Special Feature: Applied Nanoscale Morphology

Fabrication of Polymer-immobilized Colloidal Crystal Films

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ABSTRACT A fabrication method for polymer-immobilized colloidal crystal films using conventional spray coating has been developed for application of the films as practical colored materials. By controlling both the viscosity of the silica sphere-acrylic monomer dispersions and the wettability of the substrates, colloidal crystalline films with brilliant iridescent colors were successfully obtained by spray coating and UV curing. The color could be controlled by adjusting both the sphere concentration and diameter. Scanning electron microscopy was applied to study the crystal structure of the coated films, and revealed that the films are composed of highly oriented face-centered-cubic grains with (111) planes parallel to the substrate surface. A method for utilizing the colloidal crystal films as pigments was also proposed. Flakes obtained by crushing the colloidal crystal coated films were added to a commercial clear paint and coated on a substrate. The coated films exhibited iridescent colors that varies with viewing angle.

KEYWORDS Colloidal Crystal, Self-assembly, Silica, Polymeric Material, Spray Coating

1. Introduction

Jewels such as diamonds and rubies are beautiful, attracting the attention of people worldwide. Most of these are natural minerals with crystalline structures. Opals, the birthstone for October, are categorized as amorphous structures consisting of silica spheres self-assembled in three-dimensional periodic arrays in nature, and have an appeal different from other jewels because they exhibit iridescent colors. The colloidal crystals featured in this paper and explored in this work are called artificial opals, since they also consist of self-assembled monodispersed spheres and show beautiful iridescent colors. Colloidal crystals have become an important research area for application in photonics, optoelectronics, chemical and biological sensors as well as colored materials. Colloidal crystals could be used in more applications if they could be fabricated as coating films for use in conventional painting. In this paper, we report the fabrication of polymer-immobilized colloidal crystal films using a conventional spray coating method.

2. General Fabrication Methods for Colloidal Crystal Films

Colloidal crystals are three-dimensional periodic arrays of monodispersed sub-micrometer sized spheres. They exhibit iridescent colors due to Bragg diffraction of visible light when they have a periodicity on the scale of the wavelength of the light. The most common form of colloidal crystals is that formed in a water dispersion of monodispersed silica or polystyrene spheres. Periodic arrays of the spheres are assembled in the dispersion by eliminating impurity ions using an ion-exchange resin. The colloidal crystals formed in this manner, however, are unfit for use as practical materials because they are easily destroyed by stirring the dispersion. Gel immobilization of the colloidal crystals has been tried by partially replacing water with gel forming agents. However, it is still difficult to use gel-immobilized colloidal crystals in practical applications, because the structures tend to change with water evaporation.

Aside from colloidal crystals formed in dispersions, close-packed colloidal crystals fabricated by gravitational sedimentation of spheres in dispersions and by evaporation-induced capillary forces have also been studied. In addition, close-packed colloidal crystals are not strong enough to be used as practical materials. Several methods to increase the strength have therefore been proposed, including infiltration of resin into the spaces between spheres and thermal adhesion of polymer shells of core-shell spheres.
3. Polymer-immobilized Colloidal Crystal Films

Several methods for forming polymer-immobilizing colloidal crystals have been reported, including the above method using core-shell spheres. One of the methods is spin-coating of acrylic monomer dispersions of silica spheres, reported by Jang and McFarland, the main feature of which is rapid fabrication of polymer-immobilized colloidal crystal films with sizes on the order of centimeters. In addition, the Bragg wavelength can be controlled through the sphere concentration as well as the sphere diameter. The paper states that the ordered structure is induced by the shear force during spin-coating. However, the form and size of the substrate are restricted by the spin-coating apparatus, that is, the form is required to be flat and the size is limited to the order of several tens of centimeters in the conventional apparatus. Compared to spin-coating, conventional spray-coating using a handheld air-spray gun can be applied to curved surfaces and is not restricted in terms of substrate size. We attempted spray coating of acrylic monomer dispersions and we were able to successfully obtain polymer-immobilized colloidal crystal films with brilliant iridescent colors.

4. Spray-coating Fabrication of Polymer-immobilized Colloidal Crystal Films

4. 1 Preparation of Colloidal Dispersions

Monodispersed silica spheres with diameters of 150 and 200 nm were purchased from Nippon Shokubai as dry powder. Ethoxylated trimethylolpropane triacrylate (ETPTA) and tetraethylene glycol diacrylate (TEGDA) were obtained from Toagosei and Shin-Nakamura Chemical, respectively. Colloidal dispersions were prepared by dispersing the silica spheres (40 or 50 wt%) in ETPTA or TEGDA monomer using ultrasonication until they showed iridescent colors. Ethanol (5 and 10 wt%) was added to the silica-ETPTA dispersions to control their viscosity. The viscosity of the colloidal dispersions was measured with a rheometer (TA Instruments, ARES) at 25 °C, because paint viscosity in spray coating is an important parameter. Darocur 1173 provided by Toyotsu Chemical was added as a photoinitiator to the colloidal dispersions (0.5 wt%) prior to spray coating. The dispersion was fed into a handheld air-spray gun (Anset Iwata, W-71-1S) by suction and ejected toward the substrate (located high at low shear rates but decreases with increasing shear rate. In silica-ETPTA dispersions, the viscosity was reduced by adding ethanol over the whole range of shear rates investigated. On the other hand, the silica-TEGDA dispersion had a similar viscosity to the silica-ETPTA-ethanol (10 wt%) dispersion at high shear rates without adding ethanol.

4. 2 Preparation of Substrates

The wettability of substrates to paint is also one of the important parameters in spray coating, because sprayed droplets do not form a film on a substrate with poor wettability due to shedding of the droplets. The substrates used in this study were steel plates (70 × 150 mm²) painted black with melamine resin paint in order to clearly observe the colors of the colloidal crystal films prepared by spray coating. The substrates were washed with a neutral detergent and then rinsed in water, yielding a contact angle of around 30° for the silica-ETPTA dispersion. The wettability was improved by UV irradiation using an UV/ozone cleaner (Sen Lights Corporation, PL16-110). The substrates were irradiated for 15 min immediately prior to spray coating, and the contact angle subsequently decreased to less than 5°.

4. 3 Spray Coating of the Dispersions on the Substrates

Figure 1 shows the shear rate dependence of the viscosity for (40 wt%) 200 nm silica spheres-ETPTA (or TEGDA) dispersions. All the dispersions exhibited pseudoplastic flow, wherein the viscosity is extremely high at low shear rates but decreases with increasing shear rate. In silica-ETPTA dispersions, the viscosity was reduced by adding ethanol over the whole range of shear rates investigated. On the other hand, the silica-TEGDA dispersion had a similar viscosity to the silica-ETPTA-ethanol (10 wt%) dispersion at high shear rates without adding ethanol.

Fig. 1 Shear rate dependence of viscosity of (40 wt%) 200 nm silica-ETPTA (or TEGDA) dispersions with and without ethanol.
25 cm from the gun) at an air pressure of 0.3 MPa. By scanning the gun several times over the substrate, a wet colloidal dispersion film with a thickness of about 35 μm was typically obtained. After the spray coating, the coated surfaces were maintained in a horizontal position for 10 – 30 min. This procedure is important for leveling the coated surface and inducing self-assembly of the silica spheres. The substrates were then transferred to a glove box with a nitrogen atmosphere and exposed to UV radiation from a high-pressure mercury lamp for 1 min to polymerize the acrylic monomers.

Figure 2 shows photographs of the colloidal crystal films obtained by spray coating of (40 wt%) silica-ETPTA dispersions with (5 and 10 wt%) and without ethanol on the painted steel substrates. The film prepared from the dispersion without ethanol exhibited a patchy pattern due to surface roughness (Fig. 2(a)). The surface roughness decreased with increasing ethanol concentration and a smooth surface was observed on films fabricated from the dispersion with 10 wt% ethanol (Fig. 2(c)). Normal-incidence reflection spectra of the three film surfaces were measured with a multichannel spectrometer (Soma Optics, Fastevert S-2650) using a coaxial optical fiber. The obtained spectra are shown in Fig. 3. A reflection peak due to Bragg diffraction was detected at the same wavelength for all three samples, but its intensity increased with increasing ethanol concentration. Comparing to Fig. 2, it is concluded that the increase in intensity resulted from improvement of the surface roughness.

The above results indicate that the surface roughness of the films is reduced by adding ethanol to the silica-ETPTA dispersion. The viscosity of the dispersion was also reduced by the addition of ethanol. Thus, the roughness improvement was probably induced by the decrease in viscosity, because paint viscosity generally affects droplet atomization and the leveling behavior of droplets that attach to the substrate. The ethanol, however, may act as an impurity and disrupt the formation of a crystalline arrangement. We therefore tried using other acrylic monomers with lower viscosity than ETPTA. Silica-TEGDA dispersions were found to have low viscosity at a high shear rate of around 1000 s⁻¹ without adding ethanol, as shown in Fig. 1. In fact, colloidal crystal films with a flat surface and brilliant colors were fabricated by spray coating without adding ethanol. Reflection spectra and photographs of the films prepared from silica-TEGDA dispersions with different sphere diameters and concentrations are shown in Fig. 4. These data indicate that the reflection peak wavelength can be controlled not only by varying the sphere diameter but also by adjusting the sphere concentration. The film prepared from the 50 wt% dispersion showed a reflection peak at a shorter...
wavelength than that for the 40 wt% dispersion, because higher sphere concentrations correspond to shorter interparticle distances.

4.4 Structures of the Spray-coated Colloidal Crystal Films

Although the spray-coated colloidal crystal films show different colors that vary with observation angle, they exhibit a plain color when observed from a single angle, as shown in Figs. 2 and 4, and the color does not change with azimuth angle. To examine the configuration of the silica spheres in the spray-coated film, the surface and cross section of the film were observed by scanning electron microscopy (SEM). The surface SEM image shown in Fig. 5 clearly indicates that the surface of the coated film has a polycrystalline structure consisting of grains with sizes of 2-10 μm, and each of the grains has a hexagonal array of spheres, corresponding to the (111) plane of the face-centered-cubic (fcc) lattice. Figure 6 shows cross-sectional SEM images of the colloidal crystal film coated on a plastic substrate. A plastic substrate was used here because it was difficult to prepare films on steel plate substrates for cross-sectional SEM observations. The low magnification image (Fig. 6(a)) shows that the spray-coated film has a flat surface and uniform thickness (42 μm). The magnified image (Fig. 6(b)) indicates that the colloidal crystal film has a polycrystalline structure that consists of grains with widths of around 10 μm and heights of around 40 μm, which is almost the same as the film thickness. These results suggest that the spray-coated film is composed of grains that are highly oriented with the (111) planes of the fcc structure parallel to the substrate surface. This is probably the reason why the films exhibit a brilliant and plain color when observed from a single angle.

4.5 Use of the Colloidal Crystal Films as Pigments

We thus successfully obtained polymer-immobilized colloidal crystal films with brilliant structural colors by spray coating, as described above. However, there are several issues for spray coating on larger and/or curved substrates. One of the issues is the difficulty in ensuring uniform wettability on the whole surface to be coated. Inhomogeneous wettability induces uneven development of colors of the coated film, due to the uneven thickness of the film induced by the inhomogeneous wettability. Another issue is that a setting time of 10-30 min is required to make the surface flat and for the spheres to be arranged after spray coating. If the substrate has a curved or tridimensional shape, uneven development of colors will result due to the flow of coated dispersions.

Although these issues will be solved by improving...
both the surface treatment methods used and the properties of the dispersions, we propose the following quick method to avoid these problems for now, particularly when using the colloidal crystals as pigments in paint. A colloidal crystal film with uniform color can be coated on a flat substrate by a conventional method, for example, spray coating as described in this paper. If the substrate is glass, the coated film is easily peeled off from the substrate and it can then be crushed until flakes of the film with sizes of around $20 \times 50 - 200 \times 50 - 200$ μm$^3$ are formed. The flakes are added to a commercial clear paint and coated by various conventional painting methods on various substrates. Figure 7 shows photographs of a car-shaped model painted with clear paint that included the colloidal crystal flakes formed by spray coating. The painted film also changed color with viewing angle, as shown in Fig. 8, which is a characteristic of the colloidal crystals.

5. Summary

The fabrication of polymer-immobilized colloidal crystal films using a conventional spray coating method has been described. Controlling both the viscosity of the dispersions and the wettability of the substrates enabled the synthesis of colloidal crystal films with smooth surfaces and brilliant iridescent colors due to Bragg diffraction. The colors could be controlled by adjusting both the sphere concentration and diameter. Also, a method for utilizing the colloidal crystal films as pigments in conventional paint was proposed.

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Fig. 6 Cross-sectional SEM images of the colloidal crystal film coated on a plastic substrate. (a) Low magnification image, and (b) composite image of the area framed by the quadrangle in (a).

Fig. 7 Photograph of a car-shaped model coated with clear paint that included the colloidal crystal flakes.

Fig. 8 Photographs of film coated with clear paint that included colloidal crystal flakes. Photographs (a) and (b) were taken at different viewing angles.
References


Fig. 1

Figs. 2-5

Fig. 6

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