

Photonic Bandgap Composites

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This communication describes a procedure for generating robust polymeric composites which exhibit photonic bandgap (PBG) and mechanochromic properties. The PBG composites are composed of ordered arrays of self-assembled polystyrene spheres that have been repeatedly encapsulated with various polymeric systems in order to achieve two objectives: 1) lock-in the crystalline nature of the ordered arrays in a robust water-free matrix and 2) introduce a methodology for tailoring the mechanical properties of the final composite.

Since the original proposal that three dimensional periodic dielectric structures could exhibit a 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 visible photonic crystals as devices has been hindered by the difficulties in 1) creating three-dimensional (3D) periodic dielectric structures with a feature size comparable to the wavelength of visible light and 2) achieving dielectric contrasts that result in a forbidden gap that overlaps in all directions within the Brillouin zone. One approach to address these challenges 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 PBG.^[3]

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 non-aqueous media.^[4-6] At high particle concentrations, long-range electrostatic interactions between particles result in a significant inter-particle repulsion which yields the adoption of a minimum energy colloidal crystal structure with either body centered cubic (bcc) or face-centered cubic (fcc) symmetry.^[7-9] The ordering of the particles in the media results in spatial periodicities of the dielectric function that can result in both allowed and forbidden directions for electromagnetic waves of certain wavelengths to propagate. In the case of the CCAs, the ordering results in spatial periodicities that range from ca. 10^2 – 10^3 nm, resulting in the appearance of optical bandgap effects. These photonic crystals have potential applications as optical rejection filters, switches, limiters, and sensors.^[10-12]

Unfortunately, the low elastic modulus (10^{-2} – 10^{-3} Pa)^[6,13,14] exhibited by a liquid dispersion results in weak shear, gravitational, electric field, or thermal forces having the propensity to disturb the crystalline order and is a severe drawback to the practical application of CCAs in photonic devices. For instance, a liquid phase CCA will undergo a disordering when subjected to a mechanical shock, after which, the system will again self-assemble, while a permanent disordering can be induced to incur with the introduction of ionic impurities. 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 a polymerized crystalline colloidal arrays (PCCAs).^[10,12,15] The PCCA films contain at least 30 vol.-% water, resulting in their fragility and propensity for significant changes in optical performance with water content. Mechanically robust composite films composed of silica particles in acrylate polymers have exhibited band stop tuning with mechanical stress, 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.^[16-18] In this work, we present a procedure in which the optical qualities of a hydrogel based PCCA are retained in a highly durable and water-free composite. In addition, the procedure allows for the tailoring of the mechanical characteristics of the composite to suit an end-use criteria.

Figure 1 schematically illustrates the procedure for fabricating a PBG composite. The first phase requires the stabilization of a CCA through the generation of a hydrogel based PCCA. Although poly(acrylamide) and its derivatives have been established as standard PCCA matrixes,^[10] we have focused on the use of poly(ethylene glycol) (PEG) hydrogels to give unique PEG-based PCCAs.^[15,19] Hydrogels are prepared by the photoinitiated free radical polymerization of

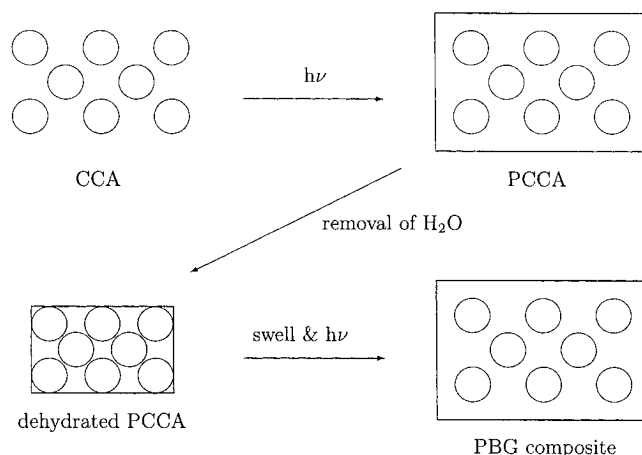


Fig. 1. Procedure for generating PBG composite: a liquid suspension of a CCA is combined with hydrophilic monomers and a photoinitiator and subsequently photopolymerized into a PCCA; the water in the hydrogel based system is removed, resulting in a dry PCCA; the dehydrated PCCA is swollen with monomers and photopolymerized into a PBG composite.

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methacrylate-functionalized PEG in the presence of an ordered CCA. Networks based on PEG tend to exhibit a wider range of amphiphilicity and may offer greater compatibility with subsequent chemistry and therefore greater versatility in tuning composite properties. Once the PCCA is generated, the long range order of the particles are stable to ionic contamination and minor mechanical deformation, though the mechanical performance of the composite is typical of a “soft” hydrogel with water contents in excess of 80 vol.-%. The next phase in the composite fabrication requires the removal of water through evaporation at ambient conditions and a subsequent vacuum exposure to remove all remaining water. This “dry” PCCA generally does not exhibit iridescence and is significantly smaller than the original hydrated PCCA. The dehydrated PCCA film is then swollen in 2-methoxyethyl acrylate (MOEA), a monomer which has a strong affinity for the PEG-based matrix of the PCCA. The reswollen PCCA film will again exhibit an angle dependant iridescence. The incorporation of a small quantity of ethylene glycol dimethacrylate (1 vol.-%) and a photoinitiator of 2,2-diethoxyacetophenone (DEAP) into the reswollen system, with subsequent photopolymerization, results in a completely water-free composite which exhibits PBG properties and improved mechanical performance relative to the hydrogel PCCA.

Figure 2 presents the reflectance spectra of a PCCA swollen in deionized water, a PCCA swollen in MOEA, and its corresponding PBG composite. All reflectance spectra were

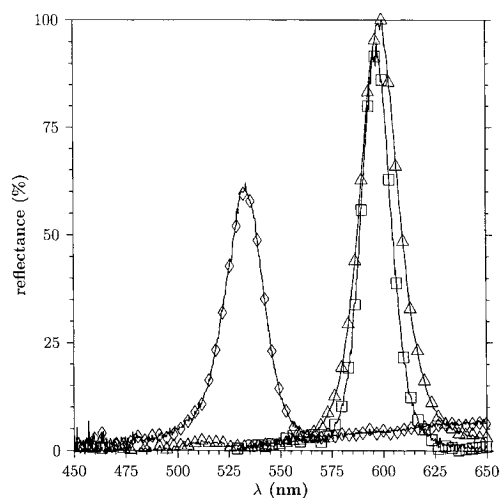


Fig. 2. Reflectance spectra, at normal incidence, of PCCA swollen in deionized water (Δ), PCCA swollen in MOEA (\square), and PBG composite (\diamond). The intensity of the curves has been scaled relative to the PCCA swollen in deionized water.

taken at a temperature of 23 °C, unless otherwise indicated. The water swollen PCCA exhibits a band stop of 600 nm, while the MOEA swollen PCCA exhibits a band stop of 597 nm. In addition, the PBG composite has a band stop at 533 nm, a ca. 64 nm reduction relative to the MOEA swollen system. A hydrated PCCA generally exhibits a higher level of swelling relative the MOEA swollen system due to the high affinity of the PEG based matrix for water, while after photopolymerization, the contraction of the poly(2-methoxyethyl

acrylate) (PMOEA) matrix tends to reduce the interparticle spacing an additional amount.

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. In the case of CCAs in which the lattice adopts a fcc symmetry, the (111) planes are parallel to the walls.^[8,9] The diffraction characteristics of these systems are most accurately predicted through the application of dynamic diffraction theory, though the Bragg diffraction equation ($\lambda_0/2 = n_c d_{hkl} \sin\theta$, where λ_0 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) is a reasonable approximation.^[20] In the experimental configuration, unpolarized light is propagated along the [111] direction of the fcc lattice, or the L-point of the reciprocal lattice.^[21] The observed band stop is then related to the lattice parameter of the conventional cubic unit cell through the Bragg equation and $a_c = \sqrt{3}d_{111}$, while the nearest neighbor distance (i.e., the primitive lattice parameter and spacing between particles at fractional coordinates 0,0,0 and 1/2,0,1/2 of the cubic unit cell) is $a = a_c/\sqrt{2}$. The 533 nm stop band observed in the composite ($n_c = 1.473$) translates into a d_{111} spacing of 181 nm. The nearest neighbor distance of the polystyrene particles is 222 nm, twice their 109 nm diameter. Obviously, the lattice contraction exhibited in the shift from the swollen state to the polymerized state does not result in the steric packing of the particles.

Dynamic mechanical thermal analysis (DMTA), operated in the torsional mode, was employed to characterize the mechanical response of the PBG composites in the temperature range of -150 °C to 125 °C and is presented in Figure 3. The low temperature shear modulus (G') exhibits a value of ca. 2×10^9 Pa and undergoes a significant drop at an onset temperature of -35 °C. At temperatures greater than this transition point, the modulus is significantly reduced relative to the value in the glassy state, exhibiting a value of ca. 3×10^5 Pa, which is characteristic of the rubbery state. In addition, the $\tan\delta$ loss response of the composite confirms the appearance of a single relaxation in this temperature range, reaching a maximum value of $\delta = 64^\circ$ at -17 °C. At the rubbery plateau,

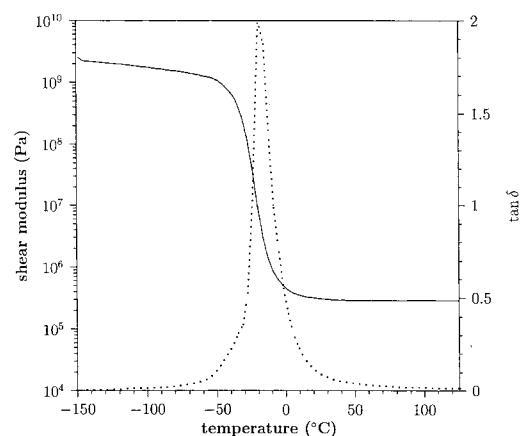


Fig. 3. Shear modulus G' (—) and loss tangent (···) of PBG composite at 1 Hz.

the modulus is relatively constant up to a temperature of 125 °C, indicative of the crosslinked nature of the matrix.

The relaxation exhibited in the dynamic mechanical response of the composite is confirmed by differential scanning calorimetry (DSC), where a maximum change in the heat flow is observed at a temperature of −39 °C (c.f., Fig. 4). As indicated in the DMTA response of the PBG

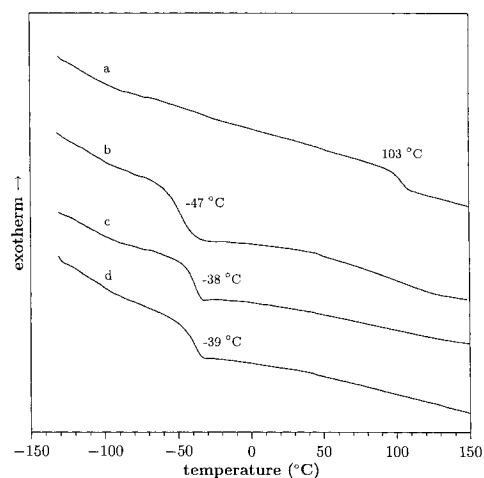


Fig. 4. Heating thermograms and observed glass transitions of a) polystyrene, b) PEGMA, c) PMOEA, and d) PBG composite; curves shifted for clarity.

composite, only one relaxation is observed between −150 °C and 125 °C. In addition, Figure 4 presents the heating thermograms of various components of the PBG composite which have been photopolymerized into lightly crosslinked homopolymers. The PBG composites are composed of a majority of polymerized MOEA (e.g., ≥80 vol.-%), therefore, the transition temperature of the composite most resembles the “pure” PMOEA, where the glass transition (T_g) of an uncrosslinked PMOEA has been previously reported in the range of −50 °C to −33 °C.^[22,23] The influence of the poly(ethylene glycol) methacrylate (PEGMA) and polystyrene in the composite is not apparent in either the DMTA or DSC analysis. The T_g of the PBG composite can be altered by copolymerization of additional acrylate monomers with MOEA, or through a complete substitution. For instance, substitution of MOEA with 2-methoxyethyl methacrylate results in a hard and glassy PBG composite at 23 °C.

It has been previously observed that PBG composites can exhibit a mechanochromic response.^[12,16,19] This mechanochromic response has been attributed to the affine deformation of the lattice, where a decrease in the wavelength of the band stop is in response to a decrease in the interplanar spacing of the particles. Unfortunately, environmentally stable (i.e., water-free) composites that exhibit 100 nm or greater band shifts and short recovery times have not been presented.

Figure 5 presents the reflectance spectra of a PBG composite film at normal incidence in the stress-free state and under a compressive loading. In the initial stress-free state, the position of the band stop is at 610 nm. Upon applying a 145 kPa

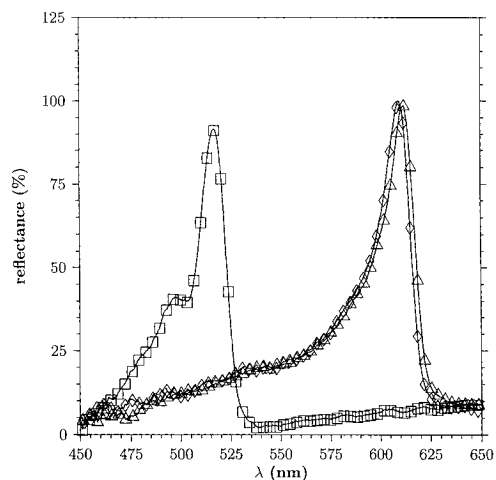


Fig. 5. Reflectance spectra of PBG composite at normal incidence: original stress-free state (\diamond), under a 145 kPa compressive stress (\square), and unloaded stress-free state (\triangle). The intensity of the curves has been scaled relative to the original stress-free state.

compressive stress, the band stop shifts down to a wavelength of 517 nm, a 93 nm variation. Additional compressive stress resulted in increasing larger band stop shifts, with shifts of 120 nm being attainable. Unfortunately, with increasing stress, the peaks became broader and less well defined due to the introduction of disorder in the array. Assuming that the band stop can be attributed to the d_{111} interplanar spacings, the strain (ϵ) associated with the 145 kPa stress is −15.2%. With compression, the short wavelength shoulder on the peak which is visible in the unstressed state becomes more clearly defined. A disordered and possibly rotated crystal is the presumed source of this shoulder. At 23 °C, the PBG composites are at a temperature above their T_g . Assuming that their mechanical response can be modeled as rubber-like and follows the relationship:

$$\sigma = G' \left(\alpha - \frac{1}{\alpha^2} \right) \quad (1)$$

where σ is the force per unit area of composite and $\alpha = \epsilon + 1$ is the deformed height to the initial height of the composite, a composite with a shear modulus of 310 kPa (c.f., Fig. 3) would strain ca. −13.5% under a 145 kPa compressive stress, in agreement with the reflectance results. In addition, the removal of the compressive stress results in the immediate return of the band stop position within 1–2 nm of the original stress-free state (c.f. Fig. 5). Repeatedly straining a PBG composite did not result in any permanent change in the observed optical characteristics, unless the film was mechanically degraded.

In summary, we have presented a methodology for stabilizing the long range order in colloidal arrays through encapsulation in a robust and water-free matrix. The flexibility in altering the mechanical properties of the final composite through monomer substitution or copolymerization of the matrix, coupled with the mechanochromic response of the PBG composites, suggests that these systems may be useful in optical sensor or switching applications.

Experimental

Crystalline Colloidal Array (CCA): Monodisperse crosslinked polystyrene particles were prepared using an emulsion polymerization procedure described elsewhere [24,25]. The resulting particles were dialyzed against deionized water and then shaken with an excess of mixed bed ion-exchange resin [19]. After the cleaning procedures, the particle diameter was measured to be 109 ± 26 nm with a Coulter N4MD dynamic light scatter (DLS). The cleaned suspension was then diluted with deionized water until an angle dependent iridescence was observed. Drying a known mass of the suspension in an oven at 80°C overnight and then under vacuum for 2 days resulted in a calculated particle density of $2.6 \times 10^{14} \text{ cm}^{-3}$.

Polymerized Crystalline Colloidal Array (PCCA): The CCAs were encapsulated in a hydrogel matrix prepared by an in situ photopolymerization procedure [19]. The matrix materials included a monomer of PEGMA, $M_n = 360$, a crosslinker of poly(ethylene glycol) dimethacrylate (PEGDMA, $M_n = 550$), and a photoinitiator of DEAP. The PEGMA and PEGDMA were stored in Nalgene containers over a mixed bed ion-exchange resin for at least 48 h prior to their use, while all other matrix materials were used as-received.

The procedure for generating a PCCA film included combining all the components of the PCCA in a Nalgene container and allowing the mixture to shake with an excess of a mixed bed ion-exchange resin for at least 2 h prior to injecting the mixture between two quartz plates separated by a $500 \mu\text{m}$ parafilm spacer. The film was then polymerized by exposing the assembly to an ultraviolet (UV) source for 4 min.

In order to fabricate the PBG composite, the resulting PCCA film was removed from the quartz plates and allowed to air dry for 2 days and then placed in a vacuum oven at 35°C . The resulting clear films were then swollen in a solution of MOEA for 2 days. To this solution, ethylene glycol dimethacrylate and DEAP was added and the formulation crosslinked by a 20 min exposure to the UV lamp. All chemicals were purchased from either Aldrich or Acros Organics.

Optical Analysis: The reflectance spectra of the composites were collected on an Ocean Optics PC2000 fiber optic spectrometer with incident light normal to the quartz plate surface. Spectra were collected between the wavelengths of 300 to 900 nm, while a Metricon 2010 prism coupler operating at 632.8 nm was employed to measure the refractive index of the PBG composites.

Thermal Analysis: The dynamic mechanical characteristics of the PBG composites were determined with a TA Instruments AR1000-N rheometer operating in the torsional mode. Scans were made at 1 Hz under a nitrogen purge and scanning rate of $5^\circ\text{C}/\text{min}$. Samples were placed in a vacuum oven at 35°C for at least 15 h prior to testing.

A differential scanning calorimeter (TA Instruments DSC 2920) equipped with liquid nitrogen cooling accessories and operating in the modulated form was employed; the reported T_g value is taken at the peak maximum in the curve of the first derivative of heat flow. The carrier gas was nitrogen at a flow rate of ca. $50 \text{ mL}/\text{min}$. Scans were made from -150°C to 150°C at a scanning rate of $10^\circ\text{C}/\text{min}$. All samples were run twice, with reported values taken from the second run.

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