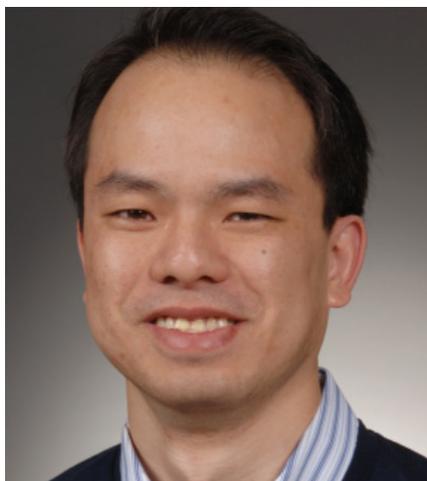




BLOCK COPOLYMER PHOTONIC GEL FOR DETECTING INTERFACIAL SEPARATION

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Introduction

Mechanochromism, which is defined as a visual color change in response to a mechanical deformation, is a phenomenon that has been observed in many polymer gel layers. Since the local deformation can be detected visually via a color change, mechanochromic materials are potentially useful for measuring separation modes of pressure adhesives, traction forces of cells, tissue deformation during surgical procedures, blast damage in body armor, as well as failure for building infrastructure.

An interesting class of polymer gels that displays mechanochromism is block copolymer photonic gels, which are nanostructured materials engineered with a photonic stopband or color whose mechanochromic properties can be tuned by adding solvents, diluents, polymers and nanoparticles. This work will demonstrate block copolymer photonic gels as sensors for detecting interfacial failure relevant to pressure sensitive adhesion. The block copolymer gels discussed are styrenic-based diblock copolymers preferentially swollen with diluents to enhance both their optical and mechanical properties. Several examples of adapting these block copolymer photonic gels as mechanochromic sensors for detecting different modes of interfacial separation will be presented.

Block copolymer photonic gels

Photonic crystals derive their color from photonic band gaps, which develop due to a periodic arrangement of at least two materials having different refractive indices (Figure 1). Unlike other photonic materials that generate color based on luminescence, photonic crystals are unique in that they generate color based on constructive interface of light at periodic interfaces.

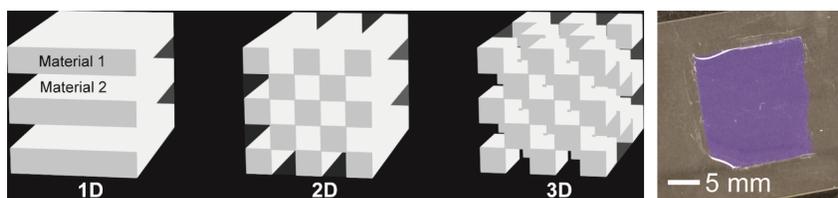


Figure 1. The left figure is a schematic representation of 1D, 2D and 3D photonic crystals. The dimensionality refers to the spatial arrangement of at least two materials with different refractive indices. Reproduced with permission.¹ Copyright 2013, John Wiley & Sons, Inc. The right figure is an optical micrograph of a block copolymer photonic gel.

The simplest photonic crystal is a 1D photonic crystal, which consists of an arrangement of layered materials with different dielectric constants or refractive indices periodic along only one direction (Figure 1). This 1D photonic crystal consists of a pair of layers of two different materials of thickness d_1 and d_2 with isotropic refractive indices n_1 and n_2 . Such a material is commonly referred to as a Bragg reflector and the stopband arises from constructive and destructive interference reflections at each material interface. Incident light is partially reflected at the interfaces created by these two materials and

the sum contribution of reflection from the layers leads to constructive interference of a certain wavelength of light.

In order to reflect a color for wavelength around 600 nm, the optical thickness for each material layer must be 150 nm. For example, a polymeric material with a typical refractive index $n \approx 1.5$ would require layer thickness of $d \approx 100$ nm. For a 1D photonic crystal consisting of two materials, the wavelength (λ) can be simply written as,

$$\lambda = 2(n_1d_1 + n_2d_2). \quad (1)$$

Based on Equation (1), it is clear that changing the thickness or refractive index or both can control the wavelength of color.

While photonic crystals have been studied for over 100 years, their application as mechanochromic sensors has only been exploited in the last decade. A main reason for the limited applications is due to traditional design of photonic crystals using inorganic or “hard materials”. Since these materials are only elastic at a few percent strains, the color change with strain is quite small to be detected practically. Compared with hard materials, polymer gel-based photonic crystals are potentially interesting as mechanochromic sensors due to their extreme elasticity. Polymer gels are either physically- or chemically-crosslinked polymer networks traditionally swollen low-molar mass solvents. However, swelling with other diluents, such as plasticizers, polymers and nanoparticles, offer a significantly larger parameter space to tailor both the optical and mechanical properties of polymer gel-based photonic crystals, which we refer to as photonic gels.

A 1D photonic gel reflects color perpendicular to the material layers, thus making it an ideal geometry for mechanochromic sensing since the color can be easily viewed normal to a surface. While a top-down fabrication strategy such as co-extrusion of polymer multilayer films is a commercially relevant approach, it has only been demonstrated for fabricating glassy and semi-crystalline polymer multilayers. For photonic gels, we use a bottom-up fabrication approach based on self-assembly of block copolymers. For a diblock copolymer composed of 2 homopolymers covalently bonded at a junction, several morphologies including the body-centered cubic, cylindrical, bicontinuous cubic, and lamellar structures can be obtained depending on the relative composition of the homopolymers (Figure 2).

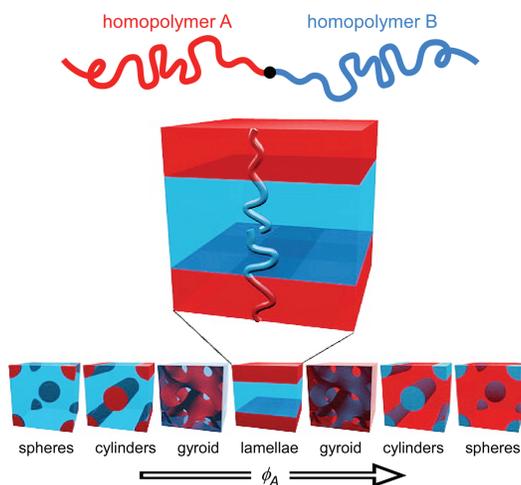


Figure 2. Block copolymer phase diagram of a diblock copolymer consisting of homopolymers A and B. Reproduced with permission.² Copyright 2007, Elsevier.

For the photonic gels discussed, we will focus on diblock copolymers where both blocks have similar molecular mass such that they self-assemble into the lamellar morphology. The size of an individual

block copolymer microdomain scales with the molecular mass or total number of monomer repeat unit (N) of the corresponding polymer. For a diblock copolymer that forms the lamellar morphology, the size of microdomain scales as $N^{2/3}$. Besides having a refractive index contrast between the respective block domains, a photonic crystal with color in the visible wavelengths requires that each homopolymer have sufficiently large number of monomer repeat units to create the necessary 100 nm domain thickness, in other words, the total molecular molar mass is about 10^6 g/mol.

Mechanochromism of block copolymer photonic gels

Mechanochromism in a photonic gel is based on changes in color due to changes in the optical path length of one or more of the domains upon the application of a mechanical deformation. Consider a photonic gel under the three basic modes of compression, tension, and shear (Figure 3a).¹ Additionally, we consider that this photonic crystal consists of two materials with different refractive indices (n_1, n_2) but similar thicknesses ($d_1 \approx d_2$) and moduli ($E_1 \approx E_2$), possesses strain-independent refractive indices, and behaves mechanically as linear-elastic materials. In all the deformation modes, the applied deformation either deforms or distorts this multilayered structure to cause a change in layer dimensions and/or refractive index, which changes the optical path length for each layer thus resulting in a change in color. However, the extent of change in color is unique to each deformation, which implies unique relationships between wavelength of color (λ) and strain (ϵ) (Figure 3b).

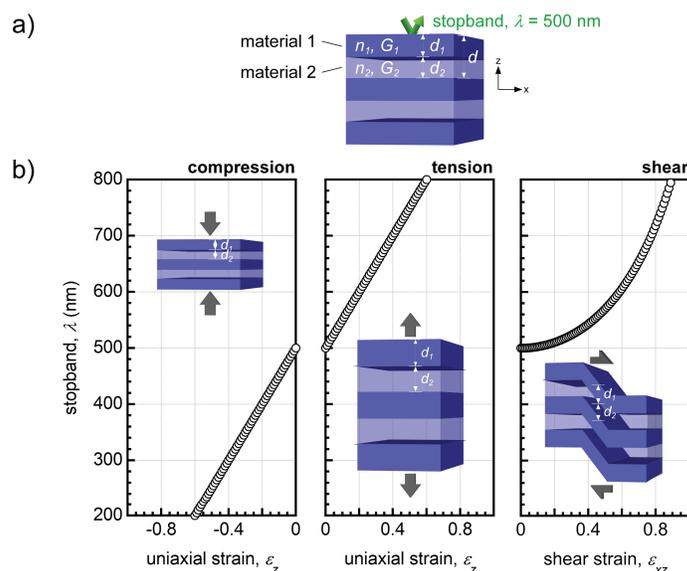


Figure 3. Three primary modes of deformation in relation to mechanochromism. a) Example of a photonic gel made up of two materials with different refractive indices (n_1, n_2) but similar layer thicknesses ($d_1 \approx d_2$) and elastic moduli ($E_1 \approx E_2$). b) The left plot shows that the color shifts to shorter wavelengths linearly with compressive strain (ϵ_z) due to reduction in optical path lengths. The center plot shows that the color shifts to longer wavelengths linearly with tensile strain (ϵ_z) due to increase in optical path lengths. The right plot shows that the color shifts to longer wavelengths nonlinearly when shear strain (ϵ_{xz}) induces changes in lamellar orientation leading to changes in the layer spacing. Reproduced with permission.¹ Copyright 2013, John Wiley & Sons, Inc.

Based on our understanding of the development of color in a photonic gel, we can develop some simple relationships between wavelength of color and mechanical deformation.¹ Uniaxial compression and tension applied along the normal to the layer thickness are similar as they can be described as a decrease or an increase in the layer thicknesses, respectively. Based on Equation (1), the stopband versus strain relationship is,

$$\lambda(\varepsilon_z) = 2n_1d_1 \cdot (1 + \varepsilon_{z,1}) + 2n_2d_2 \cdot (1 + \varepsilon_{z,2}) , \quad (2)$$

$$\varepsilon_z = \phi_1\varepsilon_{z,1} + \phi_2\varepsilon_{z,2} . \quad (3)$$

Equation (3) is obtained from the classical Reuss composite model with volume fractions of materials 1 and 2 defined as $\phi_1 = d_1/d$ and $\phi_2 = d_2/d$, respectively.

Shear is unique in that it involves a shape change as opposed to a volume change. This leads to a rotation as well as a translation of the layers, which causes an effective increase in the optical path length along the original viewing direction with strain (Figure 3c). Therefore, the wavelength of color increases nonlinearly with shear strain (ε_{xz}),

$$\lambda(\varepsilon_{xz}) = \frac{2(n_1d_1+n_2d_2)}{\cos(\tan^{-1}(\varepsilon_{xz}))} . \quad (4)$$

Mechanochromism of photonic gels for characterizing interfacial strength

Using these relationships that describe the change in color with deformation modes in photonic gels, we can apply them to understand mechanochromism of photonic gels in the context of characterizing interfacial strength.

Peel testing

Swelling with a solvent represents one of the simplest and most versatile routes to enhancing the physical, optical, and mechanical properties of polymers. However, most solvents are volatile, which causes unstable changes in polymer properties unless the overall system can be encapsulated. As a solution, Urbas and coworkers used dioctyl-phthalate, a common non-volatile plasticizer for polymers, to swell a nearly symmetric diblock of polystyrene-*b*-polyisoprene (PS-*b*-PI) of moderate molecular mass ($M_{n,PS}/M_{n,PI} = 194 \text{ kg/mol.}/197 \text{ kg/mol.}$).³ Since dioctyl phthalate is a neutral solvent for both polymer blocks, both the PS and PI microdomains swell significantly thus resulting in a photonic gel that is quite soft and viscoelastic because the glassy PS is now plasticized.

This plasticized PS-*b*-PI photonic gel is then used to measure the stress distribution in a peel test (Figure 4). A small amount of this photonic gel was placed between a rigid glass substrate and a clear flexible plastic film. Then, the clear plastic film was peeled back from the glass substrate deforming the photonic gel (Figure 4a). As shown in (Figure 4b), this deformation caused a color change at the separation edge, *i.e.* the peel front. Since the undeformed gel is violet in color, the shift to a longer wavelength at the peel front indicates that the gel is in tension. Ahead of this peel front, as indicated by the deformed region in significant color change is observed that is highly position dependent and oscillates between longer and shorter wavelengths corresponding to both tensile and compressive regions of deformation (Figure 4c).

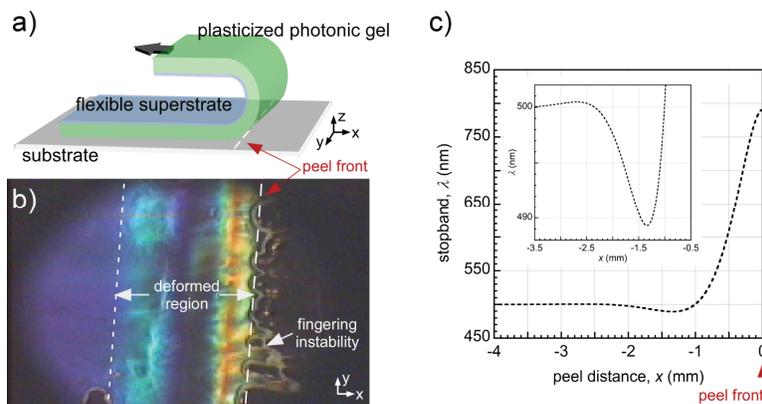


Figure 4. Peeling of a plasticized PS-*b*-PI photonic gel. a) The photonic gel layer is sandwiched between a rigid substrate and a flexible backing. This backing is then peeled away to develop a peel front. Reproduced with permission.¹ Copyright 2013, John Wiley & Sons, Inc. b) Optical micrograph of the peel testing illustrating the mechanochromic response of the photonic gel as the backing is peeled from right to left. Reproduced with permission.³ Copyright 2003, Massachusetts Institute of Technology. c) Predicted change in wavelength of color as a function of the peel distance. The inset figure magnifies the region directly behind the peel front illustrating the tensile and compressive regions of the photonic gel. Reproduced with permission.¹ Copyright 2013, John Wiley & Sons, Inc.

Contact adhesion testing

Besides peel testing, photonic gels can also potentially be used to measure interfacial strength using contact adhesion testing. Chan and coworkers demonstrated the mechanochromic response of a polystyrene-*b*-poly-2-vinylpyridine (PS-P2VP) photonic gel via contact adhesion testing.⁴ A moderately high molecular mass PS-*b*-P2VP diblock ($M_{n,S}/M_{n,P2VP} = 102$ kg/mol./97 kg/mol.) was converted to a photonic gel when exposed to an acetic acid-water solution that selectively swells the P2VP domains by protonation. Contact adhesion testing was used to study the mechanochromic response by deforming the gel uniaxially with a spherical probe and characterizing the applied compressive strain, stress and contact area (Figure 5). Due to the spherical shape of the probe, an axisymmetric strain field developed within the region of the gel in contact, which is reflected by the radially-dependent color observed in each normal incidence light (Figure 5b). The probe shape causes increases in the contact area with increasing compressive strain (ϵ_z). Both of these features are captured by the local color change of the photonic gel, which nicely demonstrated the ability of the BCP photonic gel to record local mechanical deformation. Unfortunately, the interfacial strength cannot be quantified because the probe separated from the gel surface before any tensile strain can be developed within the gel.

To describe the mechanochromic response, the position of the wavelength of color measured at the center of contact was measured as a function of compressive strain at several indentation rates. The results suggest that the color shift with increasing compressive strain appears to be insensitive to the deformation rates investigated. Importantly, the mechanochromic response is tunable with respect to the pH of the acetic acid solution. The degree of swelling of the P2VP layers, and hence the average shear modulus of the photonic gel, decreases significantly with decreasing acetic acid concentration with respect to the water content. This simple demonstration provided a straightforward means to adjust the mechanochromic sensitivity of the photonic gel depending on the particular sensing requirements. Currently, we are investigating the interfacial strength of the dioctyl phthalate plasticized PS-*b*-PI photonic gel using contact adhesion testing. Preliminary results indicate that the interfacial strength and mechanochromic property can be tuned by varying the amount of dioctyl phthalate relative to the block

polymer from 0 % by mass to 200 % by mass. This approach appears to be a pragmatic means to generate a mechanochromic pressure sensitive adhesive as the plasticizer content can be used to tune the viscoelasticity and mechanochromism of the photonic gel.

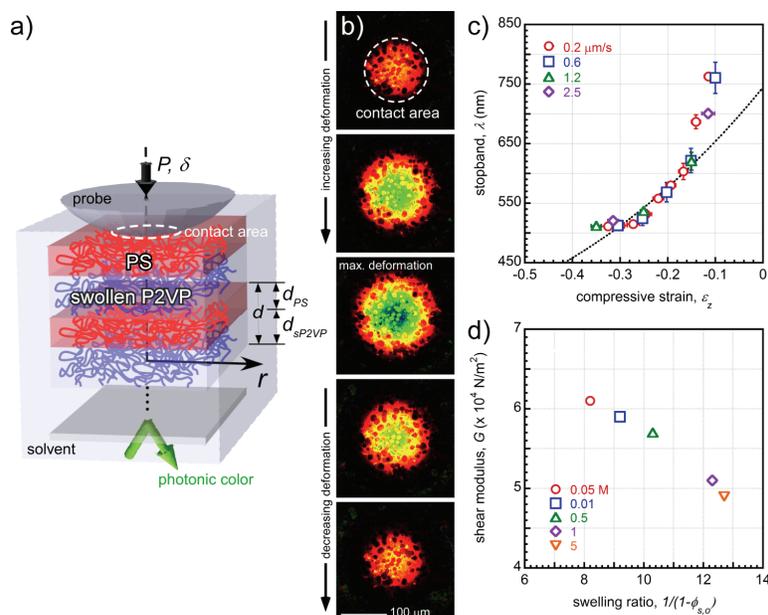


Figure 5. Mechanochromism of a polyelectrolyte PS-*b*-P2VP photonic gel swollen with an acetic acid/water solution. a) Schematic of the contact adhesion testing. b) Optical micrographs of the change in color with compression of the gel by the probe. c) Change in wavelength of color with compressive strain. d) Change in shear modulus of the gel as a function of swelling ratio. Reproduced with permission.⁴ Copyright 2011, John Wiley & Sons, Inc.

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