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Dependence of Photonic Crystal Nanocomposite Elasticity on Crystalline Colloidal Array Particle Size

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The properties of hydrogel materials depend on their network structure, which is determined predominantly by the hydrogel polymer volume fraction and the degree of hydrogel cross-linking.[1−3] In an effort to optimize the utility of our photonic crystal hydrogel materials, and to improve our understanding of these nanocomposite systems, we investigated how the mechanical properties of these photonic crystal hydrogels depend upon the diameter of the nonbonded embedded nanoparticles.

Our photonic crystal hydrogel materials contain mesoscopically periodic arrays of colloidal particles that self-assemble into highly ordered crystalline colloidal arrays (CCA), with lattice spacings that Bragg diffract visible light (Figure 1A).[4−10] The CCA are polymerized within hydrogels forming a polymerized CCA (PCCA).[11] These PCCA optically report on volume changes experienced by the hydrogels, since the observed diffraction wavelength directly depends upon the spacing between lattice planes. These PCCA have been used for chemical sensing by functionalizing them such that changes in the concentration of the analyte of interest actuate changes in the PCCA volume and, thereby, the diffraction wavelength.[12−14] Intelligent PCCA have been developed for the detection of multiple analytes, including glucose,[15−17] cations,[18−20] ammonia,[21] pH,[22] organophosphates,[23] and creatinine.[24]

The viscoelastic properties of a hydrogel are predominantly determined by the hydrogel network structure.[1,3] In the work here we develop new insight into this network structure by oscillatory shear rheometry measurements, which characterize the PCCA shear storage modulus. This modulus monitors the effective cross-link density of the PCCA hydrogels.[1,3] The effective cross-link density is derived from normal hydrogel cross-links as well as from interactions of the hydrogel network with the embedded nanoparticles.

In spite of the numerous studies that examined the impact of nanoparticle inclusions on elastomer mechanical properties, there still remains significant quantitative disagreement on the dependence of these properties on nanoparticle size.[1,3,25−43] We present here the first definitive study of how the mechanical properties of a swollen hydrogel depend upon the diameter of nonbonded embedded nanoparticles.

Monodisperse, highly charged polystyrene colloidal particles with diameters between 114 and 186 nm were used in the preparation of the PCCA studied (Table 1). Figure 1B shows a TEM micrograph of the highly charged, monodisperse 186 nm polystyrene spheres. The PCCA studied were synthesized by UV-initiated free radical polymerization of a hydrogel around the CCA. In a typical recipe, 0.1 g of acrylamide and 0.002 g of bisacrylamide were dissolved in 2.0 g of CCA. The CCA solutions used for the PCCA preparations were composed of identical weight percent particle dispersions in water to ensure constant overall polymer content within the corresponding prepolymerization solutions. For hydrogels prepared without colloidal particles, 2.0 g of deionized water was used in place of the CCA solution.

Hydrogels were prepared using nanoparticles of different diameters and were analyzed at a constant temperature. Figure 2A shows the frequency dependence of the PCCA shear storage modulus for the different size nanoparticles. The modulus increases linearly with increasing particle diameter (Figure S1, Supporting Information).

These results are somewhat surprising considering previous reports.[1,3,28,29,31,33,36,37] Filler particles are commonly utilized to improve the mechanical properties of polymers by increasing the modulus. Previous studies have shown that the extent of modulus increase depends on the particle size, with smaller particles typically giving rise to a larger modulus increase than larger particles, exactly the opposite of what we observe for our PCCA.

The difference between our results and those of previous studies most likely derives from the fundamental differences in the morphologies of the systems studied, particularly the ordered dispersion of nanoparticles and the lack of particle−matrix bonding. Previous studies used filler nanoparticles which were randomly dispersed and showed a tendency to aggregate.[29,32] Our nanoparticles are electrostatically stabilized due to the high concentration of surface immobilized acid groups. The high surface charge prevents aggregation and causes the particles to self-assemble into an fcc array which uniformly spans the material, as evident in a SEM of a PCCA (Figure 2B). Further, the extent of interfacial interaction between the filler particle and surrounding polymer matrix will impact the overall viscoelastic response of the material.[26−34,37−39,42,43] The fact that many nanoparticles have fallen out of the surface layer of our PCCA hydrogel material (Figure 2C) demonstrates the lack of covalent attachment or interfacial adhesion between the polystyrene particles and the surrounding hydrogel matrix.

The correlation between the modulus and the particle diameter can be understood by treating the shear storage modulus as the product of the contributions of three distinct components, or regions, of the PCCA (Figure 3). We postulate that each particle is surrounded by a small interfacial shell, in which there are no interactions between the particle surface and the surrounding hydrogel matrix. The nanoparticles can be thought of as a very tight spring because of the large storage modulus of the rigid polystyrene particle. The hydrogel matrix can be thought of as a smaller force constant spring, since it is more elastic than the particles. The lack of adhesion between the embedded particles and surrounding hydrogel matrix results in slip, which is equivalent to a spring with a significantly low force constant. Given a constant particle volume fraction, the PCCA containing smaller particles have a larger contribution from the interfacial shell region, owing to increased surface area, giving rise to a lower overall PCCA modulus.

Using polymer rubber theory, we can determine the effective cross-link density (v_e) from the experimentally determined shear storage modulus (G') and the polymer volume fraction (ϑ):[1]

$$G' = v_e RT\vartheta^{1/3} \quad (1)$$

The effective cross-link density of these constant polymer volume fraction PCCA scales with the modulus and thus increases as the

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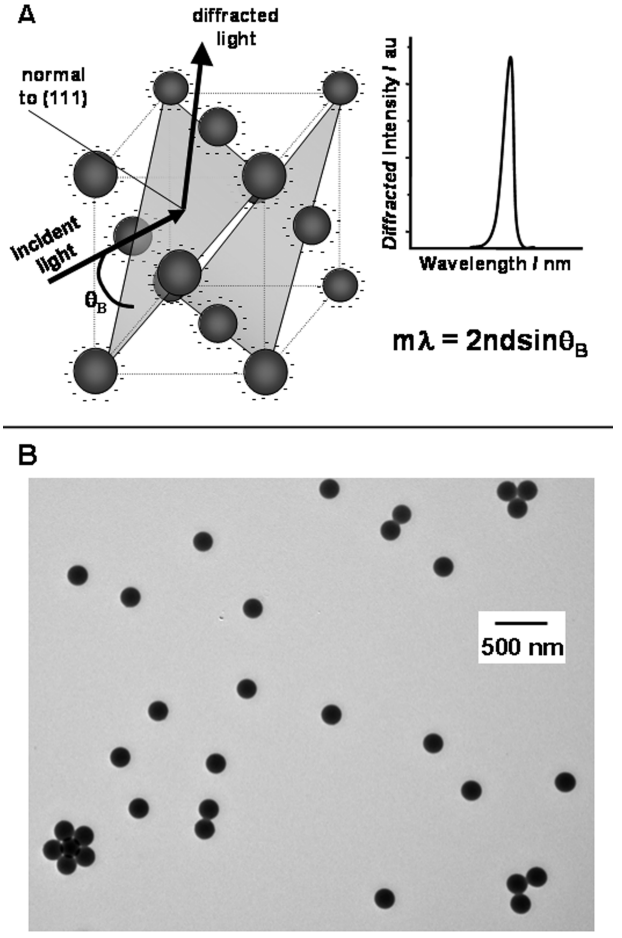

Figure 1. (A) Crystalline colloidal arrays (CCA) form due to the electrostatic repulsion between the highly charged, monodisperse polystyrene particles. The spacing between particles is such that they diffract visible light according to Bragg's law, where m is the order of diffraction, λ is the wavelength of diffraction, n is the refractive index of the system, d is the spacing between diffracting planes, and Θ_B is the Bragg glancing angle. (B) TEM of 186 nm polystyrene colloidal particles prepared via emulsion polymerization (scale bar = 500 nm).

Table 1. Hydrogel Modulus Dependence on Embedded Nanoparticle Diameter[a]

nanoparticle diameter (nm)	hydrogel G' (Pa)	hydrogel v_e (mM)
114	670	0.4
124	860	0.59
145	1090	0.75
145[b]	800	0.55
186	1590	1.09
none	190	0.21
none[b]	120	0.13

[a] Polymerized crystalline colloidal arrays (PCCA) were prepared with embedded nanoparticles of different diameters. The effective cross-link density of the hydrogel material (v_e) was calculated from the experimentally determined shear storage modulus (G'). All hydrogels were prepared with 2 wt % cross-linker. All PCCA were prepared to have constant polymer content, using 16.35 wt % crystalline colloidal array nanoparticle solutions. [b] Hydrogels prepared in the presence of oxygen.

particle diameter increases. As can be seen in Table 1, an increase of particle diameter of ~9% will result in an increase of effective cross-link density of ~28%. Since the degree of hydrogel swelling is directly related to the effective cross-link density,[1−3] the responsivity of our PCCA sensing material can be increased by utilizing smaller diameter colloidal particles.

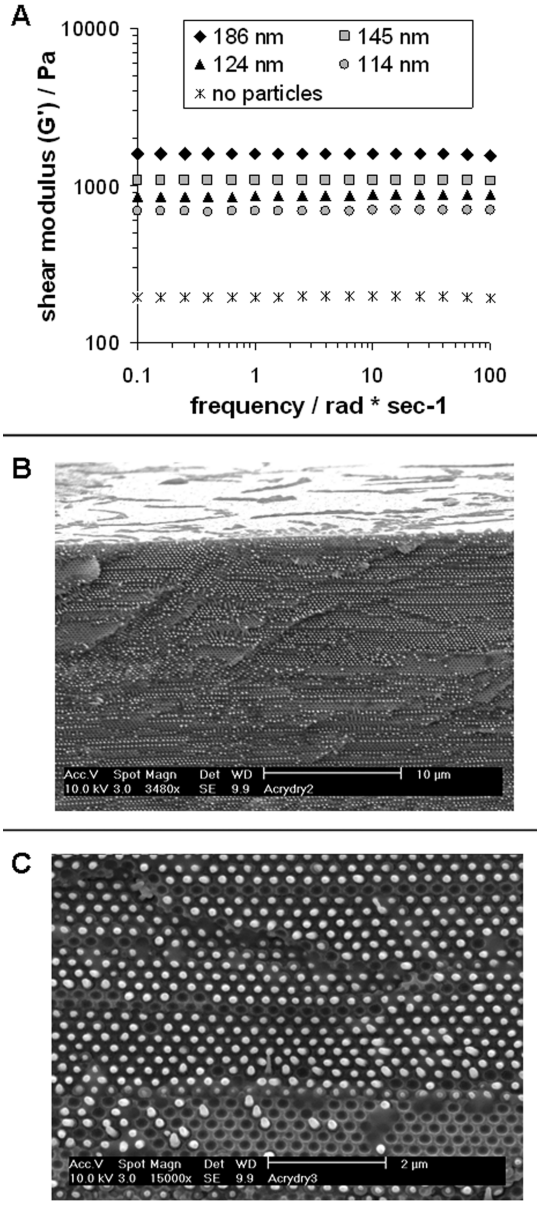

Figure 2. (A) Average values of the shear storage modulus (G'), for PCCA hydrogels prepared from nanoparticles of different diameters, as a function of angular frequency. (B) SEM of PCCA hydrogel material illustrating the long-range order of the embedded nanoparticles (scale bar: 10 μm). (C) Higher magnification SEM image of PCCA, illustrating the lack of interaction between the embedded nanoparticles and the surrounding polymer matrix (scale bar: 2 μm). The particles actually "fall out" of the surface layer of the surrounding matrix upon sample preparation.

The sensing mechanisms employed in our PCCA sensing material can be modeled by using Flory's model for the swelling of network structures,[1] where the total osmotic pressure at equilibrium is considered to be the balance of osmotic pressures arising from changes in the free energy of mixing (Π_M), the elastic free energy (Π_E), and the Donnan potential (Π_{Ion}):

$$\Pi_T = \Pi_M + \Pi_E + \Pi_{Ion} \quad (2)$$

The osmotic pressure arising from the change in the elastic free energy is determined by the effective cross-link density of the system

$$\Pi_E = -\frac{\partial \Delta G_E}{\partial V} = -RTv_e\left[\left(\frac{V_m}{V}\right)^{1/3} - \frac{1}{2}\frac{V_m}{V}\right] \quad (3)$$

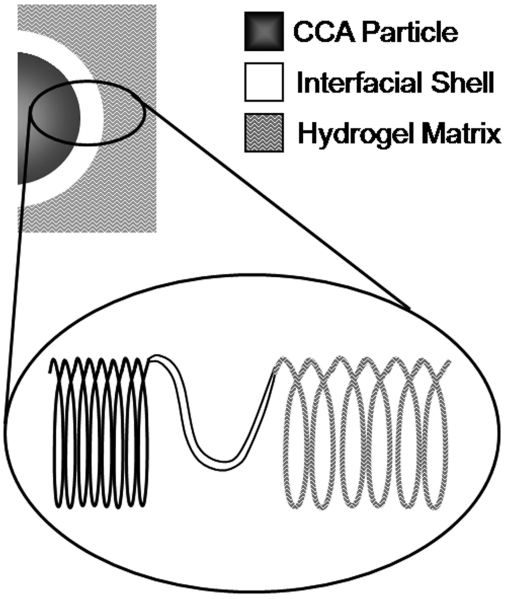

Figure 3. Illustration of proposed mechanism for decreased shear modulus with decreased nanoparticle diameter. The overall modulus can be thought of as a series of connected springs. The rigid nanoparticles contribute a very tight spring, and the surrounding hydrogel matrix contributes a smaller force constant spring as it is more elastic. The lack of adhesion between the embedded particles and surrounding hydrogel matrix, as found in the interfacial shell, results in slip which is equivalent to a spring with a very low force constant. Given a constant polymer volume fraction, the PCCA containing smaller particles have a larger contribution from the interfacial shell region, owing to increased surface area, giving rise to a lower overall PCCA storage modulus.

where R is the universal gas constant, T is the temperature, V is the current volume of the hydrogel, and V_m is the volume of the relaxed hydrogel network.

As the diffraction shift observed in a PCCA sensing material is directly related to the volume of the hydrogel, accurate determination of the effective cross-link density of our system allows modeling of our sensor response, providing increased understanding of our material and enabling a more directed approach toward material development.

We examined the effect of polymerization conditions on our materials by preparing hydrogels with and without embedded nanoparticles, in both the presence and absence of oxygen. The materials moduli were analyzed at a constant temperature, and the resulting shear storage moduli are shown in Table 1. As expected, hydrogels prepared in the absence of oxygen show higher moduli than those prepared with oxygen, as oxygen is known to quench free-radical polymerizations. It is interesting to note that the effect of oxygen exclusion is more pronounced for those hydrogel materials prepared without nanoparticle inclusions.

Also of interest is the fact that the effective cross-link density is dominated by nanoparticle inclusions, as opposed to the BisAA cross-linker. Although the absence of a reliable molecular theory makes it difficult to determine the exact mechanism of filler reinforcement, the decreased water content and reinforcement from the embedded nanoparticles in the PCCA results in a 2.5-fold increase in the effective cross-link density compared to that of hydrogels prepared without nanoparticle inclusions. The rigid nanoparticles deform less than the surrounding polymer matrix, causing the material strain to be reduced overall.[1,3,44] In addition, the volume occupied by the filler particles will affect the polymer chain distribution during polymerization and the resulting polymer chain mobility within the elastomer.[3] The modulus values for our composite material are reasonable considering values reported for other highly swollen hydrogels.[2,40,41,45−48] Further investigation of the PCCA modulus dependence on nanoparticle and monomer concentrations is currently underway in our laboratory.

In conclusion, we have presented the first quantitative study of how the mechanical properties of a swollen hydrogel depend upon the diameter of nonbonded embedded nanoparticles. We characterized the storage modulus, and thereby effective cross-link density, of our photonic crystal hydrogel material as a function of incorporated nanoparticle size and found that the storage modulus increases linearly with increasing particle diameter. This linear dependence derives primarily from the contribution of slip within the system, which varies based on the surface area of the embedded particles. We also found that the increase in storage modulus upon exclusion of oxygen during polymerization is more pronounced for hydrogels without nanoparticle inclusions and that the modulus is dominated by particle inclusions as opposed to the cross-linker. We have increased our understanding of PCCA materials, providing for a more directed approach to improved PCCA sensor material development, as the degree of swelling of the hydrogel material is directly related to the effective cross-link density.

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Supporting Information Available: Text giving the experimental details; materials; synthesis of nanoparticles; fabrication of hydrogel materials; characterization of nanoparticles and PCCA hydrogel materials; mechanical analysis of hydrogel materials; graph of modulus versus particle size. This material is available free of charge via the Internet at http://pubs.acs.org.

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