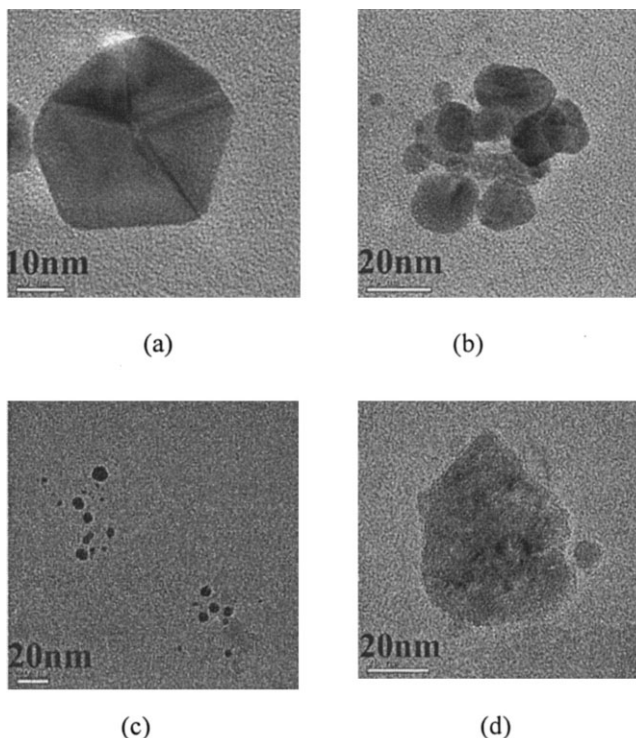


Figure 4 TEM images of KGM/Ag composites. (a): $[\text{Ag}^+] = 0.025 \text{ mol L}^{-1}$, $\omega(\text{KGM}) = 0.50\%$, $t = 60 \text{ min}$; (b): $[\text{Ag}^+] = 0.05 \text{ mol L}^{-1}$, $\omega(\text{KGM}) = 0.50\%$, $t = 60 \text{ min}$; (c): $[\text{Ag}^+] = 0.025 \text{ mol L}^{-1}$, $\omega(\text{KGM}) = 0.50\%$, $t = 30 \text{ min}$; (d): $[\text{Ag}^+] = 0.025 \text{ mol L}^{-1}$, $\omega(\text{KGM}) = 1.0\%$, $t = 60 \text{ min}$.

0.75, and 1.00%, respectively. It can be seen from Figure 3 that the width of both O—H stretching absorption peaks at approximately 3380 cm^{-1} and the bending absorption peak at approximately 1100 cm^{-1} become broader. This phenomenon may be interpreted as follows: because of the higher mass fractions of KGM used, which contain more O—H groups, the stronger interaction occurs between silver particles and O—H groups of polysaccharide may also broaden the absorption peaks.

Morphology of the nanocomposites

Figures 4(a)–4(d) represent the TEM micrographs of the KGM/Ag nanocomposites at different preparation conditions. The images of TEM indicate that Ag nanoparticles are finely dispersed in the KGM films with different shapes, such as sphere-like and star-like, respectively. The average diameters of spherical Ag particles are $9 \pm 4 \text{ nm}$, which is calculated from the diameters of a large number of individual particles. The star-like particles (Fig. 4(a)), with edge lengths of about 20 nm , are larger when compared with the spherical particles. Moreover, the proportion of star-like particles is much lower than that of spherical particles. On one hand, as a kind of polymer, the

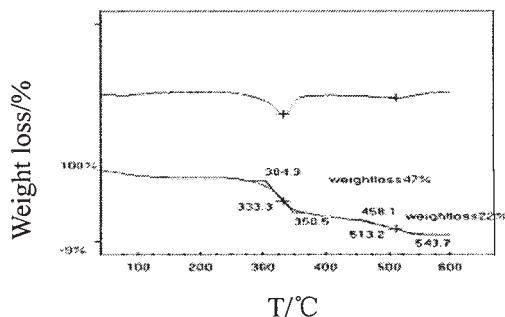


Figure 5 TG curve of KGM film.

thermal motions of chain segments of KGM can increase the chance of coalescing the resultant silver atoms to form small silver particles and then large silver particles. On the other hand, the steric effect of polymeric network of KGM prevents the silver particles from coalescing. Thus, the silver particles are restricted in the range of nanoscale.

However, there are some differences in morphology and distribution of silver particles within the nanocomposites under different preparation conditions. With the increasing concentrations of silver ions, coalescences and lumps of silver particles are present, as shown in Figures 4(a) and 4(b). This phenomenon may be due to the increasing chance of coalescing silver particle with the increasing numbers of silver atoms reduced from silver ions; With the decrease of photochemical reduction time, the sizes of silver particles are small and the shapes of silver particle are spherical, as shown in Figures 4(a) and 4(c). This can be interpreted as follows: on the effect of photoenergy, the resulting silver atoms form oligomeric clusters of larger and larger size via condensation reaction at first and then grow via reduction of silver ions on the surfaces of the clusters whose behavior is like typical colloidal particles or coalescence.¹⁷ Thus, the sizes and shapes of silver particles within the KGM films are different from the different photochemical reduction time; What is more, with the increasing concentrations of KGM, as shown in Figures 4(a) and 4(d), the films are not uniform, with poor distribution of KGM hydrosol inducing the poor film-forming characteristic (as an irregular shape on the copper grid as in Fig. 4(d)), and the sizes of silver particles, which may be difficult to be identified clearly, are small at the same time within the irregular film. (To some extent, this phenomenon also indicates that the increasing number rather than the increasing size of Ag particles might mainly cause the broadening of the IR peaks when the synthesis conditions were changed). Then, nanoscale silver particles in the KGM films with different morphologies can be prepared by controlling the concentrations of KGM, concentrations of silver ion, and photochemical reduction time.

Analysis of TG

Figures 5 and 6 indicate the TG curve of KGM film and that of KGM/Ag nanocomposites, respectively. It can be seen from Figure 5 that there exists an evident weight lost peak at 333.3°C with 47% loss of weight. Whereas there exist the first weight lost peak at 213.4°C with 20% loss of weight and the second one at 334°C with 40% loss of weight. This illustrates that the KGM and KGM/Ag films had remarkably different thermal properties. It may have something to do with the interaction between the O—H groups of KGM and the silver ions.

The mechanism of interaction between KGM and Ag

It is well known that the mechanism of photochemical reduction of silver ions is as follows: since KGM has many OH groups and O atom has unpaired electrons, the orbits of Ag ions, the outermost electron configuration of which is $4d^{10}5s^05p^0$, are sp hybridization without fully filled in general. According to the theory of coordination chemistry, the O—Ag coordination bond is formed where the unfilled orbit of Ag is occupied by the unpaired electron of O. Thus, Ag ions are dispersed uniformly within the KGM polymers. On the effect of photoirradiation, organic radicals are produced at first. Then, the Ag^+ is reduced by organic radical. The Ag atoms form oligomeric clusters of larger and larger size via condensation reactions. Then, Ag particles grow via reduction of Ag^+ or coalescence. The KGM, as a type of polymer stabilizer, can prevent the consultant Ag particles from coalescing to form further larger size because of coordination reactions of silver ions and OH groups of KGM.

CONCLUSIONS

KGM/Ag nanocomposites were prepared *in situ* via photochemical reduction of silver ions. The images of TEM indicated that Ag nanoparticles were finely dispersed in the KGM films with different shapes, such as sphere-like (average diameters of 10–30 nm) and star-

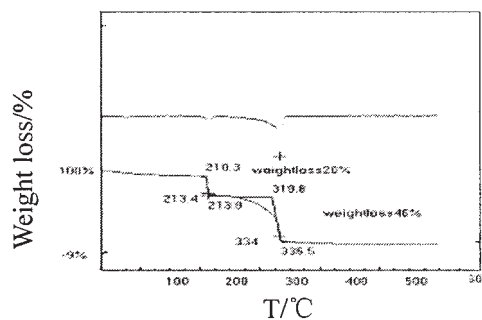


Figure 6 TG curve of KGM/Ag nanocomposites.

like (edge lengths of about 20 nm), respectively. The FTIR spectra of nanocomposites showed that the wavenumbers and the strengths of some characteristic peaks are strongly influenced by the silver nanoparticles. There existed remarkably different thermal properties between KGM and KGM/Ag films. The mechanism of interaction between KGM and Ag is attributed to the coordination of unfilled orbit of silver ion with unpaired electron of oxygen.

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