Mechanically tunable color display of photonic crystals and shape memory polymer composites

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Keywords: tunable color display, photonic crystal, shape memory polymer, composite film fabrication

Abstract
Photonic crystals (PCs) have been studied for color displays and micro-sensors due to their ability to control colors when combined with polymer matrix. Mechanically tunable color display can be fabricated via infiltration of shape memory polymer (SMP) precursor into self-assembled microsphere PC structure. In this study, infiltration of SMP precursor was studied by measuring the contact angle using single fiber tensiometer. After the SMP infiltration into PC structure, the color spectrum of SMP-PC composite was analyzed via spectrophotometer, demonstrating that mechanically tunable color display can be fabricated using shape memory polymers and photonic crystals.

1. Introduction

The composites of photonic crystals (PCs) and polymer matrix have been investigated for color displays and micro-sensors due to their ability to in-situ control colors. After colloidal crystallization, reflected colors caused by Bragg diffraction of visible light can be obtained in the composites [1-3]. Most studies of the PC composite have been performed using elastomer matrix that can tune colors under its mechanical deformation such as bending or stretch. In addition, the lattice distance of the PC composites can be controlled using voltage or PH [4-6]. The mechanically tunable PC composite display has advantages in application and control, however, its reversibility is not ensured during indirect stimulus-driven operation. Since shape memory polymers (SMPs) can recover their original shape under relatively large deformation upon external stimuli such as temperature, electric field and magnetic field, SMP matrix can be perfect candidate to ensure the reversibility of PC composites. The PC composite can be used for flexible display or indirect stimulus sensing in medical applications [7, 8].
In this study, wettability of SMP on PCs was investigated using contact angle to find right SMP that can infiltrate into PC crystals and form a matrix. The color properties of PC/SMP composites were analyzed through spectrophotometer, based on which requirements for PC/SMP composites to show tuned colors by mechanical deformation will be discussed in the followings.

2. Experimental

2.1. Contact angle measurement using tensiometer

The wettability of a liquid on a solid surface is investigated using contact angle. The contact angles of SMP precursors on polystyrene (PS) and silicon wafer with hydrophilic –OH group on its surface were measured. The SMP precursors used were mainly bisphenol-A type epoxy resins. Polydimethylsiloxane (PDMS) was used as a reference elastomer. Two types of epoxy resin (Epofix® (Struers) and YD-128 (Kukdo-chemical)) were chosen as SMP precusors. The solid polystyrene surface and silicon wafer were sliced into 10 mm x 20 mm rectangular shape for tensiometer (K100SF) scale. The advancing contact angle was measured through the plate method as shown in Figure 1 below.

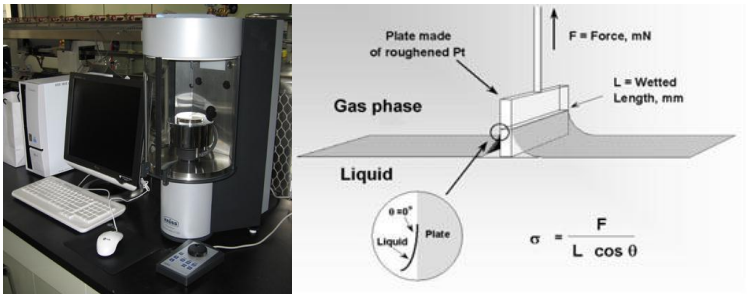

Figure 1. A tensiometer (left) and the plate method for measuring contact angle (right).

2.2. Fabrication of PC/SMP composite

PC/PC composite was fabricated via resin infiltration method, i.e., precursor of SMP was infiltration into assembled photonic crystal structure. Here, photonic crystals was prepared through evaporation of colloidal suspension or spin coating. Note that the evaporation of colloids was conducted for making amorphous crystal structure, while spin coating for close-packed structure. The size of PS microspheres in the colloids was 150 nm. For comparison purpose, larger microspheres with the diameter of 300 nm were also used. Two SMP precursors Epofix® and YD-128) were used. Jeffamine D-230 and decylamine (2:1 weight ratio) were used the cross-linking agent and softener for both of SMP precursors. The mixed SMP precursors were poured into established PC structure and crosslined. The microstructure of PC/SMP composites was observed using Scanning Electron Microscope (SEM). Detailed procedure for fabricating PC/SMP composites is schematically illustrated in Figure 2.

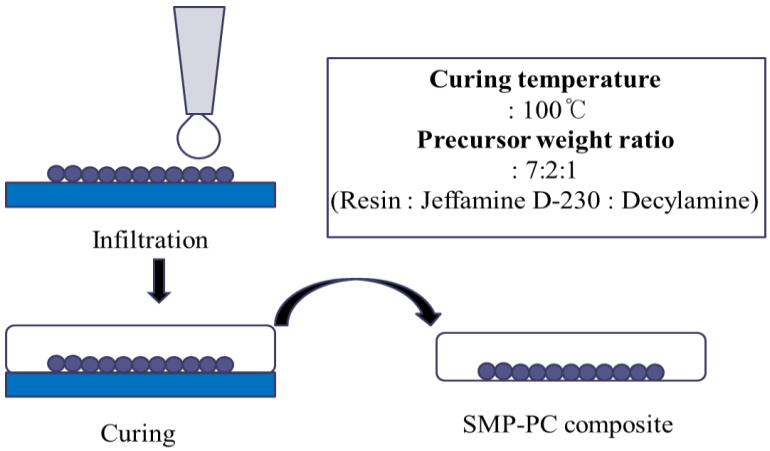

Figure 2. Schematic diagram for fabricating PC/SMP composites.

2.3. Reflection peak analysis

The reflection peak of PC/SMP composites was measured using color spectrophotometer (Colormate). For this analysis, the thickness of composite sample was about 200 μm. The PC/SMP composite films were extended at high temperature condition (above T_g) and were fixed at low temperature condition (below T_g). The reflection peak after extension was compared with undeformed case. Recovered samples were also characterized to investigate the reversibility of the PC/SMP composites in color change.

3. Results and Discussion

3.1. Contact angle measurement

The wettability of SMP precusors on solid surface is a crucial factor to fabricate uniform composites. The wettability of epoxy resin on polystyrene (PS) microsphere and silica microsphere was characterized using macroscale wettability test through a tensiometer. The contact angles of SMP precursor and PDMS against polystyrene and silicon plate with –OH group were listed in Table 1 below.

Solid	CA (YD-128)	CA (Epofix)	CA (PDMS)	γ_s (mN/m)
PS plate	112.82°	59.43°	82.77°	42
Treated Si	97.17°	48.26°	59.17°	133

Table 1. Contact angle values and surface tension of solid for experiment conducted on PS plate and treated Si plate.

The measured contact angles for YD-128 showed higher contact angle on both solid plates. The SEM image for YD-128 composite structure indicated that YD-128 wasn't well infiltrated into microsphere PC voids (see Figure 3). Epofix and PDMS showed smaller contact angle values than YD-128 case and their SEM images showed better infiltrated composite matrix into voids (Figure 3). The treated silicon surface with hydrophilic group has relatively high surface tension, so the PC composite with silica microsphere had better resin wettability than PS microsphere case.

3.2. PC/SMP composites

PC/SMP composite samples were fabricated via the infiltration of uncured SMPs between photonic microspheres. Two types of microspheres (PS and silica) were used as PC components. The SEM images of assembled microspheres after the infiltration of SMP matrix are presented in Figure 3. The PC with silica microsphere showed more fine composite structure than PS microsphere, as confirmed by the contact angle data in Table 1. To control the color of PC/SMP composites, the distance between microspheres in the PC/SMP composites need to be changed in in-situ manner. Soft matrix coating on microsphere or ultraviolet (UV) SMP curing procedure for shrinkage prevention will be studied for this purpose and detailed results will be presented at the Conference.

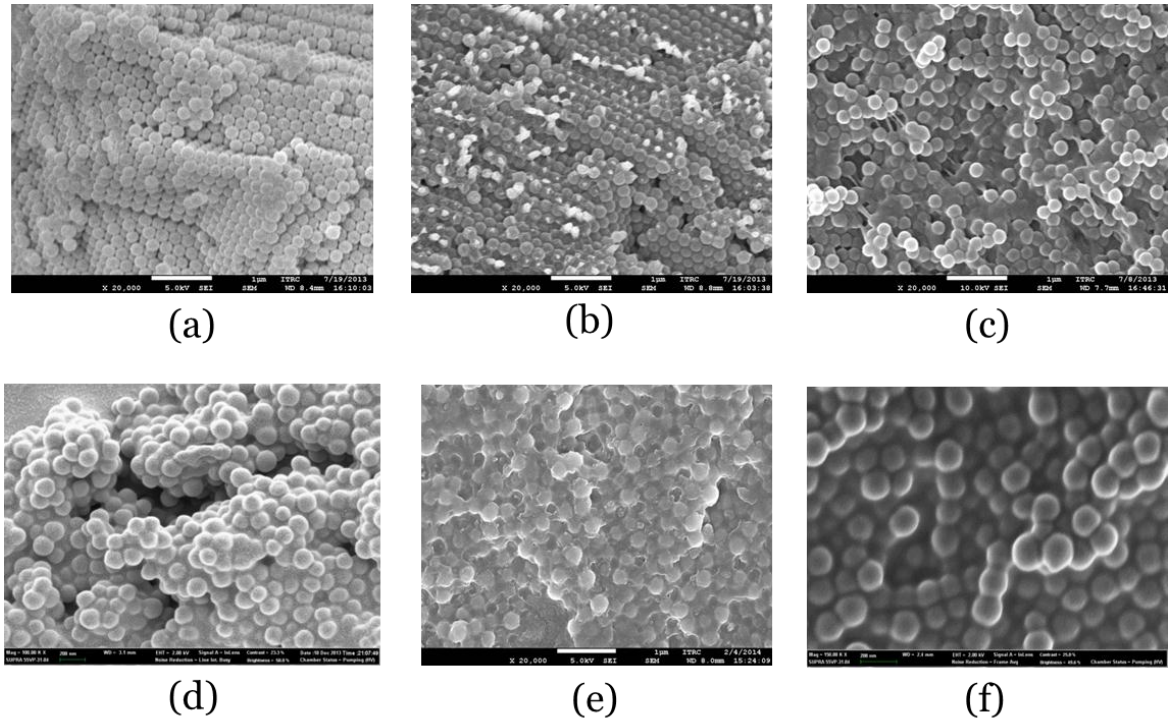

Figure 3. SEM images of PC/SMP composite. (a) YD-128 and PS microsphere composite (b) Epofix and PS microsphere composite (c) PDMS and PS microsphere composite (d) YD-128 and silica microsphere composite (e) Epofix and silica microsphere composite (f) PDMS and silica microsphere composite

3.3. Reflectance peak analysis

The reflectance spectrums of PC/SMP composites were analyzed with color spectro-photometer. The PC/SMP composite with PS microspheres did not show the wavelength contrast due to small refractive index contrast between matrix and microsphere. The sample with silica microsphere showed color peak in spectrum but remarkable wavelength peak shift wasn't found in infiltrated epoxy PC/SMP composites under constant 20% strain. The main reason for this may be insufficient spacing between microspheres. The shrinkage of the SMP matrix (epoxy type) during curing step prevented microspheres from getting moderate distance due to Poisson effect in the strained composite (see Figure 4 for detailed explanation). In face-centered cubic photonic crystal structure, Bragg diffraction lattice plane is [111] plane. Controlling the distance between adjacent [111] planes is the main factor to change color of PC/SMP composites. Efficient methods to control the plane distance in the composites are being researched and will be presented at the Conference.

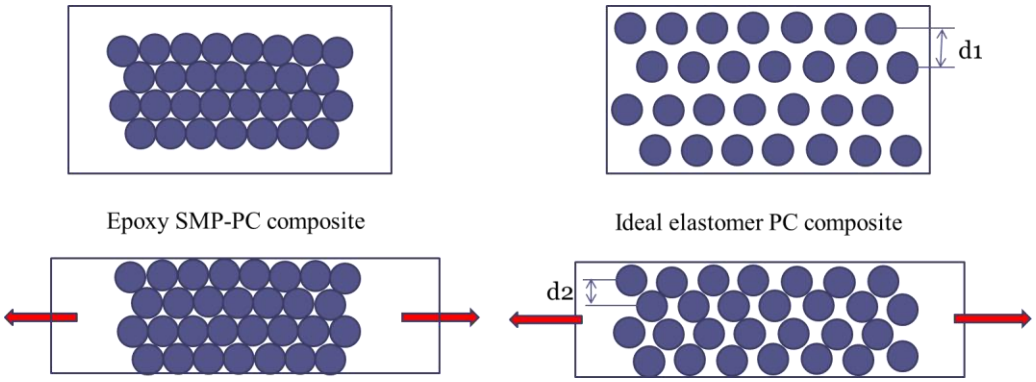

Figure 4. A Schematic diagram comparing the plane distance of PC/SMP composites and ideal PC/elastomer composites. The PC/SMP (epoxy type) composites have close packed structure, causing the plane distance to be shrunk**.**

Summary

Wettability of SMP precursors on microspheres (forming photonic crystals) were investigated using a tensiometer to explore the right conditions of SMP precursor for well infiltration into PC cyrstals. SMP precursors with contact angles lower than 90° showed excellent infiltration into PC crystals, forming uniform composites. The color spectrum of PC/SMP composites was analyzed using spectrophotometer. The color shift was not successful due to inadequate spacing between microspheres in the composites. Further experiments will be carried out to find new fabrication method to prevent the matrix shrinkage between microspheres and the, mechanically color tunable behavior of the PC/SMP composites will be investigated.

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