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Mechanochromic Response of Poly(ethylene glycol) Methacrylate Hydrogel Encapsulated Crystalline Colloidal Arrays

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1. Introduction

Since the original proposal that three-dimensional periodic dielectric structures could exhibit a photonic band gap (PBG),^{1,2} considerable attention has been focused on developing these materials into a form which is suitable for use in photonic related applications. Unfortunately, the general exploitation of optical photonic crystals as devices has been hindered by the difficulties in creating periodic dielectric structures with a feature size comparable to the wavelength of visible light. One approach to address this challenge has focused on systems which undergo self-organization at a nanometer length scale, such as colloidal crystals. Systems exhibiting self-assembly characteristics hold promise as a practical route to generating optical photonic crystals, possibly with a complete photonic band gap.^{3,4}

A crystalline colloidal array (CCA) is a three-dimensionally ordered lattice of self-assembled monodisperse colloidal particles, most commonly amorphous silica or a polymer latex, dispersed in aqueous or nonaqueous media.^{5–7} In the case of a polymer latex, at high particle concentrations ($>10^{13}/\text{cm}^3$), long-range electrostatic interactions result in a significant interparticle repulsion which yields in the adoption of a minimum energy colloidal crystal structure with either body-centered cubic (bcc) or face-centered cubic (fcc) symmetry.^{8–10} The ordering results in spatial periodicities that range from ca. 10^2 – 10^3 nm, resulting in the appearance of optical band gap effects.

Unfortunately, the low elastic modulus (10^{-2} – 10^{-3} Pa)^{7,11,12} exhibited by a liquid dispersion results in weak

shear, gravitational, electric field, or thermal forces having the propensity to disturb the crystalline order. Recently, approaches to develop robust network matrixes have been pioneered to stabilize both organic and inorganic arrays through an in situ polymerization of a monomer around the ordered arrays. Specifically, colloidal crystals composed of polymeric arrays have been stabilized through encapsulation in hydrogel networks and have been referred to as polymerized crystalline colloidal arrays (PCCA).^{3,13} PCCA films exhibit significant changes in their optical characteristics with water content; this feature has been exploited by Asher and co-workers^{13–15} in utilizing PCCAs in optical filtering and sensing applications. In addition, mechanically robust composite films composed of silica particles in acrylate polymers have been presented by Ford and co-workers^{16–18} which exhibited a mechanochromic response, though the time for the films to return to the optical characteristics of their unloaded state after the cessation of stress was 2–4 h. In particular, we have shown that poly(ethylene glycol) (PEG) derivatives are suitable matrixes for PCCA systems.¹⁹ In this work, we explore alternative PEG matrixes to extend the successful routes by which stable PCCAs can be fabricated. In addition, the mechanical performance of the resulting composites is quantified, and their mechanochromic response is demonstrated.

2. Experimental Section

2.1. Materials. Monodisperse cross-linked polystyrene particles were prepared using an emulsion polymerization procedure described elsewhere.^{20,21} The resulting latex was dialyzed against deionized water and then shaken with an excess of mixed bed ion-exchange resin to remove excess electrolyte.¹³ After the cleaning procedure, a Brookhaven BI-90 dynamic light scatterer (DLS) measured the average diameter of the particles to be 93 nm.

The crystalline colloidal arrays were encapsulated in a hydrogel matrix prepared by an in situ photopolymerization procedure described elsewhere.¹³ The matrix materials included a monomer of poly(ethylene glycol) methacrylate (PEG-MA, $M_n = 360$), a cross-linker of poly(ethylene glycol) dimethacrylate (PEG-DMA, $M_n = 550$), and a photoinitiator of 2,2-diethoxyacetophenone (DEAP) (cf. Table 1). The CCA/PEG mixture was injected between two quartz plates separated by a 250 μm Parafilm spacer and then polymerized into a PCCA through exposure to a UV source for 4 min.

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Table 1. Formulations of CCA and CCA/PEG Mixture (v/v)

	CCA	CCA/PEG
polystyrene/water (5.6×10^{13} particles/cm ³)	100	81.80
poly(ethylene glycol) methacrylate (PEG-MA)		16.35
poly(ethylene glycol) dimethacrylate (PEG-DMA)		1.65
2,2-diethoxyacetophenone (DEAP)		0.20

Table 2. Optical Characteristics of CCA, CCA/PEG Mixture, and PCCA Composite

	CCA	CCA/PEG	PCCA
ψ /polystyrene	0.0510	0.0412	0.0416
n_{matrix}	1.331	1.358	1.358
$n_{\text{composite}}$	1.344	1.367	1.368
bandstop (nm)	498.0	544.1	542.3
bandwidth _{obs} (nm)	15.0	12.5	13.0
bandwidth _{theo} ^a (nm)	8.4	6.7	6.8
d_{111} (nm)	185.2	198.9	198.3
a_c (nm)	320.9	344.6	343.4
a (nm)	226.9	243.7	242.8

^a Calculated from ref 37.

2.2. Characterization. When colloidal crystals composed of a latex are placed in a cell, the crystals orient with their most densely packed planes parallel to the walls of the container, and in the specific case of fcc symmetry, this corresponds to the [111] planes.^{9,10} The diffraction characteristics are sufficiently predicted²² through Bragg's diffraction equation, $\lambda_o = 2n_c d_{hkl} \sin \theta$, where λ_o is the wavelength of the diffracted light in air, d_{hkl} is the interplanar spacing, n_c is the refractive index of the composite, and θ is the Bragg angle. In the experimental configuration, unpolarized light is propagated along the [111] direction of the fcc lattice, or Γ -point of the reciprocal lattice.²³ The observed stop band is then related to the lattice parameter of the conventional cubic unit cell through $a_c = \sqrt{3}d_{111}$, while the nearest neighbor distance is $a = a_c/\sqrt{2}$.

The transmission spectra of the CCA, CCA/PEG mixture, and PCCA composite were collected using a Shimadzu UV3101 UV/VIS/NIR spectrophotometer. Spectra were collected between the wavelengths of 300 and 800 nm and at a temperature of ca. 25 °C. In addition, an Ocean Optics PC2000 fiber-optic spectrometer was employed for reflectance measurements.

The mechanical characteristics of the PCCA films were determined at a temperature of ca. 23 °C with a Perkin-Elmer thermomechanical analyzer (TMA) model 7 in compression mode. A quartz assembly was employed with a probe diameter of 7 mm.

3. Results and Discussion

3.1. Optical Measurements. Table 2 presents the volume fraction (ψ) of the polystyrene particles, the refractive indexes, the wavelength of the observed stop bands (λ_o), and the observed and calculated bandwidths of the CCA suspension, CCA/PEG mixture, and PCCA composite. According to phase diagrams of ordered colloidal suspensions,^{9,10} the CCA and CCA/PEG mixture contained polystyrene volume fractions that would result in a fcc lattice.

In comparing the CCA with its corresponding CCA/PEG mixture, the reduced polystyrene content of the mixture results in an increase in both the interparticle spacing and wavelength position of the stop band. The nearest neighbor distance of the particles increases by 7% with a decrease in ψ /polystyrene from 0.0510 to 0.0412, a 19% reduction in polystyrene content. The tendency of electrostatically stabilized CCAs to shift their stop band with polystyrene content has been previously observed.⁵

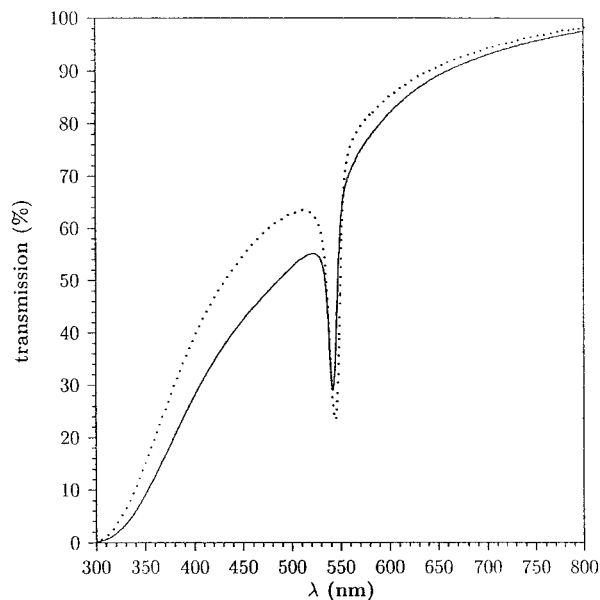


Figure 1. Transmission spectra of CCA/PEG mixture (dotted line) and corresponding PCCA composite (solid line); incident light was normal to the 250 μm thick films.

Note that for the CCA/PEG mixture the value for a is 162% larger than a nearest neighbor distance based solely on intimate contact of the particles and shows the prominence of double-layer effects.⁷

Figure 1 presents the transmission spectra of CCA/PEG and its resulting composite after the mixture had been photopolymerized. The PCCA composite exhibits a decrease of ca. 2 nm in the wavelength of the stop band (cf. Table 2) and a slight increase in the bandwidth relative to the liquid CCA/PEG mixture. In addition, the pass bands exhibit a decrease in transmission for the composite, relative to the mixture, with the decrease being significant at shorter wavelengths.²⁴

The changes in the optical behavior exhibited by the CCA/PEG mixture and PCCA are typical for the photopolymerization of a CCA/PEG into a PCCA. This suggests that the creation of a polymer network around the ordered particles does not significantly disrupt the long-range order.¹³ In general, photopolymerization of CCA/PEG mixtures into the composites results in a minor alteration of the stop band positioning, with changes being under 6 nm. The bandwidths are observed to be within the range of 12–15 nm, while calculations predict smaller values falling within the range of 6–9 nm (cf. Table 2). The observed bandwidths are ca. 2 times larger than predicted, and it is speculated that lattice distortions and defects are responsible.²⁵

Recent studies on sterically packed colloidal crystals reveal that defects in the lattice significantly alter the optical properties of the material.^{26–28} Strongly localized photonic bandtail states appear due to the presence of defects which yield an enhanced transmission at the photonic band gap, creating a stop band which becomes shallower with disorder. In addition, the appearance of

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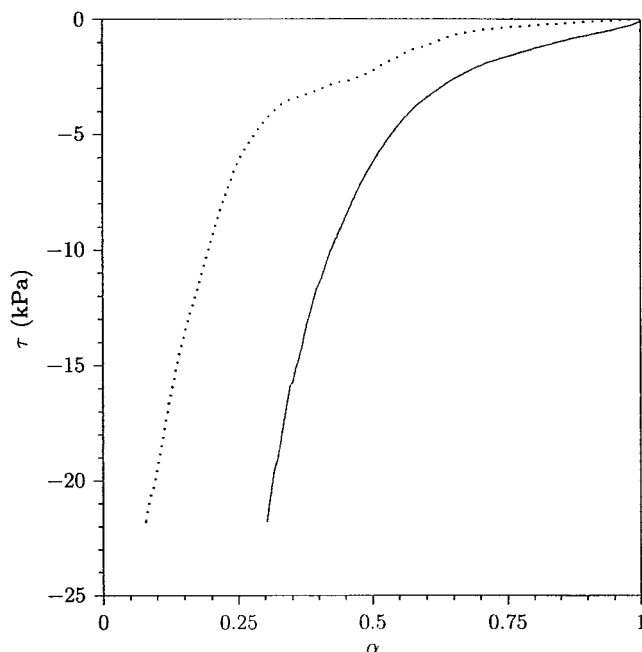


Figure 2. Mechanical response of PCCA (solid line) and unfilled hydrogel (dotted line).

defects leads to an exponential decay in light intensity with thickness not only within the former gap of the periodic structure but also in the former pass bands, thus broadening the gap and decreasing the transmission in the pass bands. These characteristics are observed in Figure 1, where the stronger attenuation in the stop band and the higher transmission in the pass bands are achieved with the original CCA/PEG mixture relative to the composite. These characteristics suggest that the photopolymerization results in some level of defect generation.

3.2. Mechanical Measurements. Hydrogels are solids composed of hydrophilic polymers which are lightly cross-linked and water swollen and, in their highly swollen state, exhibit a mechanical response that is characteristic of a "traditional" rubber.^{29,30} Figure 2 presents the stress-strain response for the PCCA composite as well as for an unfilled hydrogel of the same formulation as the PCCA except that the CCA component has been replaced by water. For these systems, τ is the force per unit area of hydrogel and $\alpha = h/h_0$ is the ratio of deformed sample height to initial height. The mechanical behavior of these systems is similar to the general characteristic of rubber elastic behavior, such as high compressibility generated by a low mechanical stress that is completely recoverable.

Plotting τ as function of $(\alpha - \alpha^{-2})$ for low strains results in a straight line with slope proportional to the effective cross-link density.³⁰⁻³⁴ The modulus of the PCCA composite and corresponding hydrogel was 2.01 and 0.39 kPa, respectively, while the effective cross-link density was 0.46 and 0.09 mol/m³, respectively. As suggested by Figure 2, the reinforcing polystyrene particles and lower water content in the PCCA composite result in a significantly higher modulus value and greater effective cross-link density relative to the values for the unfilled hydrogel.

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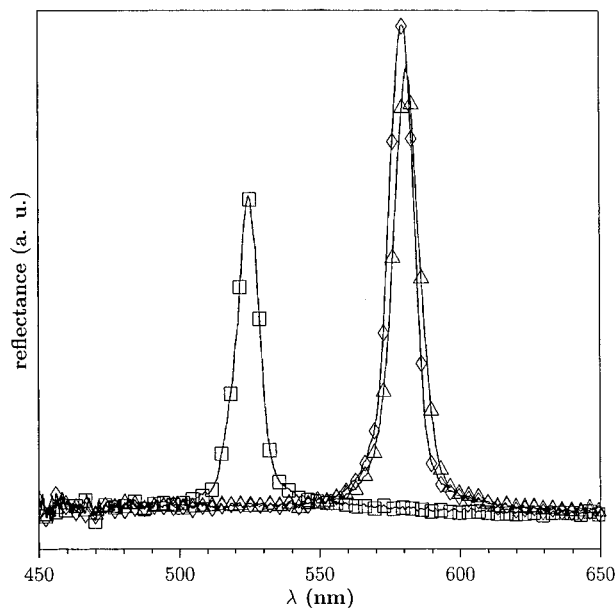


Figure 3. Reflectance spectra of PCCA composite with compressive loading: original stress-free state (\diamond), under a ca. 1 kPa load (\square), and unloaded stress-free state (\triangle).

The modulus values for the composites are typical for highly swollen hydrogels²⁹ but are low relative to those of typical engineering polymers.³⁵ Nonetheless, the encapsulation of the arrays with a "soft" hydrogel is sufficient to render the order stable to mechanical deformation.¹³

3.3. Mechanochromic Response. During the mechanical testing of the PCCA films, the observation was made that the films exhibited color changes with deformation. We attribute this response to the compression of the lattice, where in section 3.1, the nearest neighbor distance for the particles in the PCCA was calculated to be 2.6 times greater than the distance based on the intimate contact of the particles (cf. Table 2). Obviously, there is sufficient volume between particles to allow for the compression of the lattice, while maintaining their long-range order.^{13,36} To explore this phenomenon more thoroughly, the PCCA composite was removed from the plates and placed in a dish with an excess of deionized water for a number of weeks. The film was then placed over an optical probe in which the reflectance spectra of the films could be observed at normal incidence. Figure 3 presents the reflectance spectra of a water-swollen PCCA film in the stress-free state and under a compressive loading. In the initial stress-free state, the swelling of the films has resulted in a stop band movement from 542 to 580 nm. Upon application of a ca. 1 kPa compressive load, the stop band shifts down to 525 nm, a 55 nm variation. The peak of the stressed film is 65% of the original height in the stress-free state, though the bandwidth is maintained at 10 nm. It is speculated that the contraction of the lattice under loading introduces disorder which enhances the transmission at the photonic band gap, reducing the reflectivity.²⁶⁻²⁸ A 1 kPa compressive stress on the original unswollen PCCA films translates into a strain of ca. 15% (cf. Figure 2), while the nearest neighbor distance (a) calculated from the stop band shift is estimated to reduce by ca. 10%. In Figure 3, the removal of the load allows the film to immediately regain the optical char-

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acteristics of the original stress-free state with a slight diminishing of the peak height, which after a few minutes again superimposes the original peak.

4. Conclusion

The transformation of a crystalline colloidal array into a composite film through the in situ polymerization of a poly(ethylene glycol) derivative around the arrays results in a robust material with a shear modulus of ca. 2 kPa. The coupling of the mechanical and optical properties of

the composite results in a photonic crystal which exhibits a mechanochromic response, where an applied ca. 1 kPa compressive stress results in a stop band shift of ca. 55 nm that is completely reversible.

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