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Structure-Property Relationships of Gradient Hydrogels – WTC 2021, Lyon

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Gradient structures are ubiquitous in nature and play an important role in the function and properties of these biological materials. To understand the relationship between the structure and property of gradient systems, polyacrylamide hydrogels were used as a synthetic model and a crosslinking gradient was formed via oxygen-inhibited free radical polymerization. A computational model was developed to predict the thickness of the surface gradient layer, and the results were compared to nano- and microindentation experiments as well as friction coefficient measurements.

Keywords (from 3 to 5 max): gradients, hydrogels, friction, contact mechanics

1. Introduction

Hierarchical structures are ubiquitous in nature and biological systems. One commonly studied system is articular cartilage, which is composed of an extracellular matrix with compositional and structural gradients due to heterogeneous distribution of collagen and proteoglycans. [1] This system possesses extremely low coefficients of friction (0.0001-0.001) while still being able to withstand high contact pressures. [2] Understanding the relationship between the microstructure and properties of these gradient systems will lend insight into the development of synthetic designs that better mimic biology. Hydrogels are often used as synthetic models due to their easily tunable mesh size through control of the monomer and crosslinking ratio. Previous studies have shown that mesh size scales with elastic modulus and friction coefficient to the -3 and -1 power, respectively [3]; however it is still an open question as to the role of the gradient structure in the tribological and mechanical properties of a hydrogel.

2. Methods

2.1 Hydrogel preparation
Polyacrylamide (PAAm) hydrogels were synthesized through free radical polymerization in an oxygen-rich environment ("O_2 cast") to form a crosslinking density gradient through the thickness of the sample. Polymer concentration (3.75 wt%, 7.5 wt%, and 17.5 wt%) was varied while keeping the ratio between monomer and crosslinker concentration constant. Hydrogels with uniform crosslinking density were polymerized in a nitrogen-rich environment ("N_2 cast").

2.2 Characterization
Nanoindentations and microindentation experiments were completed using atomic force microscopy and a custom-built microtribometer. Friction coefficient experiments were also performed with the microtribometer.

2.3 Contact mechanics
A porohyperelastic contact mechanics model combining concepts from Winkler foundation mechanics, fluid draining, and polymer physics was utilized to determine the elastic modulus of these gradient structures.

$$F = \frac{8\pi RtE}{5}\left[\left(\frac{t}{t-z_o}\right)^{\frac{5}{4}} - 1\right] \quad (1)$$

2.4 Surface gradient layer determination
To predict the thickness of the gradient layer at the surface of the hydrogel, a computational model was developed using the reaction kinetics of free radical polymerization combined with oxygen diffusion calculations.

2.5 Results

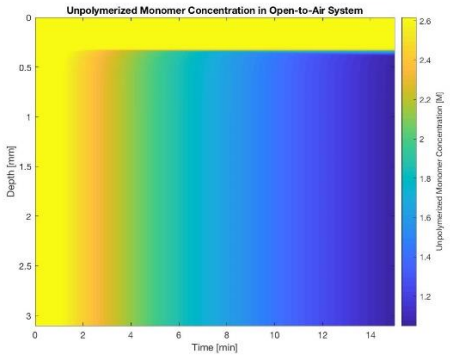

Figure 1: Computational model displaying the depth of unreacted monomer in the O_2 cast PAAm hydrogel system. After 15 min of polymerization, the surface gradient layer thickness is predicted to be 75 μm.

3. Discussion

The O_2 cast hydrogels exhibited lower friction coefficients and elastic moduli values as compared to the N_2 cast hydrogels, which indicates a difference in surface structure.

4. References

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