Elucidation of Structure from the Surface Physics of Soft Hydrogels

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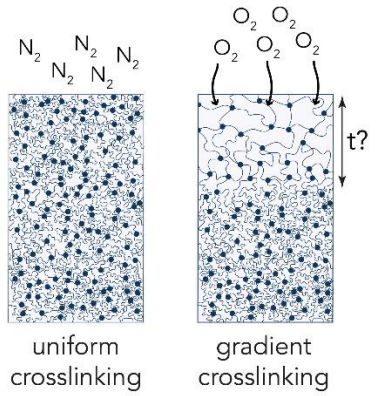
Hierarchical structures are ubiquitous in nature and biological systems. One commonly studied system is articular cartilage, which is coated by an extracellular matrix with compositional and structural gradients due to the heterogeneous distribution of collagen and proteoglycans.[1] To mimic these biological structures, hydrogels are often used due to their easily tunable mesh size (average spacing between polymer chains). Recent studies have suggested that the mesh size at the hydrogel surface may also be influenced by environmental conditions, such as the atmospheric composition or surface energy of the casting mold, leading to a mesh size that is drastically different at the surface relative to the bulk.[2,3]



Schematic demonstrating the differences in architecture between the uniformly crosslinked hydrogel and surface gradient hydrogel.

This work seeks to exploit this phenomenon to create poly(acrylamide) (PAAm) hydrogels with surface gradient layers by inhibiting the polymerization process through exposure to atmospheric oxygen. These "surface gradient" hydrogels possessed a gradient in crosslinking density at the surface of the sample and were compared to hydrogels with comparatively uniform crosslinking density. Using a custom-built microtribometer, the surfaces of the hydrogels were probed to elucidate structural and mechanical differences. A contact mechanics model combining concepts from Winkler foundation mechanics, fluid draining, and polymer physics was developed to determine the elastic modulus of the hydrogels as well as predict the thickness of the surface gradient layer. The results were compared to those predicted by a computational model that used reaction kinetics of free radical polymerization combined with oxygen diffusion calculations.

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