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Flexible Polymer Opal Films Prepared by Slide Coating from Alcoholic Media

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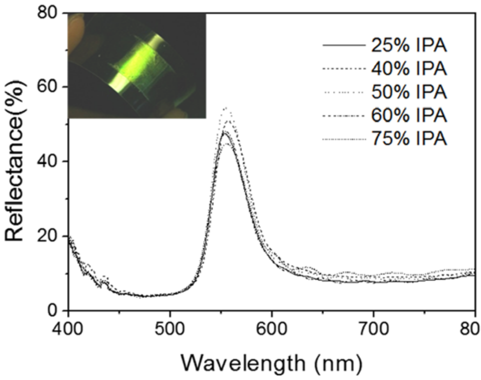

Abstract: In this study, we investigated the fabrication of a colloidal photonic crystal film on flexible substrate, which can be used as a scaffold material for various photonic applications. A thin polyethylene terephthalate (PET) film was treated by oxygen plasma and then used as a flexible substrate. The surface characterizations revealed that the surface roughness increased, and that the treated PET film was rendered hydrophilic. The contact angles of the films with water/isopropyl alcohol (IPA) mixtures at five different weight ratios (25%, 40%, 50%, 60%, and 75% of IPA) prepared on both treated and non-treated PET films were measured. The results indicated that water/IPA wets on oxygen plasma-treated PET film. The colloidal dispersions were prepared in five different water/IPA mixtures, and slide coating was carried out on both PET films aided by hot air to promote opal formation. Serious dewetting of opal film was observed on the non-treated PET film, except that with a 75% IPA. However, the treated PET film enabled the formation of high-quality opal film, regardless of IPA content in colloidal dispersion. The optical properties and surface morphologies of opal films on flexible PET film were confirmed by reflectance spectra and scanning electron microscopy images of the respective films.

Keywords: slide coating, flexible substrate, PET film, oxygen plasma treatment, opal, photonic crystal.

1. Introduction

Photonic crystals are naturally occurring colored materials found in peacock feather and opal gemstone, among others. These crystals exhibit angle-dependent reflective colors from the periodic structures within the materials. Recently, researchers have attempted to mimic natural photonic crystals because they can be used as scaffolds for various photonic devices, such as microlasers,[1,2] optical waveguides, and chemical sensors.[3,4] Among various methods for fabricating artificial photonic crystals, colloidal crystallization is a relatively simple and fast way to produce artificial opals, which can be utilized as three-dimensional (3D) scaffolds for many applications; thus, they have been extensively studied in the literature.[3-8] Artificial opal films can be created through the self-assembly process of the submicron-sized colloidal spheres dispersed in water. The colloidal particles with narrow size distribution are closely packed into the opalline face centered cubic (fcc) structure through the strong capillary force of evaporating water, and the resulting artificial opal exhibits brilliant structural colors by Bragg diffraction of visible light from [111] fcc facets. To fabricate opal films, various methods can be used, such as dip coating,[9-12] direct coating,[13,14] capillary method,[5,8,15,16] and so on. Recently, we developed a direct coating method, by which a polymeric opal film with standard slide glass size (2×6 cm^2) can be formed in 30 minutes.[17] In this slide coating method, hot air is blown on to the wet, as-coated colloidal film to accelerate water drying. Furthermore, the aqueous dispersion of the colloid is coated onto the hydrophilic glass substrate. However, if the opal films are to be coated on a flexible polymer substrate, the wettability of the colloidal dispersion on the polymeric substrate should be considered. Thus, in this study, we demonstrate the slide-coating of the polymer particle dispersions in water/alcohol mixture on flexible polyethylene terephthalate (PET) film by controlling the alcohol content and the surface polarity of the substrate.

2. Experimental

2.1. Materials

Styrene, potassium persulfate (PPS), and sodium dodecylsulfate (SDS) were purchased from Aldrich. A semipermeable cel-

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lulose membrane (MWCO 12,000-14,000) was supplied by MFPI Co.. Deionized (DI) water was prepared by water purification system (Humantech Co.) PET film (Mylar®) was purchased from Dupont Industrial Chemistry.

2.2. Synthesis of PS particles

Polystyrene (PS) colloidal particles with an average diameter of 260 nm were synthesized by emulsion polymerization method, using PPS as a radical initiator and SDS as a surfactant in water.[18] As-prepared PS particles were purified by dialysis using a semipermeable cellulose membrane (MWCO 12,000-14,000) within DI water for 2 weeks; the solid content of the final dispersions was 12 wt%. The average diameter of the PS colloid was characterized by scanning electron microscopy (SEM, S-4700, HITACHI).

2.3. Slide coating of PS opal fims on flexible PET substrate

The slide coating apparatus consisted of a top glass slide and a bottom substrate with Teflon® tape spacers (thickness: ~200 μm) attached on each side of a substrate, which was slowly pulled out by a syringe pump (KD scientific) at a preprogramed speed. In this study, Mylar® film (thickness: ~100 μm) was used as a flexible PET film, which was fixed on a glass slide and used as a bottom substrate. An aqueous PS dispersion was mixed with isopropyl alcohol (IPA, 99%, Aldrich) at various weight ratios (25%, 40%, 50%, 60%, and 75% of IPA), and then infiltrated into a thin space between the top and bottom slides. As the bottom substrate was pulled out, the colloidal crystallization took place at the drying front aided by hot air blown onto the drying colloidal film. Before the slide coating, the PET film was treated by 200 W oxygen plasma (covance, FEMTO SCIENCE) for 3 min.[19]

2.4. Characterizations

Wettability of a PET film was confirmed by contact angle measurement (PNX300, Surface Electro Optics), and its surface was characterized by X-ray photoelectron spectroscopy (XPS, ThermoVG, Sigma Probe) as well as atomic force microscopy (AFM, NanoScope IV, Digital Instruments). The coated colloidal crystal films were analyzed by SEM and a digital single lens reflex (DSLR) camera (DSLR-A550, SONY). The reflectance of a film was measured using a fiber-optic UV-Vis spectrometer (AvaSpec, Avantes), which was connected to the reflected light microscopy (L2003A, Bimeince) through an objective lens (20x/0.30NA). In all measurements, the raw data of reflected signal from the sample were referenced by a silver mirror (Edmund Optics).

3. Results and discussion

The slide coating of PS colloidal dispersion from water/IPA mixture is schematically illustrated in Figure 1(a). As a flexible substrate is continuously pulled out, air-exposed colloidal dispersion is instantly subjected to drying through the hot air blown onto the wet colloidal film. At a drying front, capillary forces are variously exerted on each particle, as indicated by the arrow (F_a–F_d) in Figure 1(b), depending on the curvature (r) of liquid menisci formed at the three phase interfaces of particle/liquid/air. This process helps determine the net driving forces so that the colloidal particles are closely packed with one another. The curvature r is given by the wettability of the liquid on a substrate. Noting that the capillary force at the three phase interface is given by $F=2\pi r\gamma$ (γ:surface tension), a driving force for opal formation is larger in water than in the water/IPA mixture owing to the larger surface tension of water than that of IPA ($\gamma_{water}=72.8$ *vs.* $\gamma_{IPA}=28.0$). If a colloidal dispersion is coated on a substrate, which is less hydrophilic than a glass slide, the wettability of a given liquid as well as the interaction between the colloidal particle and the substrate can affect the packing of colloidal particles and, consequently, the quality of the opal film. The PET film used in this study is a nonpolar flexible film on which water does not wet. Therefore, a PET film was treated by using 200 W oxygen plasma for 3 min to render the surface hydrophilic. In Figure 2, the contact angles of the different water/IPA mixtures on three different substrates are plotted. As can be seen, a lower contact angle is obtained on a plasma-treated PET film than on a slide glass, which is a typical hydrophilic substrate; at the same time, better wettability with the

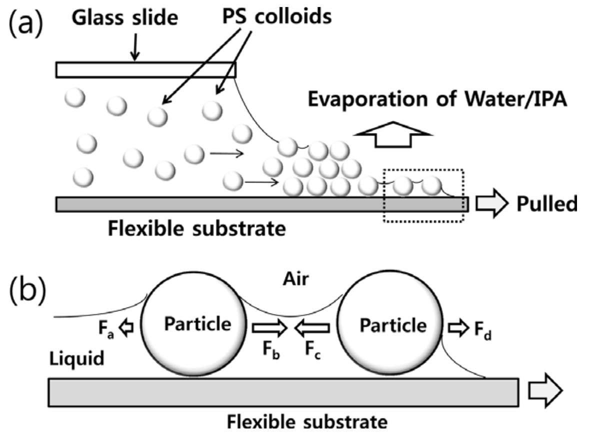

Figure 1. (a) Schematic illustration of slide coating of polymeric particle dispersion in water/IPA mixture. (b) Capillary forces exerted to each particle.

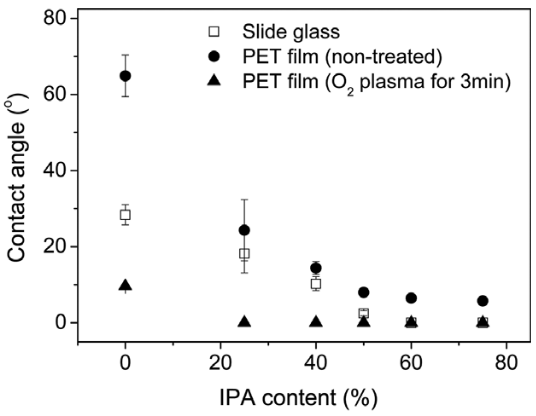

Figure 2. Contact angles of the water/IPA mixture on three different substrates.

water/IPA mixtures of all compositions can be observed. At a high IPA content, contact angles on both slide glass and plasma-treated PET film approach zero degree, implying that the water/IPA mixtures are completely wet on both substrates.

The physical/chemical rendering on PET film by oxygen plasma treatment was analyzed by tapping mode AFM and XPS. In Figure 3(a) and (b), it is compared that the surface of a plasma-treated film is rougher than that of a non-treated PET film. Figure 3(c) and(d) show that oxygen content on a film surface significantly increases after plasma treatment as a result of the formation of oxygen-containing functional groups, such as -OH, -COOH, and so on.

PS colloidal dispersions in the water/IPA mixtures with various IPA contents were slide-coated on both treated and non-treated PET films. Shown in Figures 4(a–e) are the coated opal films on non-treated PET films, and Figures 4(f–j) show those on treated films. On non-treated PET films, only a colloidal dispersion with 75% IPA is coated well, whereas other dispersions suffer from the dewetting of the opal film. Dewetting becomes less serious with increasing IPA in the mixed dispersant. Yet, despite the dewetting, the dried colloidal particles from every liquid mixture show green reflective colors, because the drying of colloidal dispersions ends up forming opalline structures anyway. However, the color of an opal film from 75% IPA appeared to be more yellowish than those of other films, implying that there is a significant contribution of the reflectance of higher wavelength light. In our previous investigation, higher content of alcohol weakens the capillary force of liquid at the meniscus between particles to result in less ordered opal arrays which will broaden the reflectance spectrum.[20] It is noteworthy that the same series of colloidal films on the plasma-treated PET films do not exhibit serious dewetting, and more importantly, an opal film is perfectly coated from a 75% IPA dispersant without any significant change in structural color.

The strong reflective color from every film implies that the opalline structures are obtained for all of them. To extract more quantitative data, reflectance measurements were carried out on the opal films. Figures 5(a) and 5(b) show the reflectance spectra of the slide-coated opal films on non-treated PET films and plasma-treated PET films, respectively. As can be seen, the peak reflectances on the treated films are stronger than those on the non-treated PET films by more than 20%. Meanwhile, the inset figures in Figures 5(a) and 5(b) respectively show the photographs of the opal films from 75% IPA dispersions while each flexible substrate is bent.

Each coated film was annealed at 90 °C for 1 h so that the colloidal particles can be slightly connected to one another, and no delamination of the opal film was observed from the substrate. From this result, we again confirmed that an oxygen plasma-treated PET film is very useful as a substrate for opal film.

In Figure 6, the different defect densities of colloidal packing structures from five dispersions are confirmed by SEM; the typical surface morphologies of opal films on the plasma-

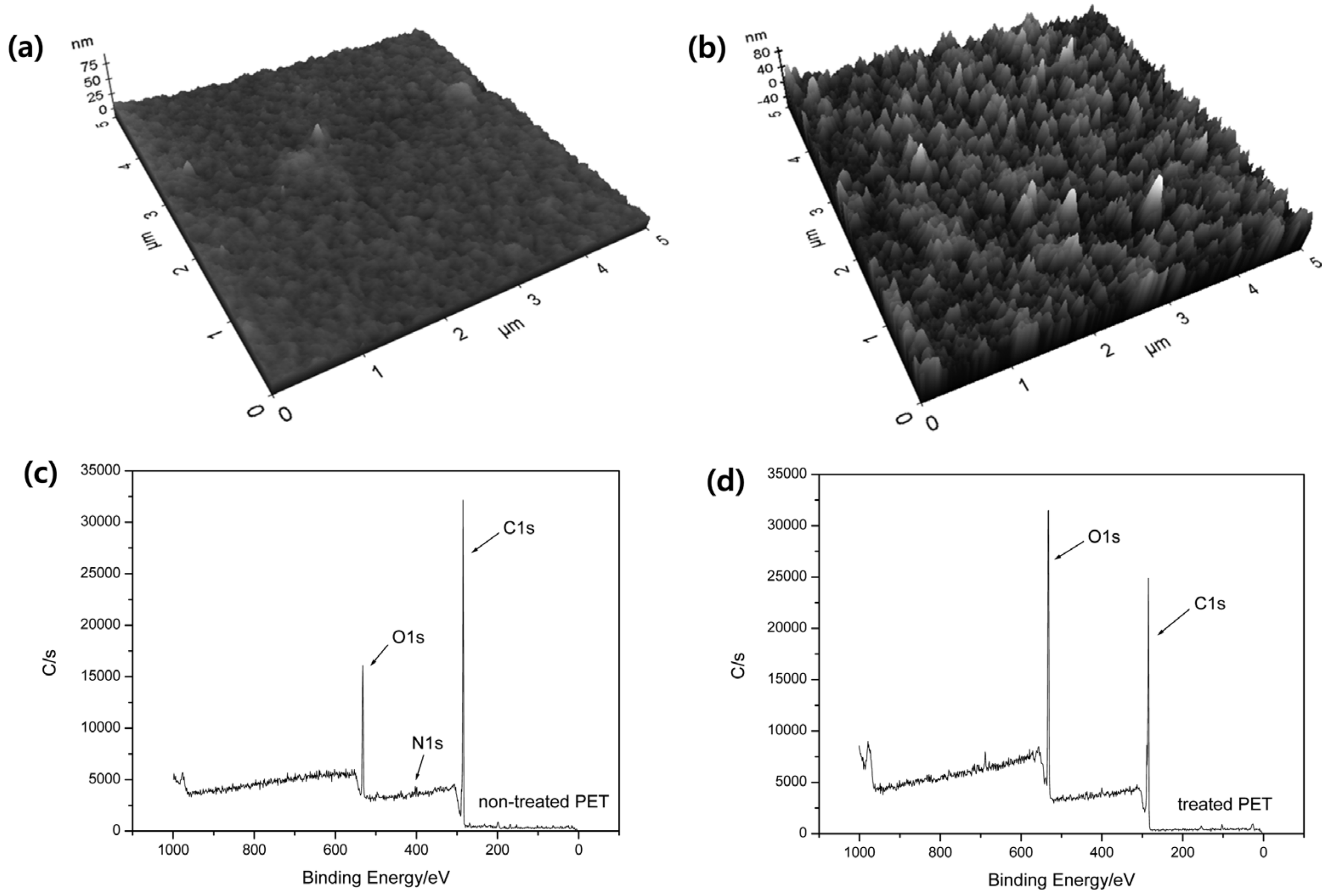

Figure 3. (a, b) AFM Images and (c, d) XPS spectra of (a, c): non-treated PET film, (b, d) oxygen plasma-treated PET film.

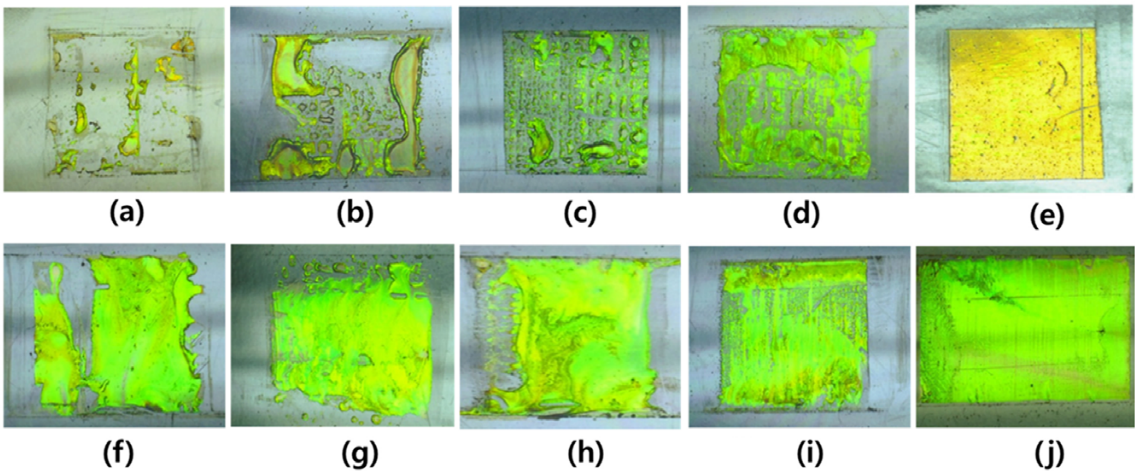

Figure 4. Photographs of opal films that were slide-coated on (a–e): non-treated PET film, (f–j) plasma-treated PET film. IPA contents in dispersing media increased from left to right (25%, 40%, 50%, 60%, 75%).

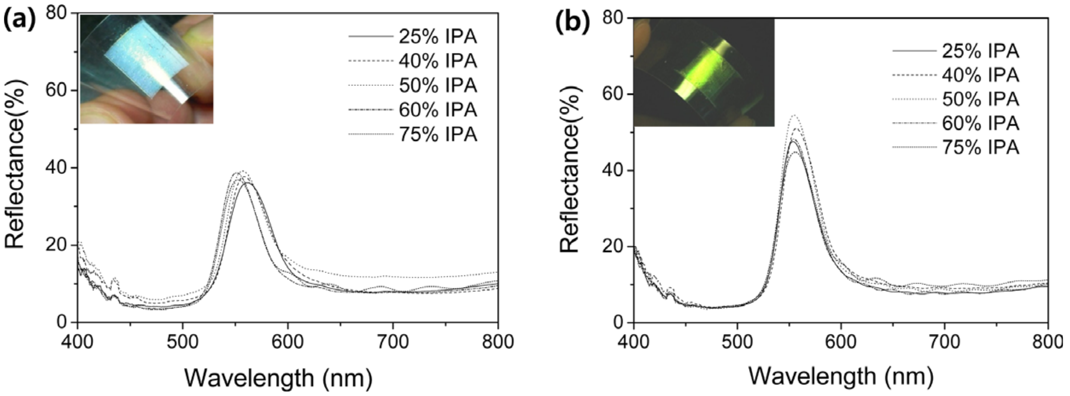

Figure 5. Reflectance spectra from the opal films from different dispersing media on flexible substrates of (a) non-treated PET film, (b) plasma-treated PET film. Inset figures in (a) and (b) are the photographs of the opal films from 75% IPA on each film with bending.

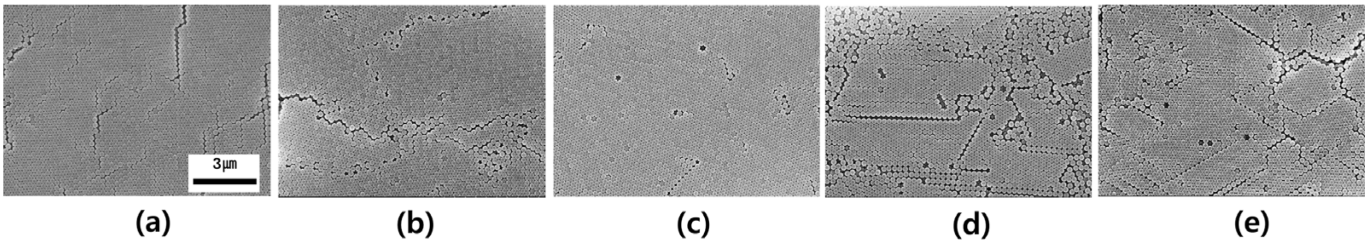

Figure 6. SEM Micrographs of opal films that were slide-coated on the plasma-treated PET films. As can be seen, IPA contents in dispersing media increased from left to right (25%, 40%, 50%, 60%, 75%).

treated PET films are also shown in the figure. Although some linear defects are observed at the films from high IPA content cases (*i.e.*, 60%, 75%), overall packing structures are not significantly deteriorated by the increased IPA content, which should have weakened the capillary forces of the liquid mixtures for colloidal arrangement.[21,22]

In our previous investigation, in which the colloidal dispersion in water/alcohol mixture was slide-coated on a glass substrate, we observed that a dispersion with high IPA content significantly increased the defect density.[20] However, in the current study, the quality of opal film from a high IPA content (*i.e.*, 75%) appears to be not much deteriorated on the plasma-treated PET film, as revealed by both the reflectance spectrum and SEM images. The improved colloidal arrangement on a treated PET film at a high IPA content may have resulted from the better wettability of the mixed liquid on a treated PET film than on a glass, which evidently affects the colloidal assembly process upon evaporation of the liquid.

4. Conclusions

The rapid fabrication of colloidal opal film on a flexible substrate is investigated. After O_2 plasma treatment of flexible PET film surface, the wettabily of the water/IPA mixture improved than on a glass substrate as demonstrated by the contact angle measurements. Results showed a high-quality opal film obtained by slide-coating colloidal dispersion in the water/IPA mixture on a treated PET film without a dewetting problem. With further optimization, the opal film on a flexible substrate is expected to promote the development of many promising applications, such as an esthetic coating and a template film for various photonic sensors.

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