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Research Article

Synthesis of Photochromic AgCl-Urethane Resin Composite Films

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AgCl-resin photochromic composite films were prepared using $AgNO_3$, HCl-EtOH, $CuCl_2$ solution, and a liquid-state urethane resin as starting materials. The obtained composite films showed a photochromic property. The rate of darkening of the composite film increased after mixing with $CuCl_2$. The AgCl particle size in the film without heat treatment was 6–20 nm, and that of the heat-treated film was 25–80 nm; these results were confirmed using TEM observations. The fading rate of the film without heat treatment was higher than that of the heat-treated films.

1. Introduction

A glass substrate doped with silver halide shows a photochromic property [1, 2]. This phenomenon is effective for controlling the transmittance of solar light through glass win-dows. To form a photochromic glass window, glass is fused at temperatures higher than 1,300–1,500°C and shaped. Then the precursor glass must be annealed at 550–700°C to deposit silver halide microcrystals from the homogeneous glass. For that reason, it is difficult to produce large flat glass sheets economically. In addition, the resulting photochromic glass is heavy. Consequently, the use of photochromic glasses is limited. However, photochromic materials containing AgCl nanoparticles have been fabricated not as glasses, but as films [3] and hybrid materials [4].

Previous reports have described studies of light-selective composite films: an ITO-urethane resin IR-opaque composite film [5], a ZnO-urethane resin UV-opaque composite film [6], and a VO_2-resin thermochromic composite film [7]. To synthesize a composite film, a fabrication process is advantageous for synthesizing glasses because of its lower temperature process. Furthermore, the resulting composite film is very lightweight. Therefore, the authors attempted to fabricate a photochromic composite film in this study.

In this investigation, a urethane resin was used as a matrix, with $AgNO_3$ and HCl-ethanol used as fillers, and AgCl-urethane resin photochromic composites fabricated using these starting materials. Liquid type urethane resin shows a photocuring property, and the cured urethane resin shows high transmittance at the visible wavelength region. The photochromic property of the resulting composite films was evaluated. Then, using Cu (the source of $CuCl_2$) as a sensitizer, a composite film was synthesized. The photochromic property of the composite was investigated with and without the Cu sensitizer.

2. Experimental

$AgNO_3$ (99.5%; Wako Pure Chemical Industries Ltd., Osaka, Japan), HCl-EtOH (0.1 mol/L; Sigma-Aldrich Japan K. K., Tokyo, Japan), $CuCl_2$ (95%; Wako Pure Chemical Industries Ltd., Osaka, Japan), and a liquid state urethane resin (M-40, density of 1.15 g/cm^3; Asahi Kasei Chemicals Corp., Tokyo, Japan) were used as starting materials. $AgNO_3$ powder was dissolved into ethanol at a concentration of 0.1 mol/L, and $CuCl_2$ powder was dissolved into the solution at a Cu/Ag ratio of 0.1. The prepared solution was mixed with a liquid urethane resin, and HCl-EtOH solution was added sequentially to the mixture solution. The preparation conditions are presented in Table 1. These mixtures were stirred well. Then the precursor solution was prepared. The mixture was degassed for 30 min. Then the mixture was formed to 1 mm thickness using slide glasses. The precursor films were cured using UV-light irradiation, thereby producing composite

Table 1: Synthesis conditions of AgCl-resin photochromic composite films.

Sample	Urethane (g)	$AgNO_3$-EtOH (0.1 mol/L, mL)	HCl-EtOH (0.1 mol/L, mL)	$CuCl_2$-EtOH (0.1 mol/L, mL)	Heat treatment
1	20	1.0	1.0	—	Yes
2	20	1.0	1.0	0.1	Yes
3	20	1.0	1.0	0.1	No

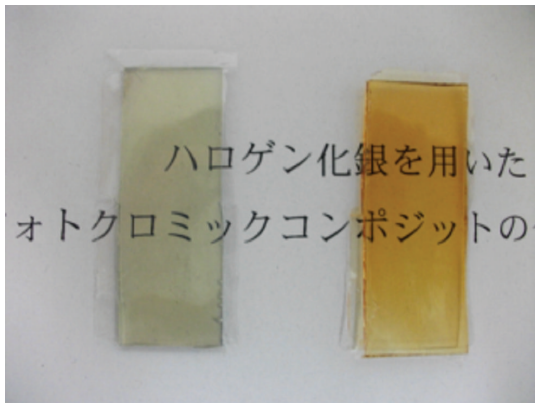

Figure 1: Photographs of composite films (Sample 1 in Table 1) before and after UV irradiation.

films. Furthermore, to confirm heat treatment effects, heat treatment of the composite films was conducted at 120°C for 10 min using a hotplate.

Transmittance of the obtained composite film was measured using a spectrophotometer (UV-1600; Shimadzu Corp.) at a wavelength range of 200–1,100 nm. To evaluate the photochromic property, transmittance measurements were conducted using UV-visible light irradiation of the resulting films. The microstructure and the composite film particles were observed using transmission electron microscopy (TEM, EM-002B; Topcon Corp.).

3. Results and Discussion

The as-prepared films were brown because the precursor films had been cured by UV-light irradiation and the composite film was colored. The darkened films faded with heat treatment at 120°C for 10 min. The resulting transparent films were used to evaluate the photochromic property. The films were irradiated by UV-light and become dark. Then their photochromic properties were observed. Figure 1 presents photographs of the composite films before and after UV irradiation. The fabrication conditions of the sample were those of sample number of "1" in Table 1. Hereinafter, sample number "n (integer)" signifies the sample number shown in Table 1. As the photograph shows, the transparent composite film was colored by UV irradiation. Therefore, the resulting composite film shows a photochromic property.

Two composite films were prepared with or without $CuCl_2$ as the sensitizer. The samples were "1" and "2" presented in Table 1. Figure 2(a) shows the dependence of the transmittance on UV-light irradiation time at 420 nm wavelength. For 10 min UV irradiation, the transmittance of the composite film without adding $CuCl_2$ (Sample 1) decreased from 50% to 10%. However, that of the Cu-added film (Sample 2) varied from 50% to 0% for 4 min. The rate of darkening of the film containing copper was much higher than that without the Cu-containing film. In general, for photochromic glass, Cu_2O or CuO was used as the sensitizer [2, 8]. However, the photosensitivity rate of the synthesized composite films in this study was increased by mixing $CuCl_2$ as the sensitizer. These results show that $CuCl_2$ is useful as a sensitizer for the preparation of composite films.

Figure 2(b) presents the fading property of the colored composite films. The fading rate of the composite film without added copper was very low: the composite film with copper retained transmittance of 0% even after 1 month.

Precursor composite films were synthesized with $AgNO_3$, HCl-EtOH, and $CuCl_2$. To evaluate the heat-treatment effect, a film was prepared without heat treatment (Sample 3 in Table 1). The as-prepared film was faded in a dark room for 1 week. Figure 3 shows the photochromic property of the as-prepared and heat-treated films. The darkening properties of both films were very similar, and the transparent films became colored during 10 min UV irradiation. The transmittance of the colored composite film with heat treatment faded by 10%–30% during 1 week, and the no-heating film faded by 10%–60% in 5 days. The fading rate of the film without heat treatment was much higher than that of the film with heat treatment.

Figures 4(a) and 4(b) portray TEM bright field images of as-prepared and heat-treated composite films. The TEM images show that the AgCl particle size in the as-prepared film was 6–20 nm, and that in the heat-treated film was 25–80 nm. In general, the particle size range of AgCl in photochromic glasses is 5–30 nm [8]. The AgCl particle sizes of the composite films without heat treatment were close to the AgCl size of the photochromic glasses. Therefore, the coloring and the fading rates of the films without heat treatment were higher than those of the heat-treated films.

4. Conclusion

Photochromic composite films were synthesized with silver chloride particles dispersed in a urethane resin matrix using $AgNO_3$, HCl, and $CuCl_2$ ethanol solutions. The rate of darkening for the film containing $CuCl_2$ was higher than that of films without $CuCl_2$, which shows that $CuCl_2$ in the AgCl-composite film acted as a sensitizer. The rate of fading of the film without heat treatment was higher than that of the heat-treated films. The particle size of the film without heat treatment was 6–20 nm, which is similar to the microcrystal

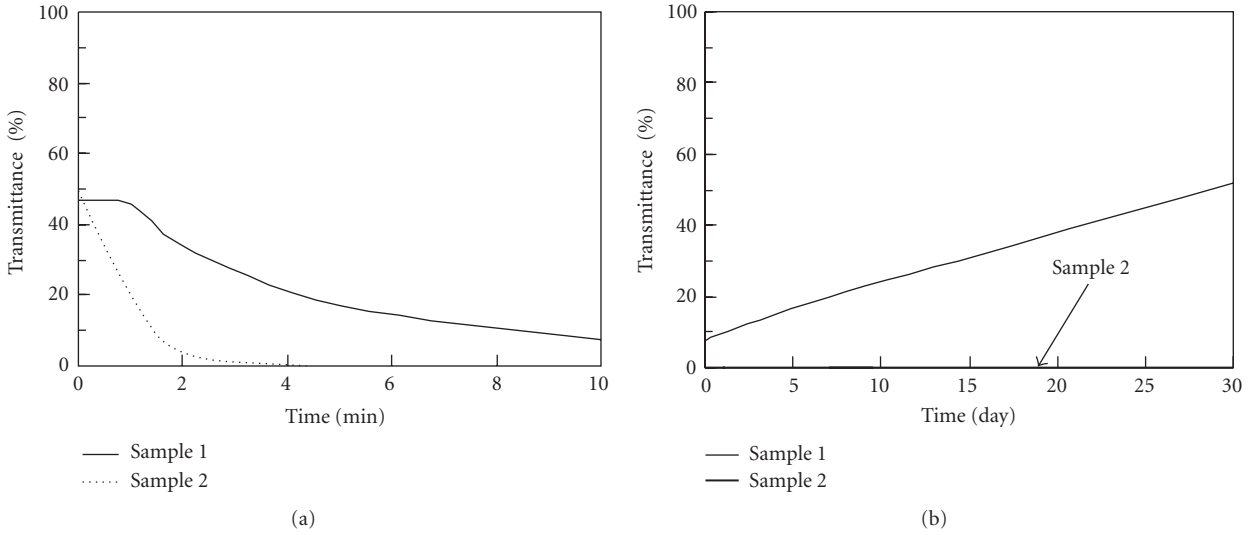

Figure 2: Time dependence of the transmittance of the films with (Sample 2) and without (Sample 1) $CuCl_2$, at 420 nm wavelength. (a) shows the darkening property. (b) shows the fading property.

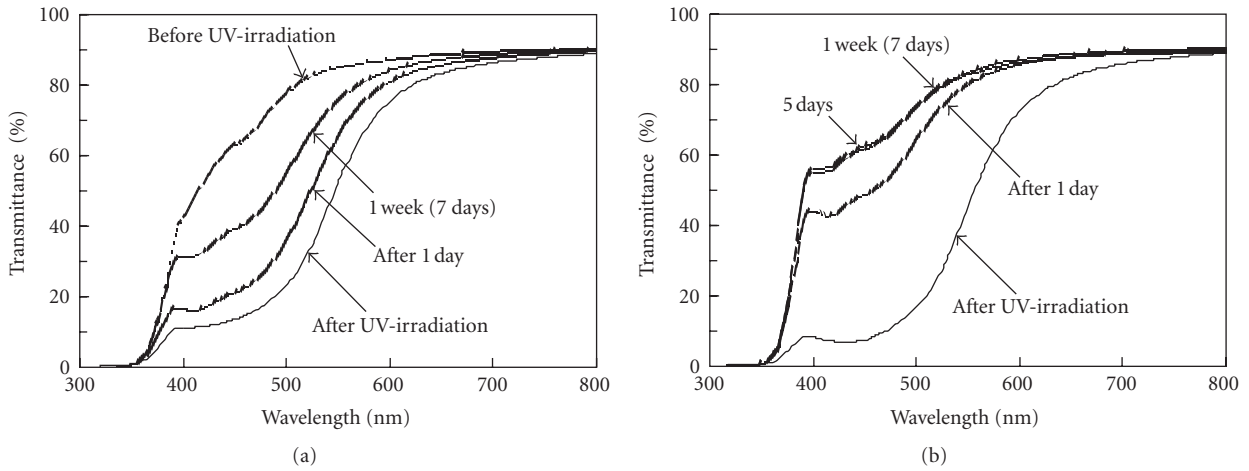

Figure 3: Photochromic property of the (a) heat-treated (Sample 2) film and the (b) as-prepared (Sample 3) film.

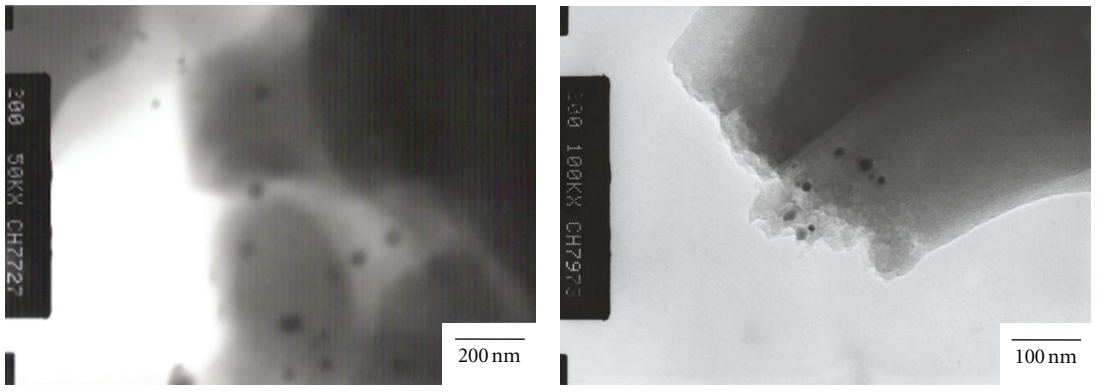

Figure 4: TEM image of (a) the heat-treated (Sample 2) and (b) the as-prepared (Sample 3) films.

size of the AgCl photochromic glass. Therefore, it is inferred that the coloring and the fading rates of the films without heat treatment were higher than those of the heat-treated films.

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