

## Introduction of Ag and Ag<sub>2</sub>S Nanoparticles into Nylon 6 Film and Fiber

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**ABSTRACT:** Nylon 6 doped with Ag nanoparticles (nylon 6/Ag) was prepared by immersion of nylon 6 in aqueous AgNO<sub>3</sub> solution followed by reductive treatment by heating under H<sub>2</sub> gas or immersing in an aqueous NaBH<sub>4</sub> solution. As a result of either reductions, Ag nanoparticles below 10 nm in diameter were successfully dispersed within the nylon 6 matrix. The Ag content and the dispersion state of the Ag nanoparticles can be varied by the concentration of the AgNO<sub>3</sub> solutions and the reduction methods, respectively. From the results of the absorbed Ag<sup>+</sup> content in nylon 6 *via* immersion in AgNO<sub>3</sub> solution, nylon 6 was found to have some affinity for silver ion. Nylon 6 doped with Ag<sub>2</sub>S nanoparticles (nylon 6/Ag<sub>2</sub>S) was also prepared by immersion in AgNO<sub>3</sub> aqueous solution and the following immersion of Na<sub>2</sub>S aqueous solution. Ag<sub>2</sub>S particles having several nanometers in diameter were dispersed in nylon 6. The nylon 6/Ag<sub>2</sub>S film showed strong photoluminescence in the near infrared region.

**KEY WORDS** Nylon 6 / Ag / Ag<sub>2</sub>S / Nanocomposite / Nanoparticle /

Organic/inorganic composite materials consisting of polymers doped with metal or semiconductor nanoparticles, which possess characteristic optical properties, such as non-linear optical and laser amplification properties, have attracted increasing interest for potential application as novel photonics devices.<sup>1-4</sup> In contrast to inorganic matrices such as glasses or ceramics, the use of organic polymers as a matrix has the advantages of processability and ease of handling of the composite materials.<sup>2</sup> Specifically, the polymer matrices can be molded at lower temperatures, are generally flexible, and show higher toughness than inorganic matrices. Furthermore, various inorganic compounds for doping components can be readily introduced in the polymer matrices using *in-situ* reactions under mild conditions.<sup>2</sup>

Some of the authors have previously reported on the preparation and characterization of Au nanoparticles dispersed within nylon 11 thin films using the thermal relaxation technique.<sup>5-7</sup> Their methodology relied on consecutive evaporations of the polymer and Au, with a subsequent heat treatment at temperatures above the glass transition temperature of a matrix polymer. Using similar techniques, Ag nanoparticles in nylon 11 (nylon 11/Ag) composite films have been prepared.<sup>6,8,9</sup> Similarly as that of Au nanoparticles, it is well known that Ag nanoparticles possess interesting optical properties: for example, surface plasmon resonance (SPR) in the state of nanoparticle.<sup>6,8-12</sup> Additionally, Ag nanoparticles in nylon 11/Ag can be converted into Ag<sub>2</sub>S nanoparticles by exposing to a mix-

ture of H<sub>2</sub>S and O<sub>2</sub> gases.<sup>8</sup> As a note, Ag<sub>2</sub>S is a desirable semiconductor with photoimaging and photodetection properties,<sup>13</sup> photoluminescence,<sup>14</sup> and super ionic conductivity by mixing with silver iodide.<sup>15</sup> In the thermal relaxation process, it has been shown that nanoparticles of noble metals such as Au, Ag, Pt, and Pd can penetrate into nylon 11, but not into nonpolar polymer matrices such as polyethylene.<sup>16</sup> This difference implies that the polar amide groups of nylon 11 play an important role in allowing the penetration of the metal particles within the polymer matrix. In addition, the existence of interactions between the polyamides and Ag metal nanoparticles has been noted in some papers. Yamaguchi *et al.* reported the stabilization (at least 6 months) of Ag nanoparticles in nylon 11/*m*-cresol solutions without any aggregation and precipitation.<sup>17</sup> Manna *et al.* showed that the wavenumbers of amide II and III bands of poly(amido amine) dendrimer were changed by introduction Ag nanoparticles in FT-IR results.<sup>18</sup>

It is advantageous, therefore, to utilize polyamides as a dispersive media of metal nanoparticles. Herein, we report on a simple technique for the preparation of nylon 6 composites containing Ag or Ag<sub>2</sub>S nanoparticles, along with their structural and optical properties.

### EXPERIMENTAL

#### *Preparation of Composites*

Commercially available nylon 6 film (thickness, 15 μm) and fiber (diameter, 300 μm) were supplied by

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Unitika Co., Ltd. AgNO<sub>3</sub>, NaBH<sub>4</sub>, and Na<sub>2</sub>S·9H<sub>2</sub>O were purchased from Wako Pure Chemical Co., Ltd.

For the preparation of Ag nanoparticles in nylon 6 (nylon 6/Ag), nylon 6 was immersed in aqueous AgNO<sub>3</sub> solutions of prescribed molar concentrations at room temperature for 2 h. Subsequently, Ag<sup>+</sup> ions that absorbed within nylon 6 were reduced to Ag metal by heat treatment at a constant temperature for 30 min under a flow of H<sub>2</sub> gas or by NaBH<sub>4</sub> as a reducing agent. For the preparation of Ag<sub>2</sub>S nanoparticles in nylon 6 (nylon 6/Ag<sub>2</sub>S), nylon 6 films were immersed in an aqueous AgNO<sub>3</sub> solution, then placed in an aqueous Na<sub>2</sub>S·9H<sub>2</sub>O solution (10% w/w) at room temperature for 2 h, and finally washed several times with distilled water.

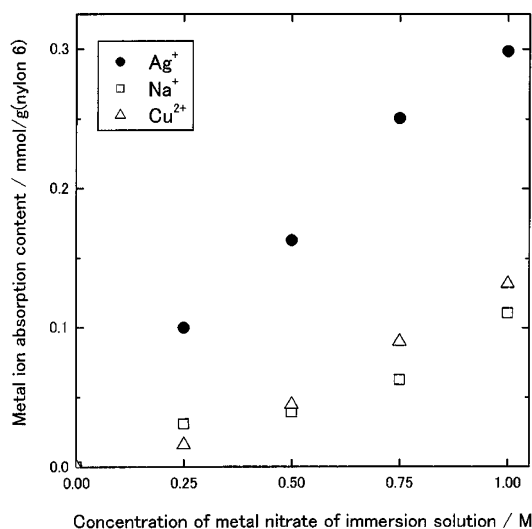
### Measurements

Atomic absorption analysis was carried out using a Hitachi A-1000 in order to quantify the metal content in the nylon 6 films. Transmission electron microscopy (TEM) analysis was performed using a JEOL JEM-2010 transmission electron microscope operating at 200 kV. A thin section (*ca.* 100 nm in thickness) for the TEM studies was obtained by the conventional microtome technique. Ultraviolet-visible (UV-vis) absorption spectroscopy was carried out using a Hitachi U-3500 UV-VIS-NIR recording spectrophotometer.

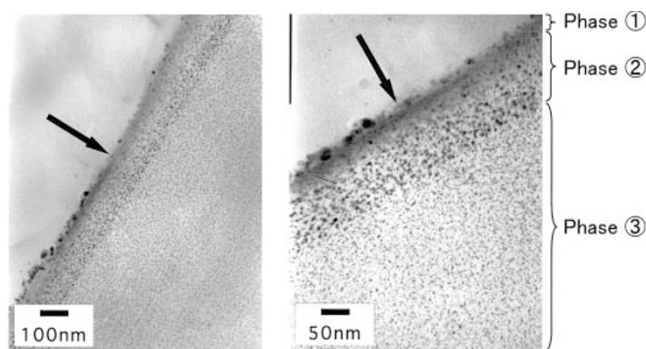
## RESULTS AND DISCUSSION

### Nylon 6/Ag Composites

Since it is well known that silver nitrate can coagulate proteins, and that Ag<sup>+</sup> ions have an affinity for polypeptides,<sup>19</sup> it was expected that the amide groups of nylon 6 will show some interactions with the Ag<sup>+</sup> ions. The absorbed metal ion content in nylon 6 films was determined after 1 h immersions in aqueous solutions of different metal nitrates at various concentrations. As shown in Figure 1, increased absorbed ion contents were observed with higher concentrations of the metal nitrates of the solutions. It must be noted that nylon 6, when immersed in ionic aqueous solutions, can contain several percentage of water that could introduce the metal ions. It is also evident from Figure 1 that nearly equivalent molar quantities of Na<sup>+</sup> and Cu<sup>2+</sup> ions were absorbed, whereas the quantity of Ag<sup>+</sup> ions was more than two-fold that of other ions. Although this selectivity may indicate the existence of interactions between Ag<sup>+</sup> ions and nylon 6, it is important to note that the interactions are not very significant, since the Ag<sup>+</sup> ions can be almost entirely removed from the film by washing with distilled water for only 20 s. Ag<sup>+</sup> ion was found to disperse homogeneously within a film,



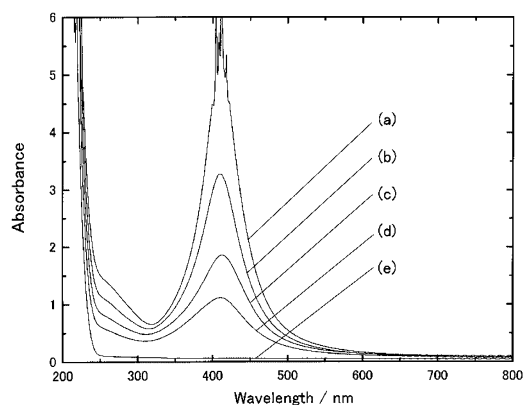
**Figure 1.** Absorbed metal ion content in nylon 6 film after immersion in aqueous solutions of different metal nitrates at various concentrations for 1 h.



**Figure 2.** Cross-sectional TEM images of the nylon 6/Ag film under various magnifications.

which was confirmed from elemental mapping analysis of Ag by an energy dispersive X-Ray analyzer.

Upon heat treatment at a certain constant temperature above 70 °C under a flow of H<sub>2</sub> gas, the color of the Ag<sup>+</sup>-absorbed nylon 6 films changed from colorless to transparent yellow or brown, showing the occurrence of SPR of Ag metal nanoparticles. The formation of Ag metal was confirmed by X-Ray diffraction. In this case, H<sub>2</sub> acted as the reducing agent for the Ag<sup>+</sup> ions. The heat treatment temperature of 70 °C agreed with the softening temperature of nylon 6 investigated by dynamic elastic mechanical analysis, and the color of the films grew rich with increase of heat treatment temperature. This may indicate that there is the relation of the reduction of Ag<sup>+</sup> with thermal molecular motion of nylon 6. The cross-sectional TEM images of the nylon 6/Ag film under various magnifications are shown in Figure 2 (arrows indicate the surface of the composite film). The composite films were prepared by immersion in an aqueous 1 M AgNO<sub>3</sub> solution, followed by heat treatment at 100 °C under a flow of H<sub>2</sub>

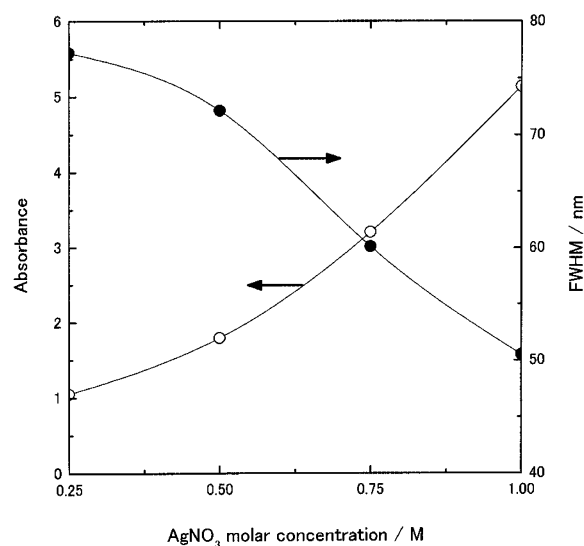


**Figure 3.** UV-vis spectra of nylon 6/Ag films prepared from immersion in solutions with  $\text{AgNO}_3$  concentrations of (a) 1 M, (b) 0.75 M, (c) 0.5 M, (d) 0.25 M, and (e) neat nylon 6.

gas for 30 min. Ag particles with diameters that are sufficiently small for exhibiting SPR absorption were dispersed within the composite. Absorbed  $\text{Ag}^+$  ion of 83% in the nylon 6 film was remained after reduction to Ag particles. As shown in Figure 2, three phases were observed for the film: phase ①, which is dark and contains significant amounts of Ag metal that can be considered as a thin continuous layer of Ag metal; phase ② which is the inner *ca.* 100 nm region of the film surface and contains larger Ag particles (*ca.* 5–10 nm) with a relatively wide size distribution, and phase ③, which is the inner part of the film consisting of homogeneously dispersed smaller particles (*ca.* 3 nm) with a narrow size distribution. The formation these phases can be attributed to the difference in the degree of penetration of  $\text{H}_2$  between the surface and inner part of the film. Since  $\text{H}_2$  gas can penetrate more readily at the film surface than at the interior of the film, the reduction of  $\text{Ag}^+$  ions to Ag metal proceeds faster resulting in the reduction of more  $\text{Ag}^+$  ions and the growth of Ag particles at the film surface. Alternately, the formation of the phases can be attributed to the initial skin phase on the film surface. Since the nylon 6 films were prepared by biaxial stretching, their surfaces are comparable to the sheath-and-core structures that are observed in well-stretched fibers. However, our results are inconclusive, and further studies to investigate the mechanisms of formation are currently underway.

The UV-vis spectra of the nylon 6/Ag films prepared by immersion in aqueous solutions at different  $\text{AgNO}_3$  concentrations are shown in Figure 3. Typically, the absorption maximum for the SPR peak of Ag nanoparticles in films are observed at 410 nm.<sup>6, 8–12</sup> Accordingly, the observance of SPR peaks indicated that the size of the Ag nanoparticles are much smaller than the mean free path of the electrons in bulk silver (*ca.* 52 nm),<sup>20</sup> as shown in Figure 2.

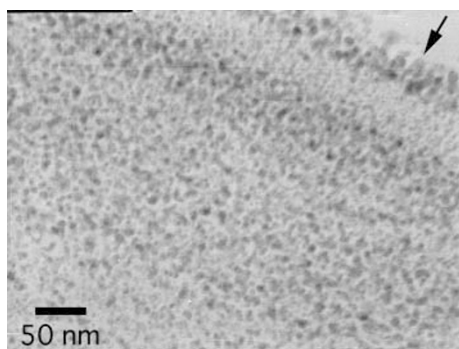
The dependences of the absorbance and full widths



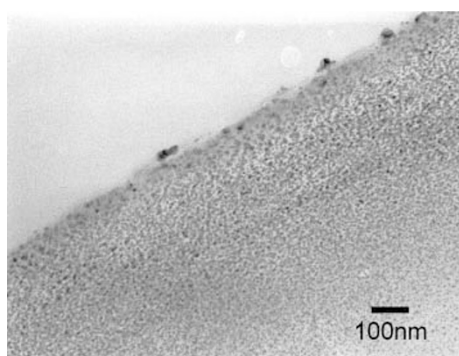
**Figure 4.** Dependences of absorbances and full widths at half-maximum (FWHM) of the SPR peak of Ag nanoparticles on the concentrations of the  $\text{AgNO}_3$  solutions.

at half-maximum (FWHM) of the SPR peaks (Ag nanoparticles obtained from Figure 3) on the concentrations of the  $\text{AgNO}_3$ -immersion solutions are shown in Figure 4. A correlation between higher  $\text{AgNO}_3$  concentrations of the immersion solution and greater absorbances of the SPR peaks indicates that exposure of the nylon 6 film to  $\text{AgNO}_3$  solutions with high concentrations can introduce larger amounts of Ag nanoparticles into nylon 6 matrix. Accordingly, the amount of Ag particles introduced in the nylon 6 film can be controlled by the concentration of the  $\text{AgNO}_3$  immersion solution. The FWHM of the absorption band decreased with higher concentrations of the  $\text{AgNO}_3$  solution. The wavelength of the SPR peak maximum for each spectrum was almost comparable regardless of the concentrations of the  $\text{AgNO}_3$  solution. Kreibig and Fragstein have determined the spectral peak positions and FWHMs of the theoretical absorption curves of Ag particles embedded in a glass matrix taking into account the mean free path effect.<sup>20</sup> Their results show that the peak positions are constant if the particles diameters are between 4 and 15 nm, and that the FWHM decreases with increasing particle diameters (below *ca.* 20 nm). Thus, the decrease of FWHMs in Figure 4 with higher concentrations of the  $\text{AgNO}_3$  solutions can be explained as the increasing diameters of the Ag nanoparticles within the composite.

The cross-sectional TEM image of an nylon 6/Ag fiber that was prepared by immersion in an aqueous 1 M  $\text{AgNO}_3$  solution and then in an aqueous  $\text{NaBH}_4$  (5% w/w) solution at room temperature is shown in Figure 5.  $\text{NaBH}_4$  is a strong reducing agent and readily reduced  $\text{Ag}^+$  ion to Ag metal. In this figure, the Ag nanoparticles were localized on the surface of the



**Figure 5.** Cross-sectional TEM image of nylon 6/Ag fiber.



**Figure 6.** Cross-sectional TEM image of nylon 6/Ag<sub>2</sub>S film.

fibers. Introduction of Ag nanoparticles on the surface of the materials led to excellent antibacterial activities against *Staphylococcus aureus* and *Klebsiella pneumoniae*.<sup>21</sup> The formation of localized Ag nanoparticles can be explained by the highly mobile Ag<sup>+</sup> ions, which can readily migrate to the film surface in nylon 6 matrix plasticized with water and react with NaBH<sub>4</sub> at the interface between the film and the aqueous NaBH<sub>4</sub> solution. This reduction using NaBH<sub>4</sub> is a relatively simple procedure, with a beneficial effect on the localization of Ag nanoparticles in the surface area of nylon 6 fibers and films.

#### Nylon 6/Ag<sub>2</sub>S Composites

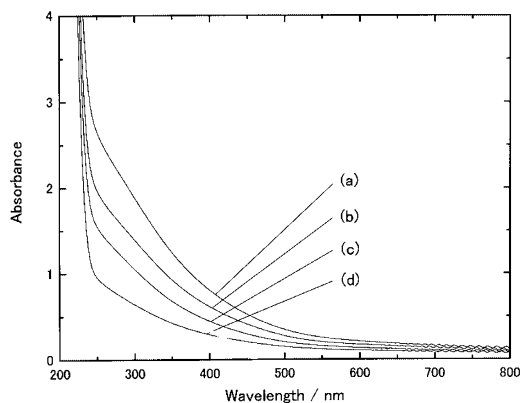
When the Ag<sup>+</sup>-absorbed nylon 6 films were immersed in aqueous AgNO<sub>3</sub> solutions at different concentrations, followed by an aqueous sodium sulfide solution, the color of the films changed from colorless to pale brown or brown. The cross-sectional TEM image of the nylon 6/Ag<sub>2</sub>S film is shown in Figure 6 (arrow indicates the film surface). The composite film in this figure was prepared by immersion of nylon 6 films in an aqueous 1 M AgNO<sub>3</sub> solution, followed by immersion in an aqueous Na<sub>2</sub>S · 9H<sub>2</sub>O solution (10% w/w) at room temperature for 2 h. The formation of β-Ag<sub>2</sub>S, which is the stable crystal form at room temperature, was confirmed using X-Ray diffraction measurements and X-Ray photoelectron spectroscopy. It is, therefore,

reasonable to suggest that most of the Ag<sup>+</sup> ions absorbed in nylon 6 reacted with the S<sup>2-</sup> ions and were deposited as spherical β-Ag<sub>2</sub>S particles within the composite. Absorbed Ag<sup>+</sup> ion of 70% in the nylon 6 film was remained after the sulfuration to Ag<sub>2</sub>S. The Ag<sub>2</sub>S particles were dispersed within the composite with a gradient density; specifically, the number of particles decreases gradually from the film surface, in which the particles exist densely in the vicinity of the film surface. The Ag<sub>2</sub>S particles near surface of the film have diameters of ca. 5–10 nm with a relatively wide size distribution, whereas smaller particles (below 5 nm) are found inside the film. The gradient distribution of the Ag<sub>2</sub>S particles may be attributed to the sulfuration of Ag<sup>+</sup> ions in the aqueous Na<sub>2</sub>S solution, in which the H<sub>2</sub>O molecules in the solution enables the Ag<sup>+</sup> ions to migrate to the surface of the film to facilitate the subsequent sulfuration of the Ag<sup>+</sup> ions by Na<sub>2</sub>S. The growth of the Ag<sub>2</sub>S particles can, therefore, occur more readily in the vicinity of the surface than the inner part of the film.

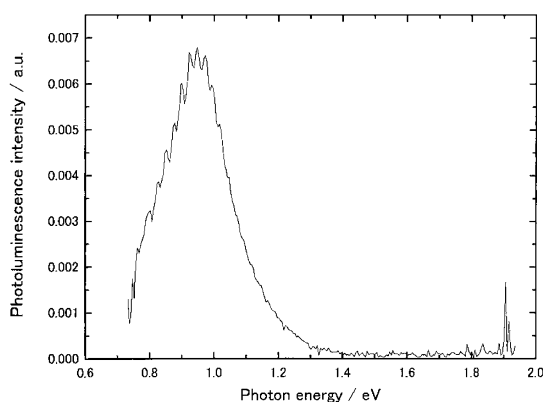
The UV-vis spectra of the nylon 6/Ag<sub>2</sub>S films prepared from immersions at various AgNO<sub>3</sub> concentrations are shown in Figure 7. The absorption intensities were dependent on the concentrations of the AgNO<sub>3</sub> solutions. The shapes of the absorption spectra were similar to those of β-Ag<sub>2</sub>S nanoparticles in nylon 11.<sup>16</sup> As a note, Ag<sub>2</sub>S is a semiconductor with an optical band gap of 0.9–1.1 eV, and can be used as an adsorber layer in thin film solar cells.<sup>22–24</sup> Absorption edge in the shorter wavelength region was due to electron transition from the valence band towards the conduction band. The interband transition was essentially a charge transfer from 3p(S) to 5s(Ag).<sup>14</sup> Estimation was unsuccessful in obtaining values for the optical band gap energy of the Ag<sub>2</sub>S particles from the absorption data, shown in figure 5, because of the interference fringes of visible lights at wavelengths above 650 nm, which was caused by the uniform thickness of the nylon 6 film.

The photoluminescence spectrum of the nylon 6/Ag<sub>2</sub>S film prepared from aqueous 1 M AgNO<sub>3</sub> solution is shown in Figure 8. Photoluminescence spectrum was measured using Ar laser (488 nm, 20 mW) as the excitation light. Strong fluorescence was observed and the photon energy at the peak maximum was ca. 0.95 eV, which corresponded to ca. 1310 nm. The peak width was relatively wide indicating a wide size distribution of the Ag<sub>2</sub>S particles, as supported by the TEM results.

The methodology described in this study is relatively simple and can be applicable for the preparation of polymer/inorganic nanocomposites. Furthermore, this method could be applied for the preparation of other



**Figure 7.** UV-vis spectra of nylon 6/Ag<sub>2</sub>S films prepared from immersion in solutions with AgNO<sub>3</sub> concentrations of (a) 1 M, (b) 0.75 M, (c) 0.5 M, and (d) 0.25 M.



**Figure 8.** Photoluminescence spectrum of nylon 6/Ag<sub>2</sub>S film prepared from aqueous 1 M AgNO<sub>3</sub> solution.

semiconducting silver halogenides, such as AgCl and AgBr, in nylon 6 films.

## CONCLUSIONS

Simple methodologies were developed for the preparation of nylon 6 composite films containing Ag and Ag<sub>2</sub>S nanoparticles. Nylon 6/Ag composite films were prepared by reduction of Ag<sup>+</sup> ions to Ag metal using H<sub>2</sub> or NaBH<sub>4</sub> as reducing agents. The Ag nanoparticles in the composite were formed with larger particles distributed near the film surface, while relatively smaller particles were located in the inner parts the film. For nylon 6/Ag<sub>2</sub>S composites, β-Ag<sub>2</sub>S nanoparticles were formed by the sulfuration of Ag<sup>+</sup> ions with Na<sub>2</sub>S. The particles were dispersed densely in the vicinity of the film surface, with the number of the particles decreasing gradually away from the film surface. Nylon 6/Ag<sub>2</sub>S film exhibited a strong photoluminescence peak at around 1310 nm.

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