Chemomechanics of Self-Oscillating Gels
by
Irene Chou Chen

Submitted to the Department of Chemical Engineering
on May 9, 2013, in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy in Chemical Engineering

Abstract

Biological materials such as cardiac and skin tissue exhibit the unique capacity to transduce mechanical stimuli into propagating electrical and chemical signals throughout the body. Few synthetic materials have been engineered to produce communicative chemical signals in response to mechanical input, though such synthetic material analogues could enable devices that mimic biological tissues and pressure sensitive processes whereby molecular mechanoreceptors enable rapid and localized transmission of chemical signals. In this thesis, self-oscillating polymer gels comprising N-isopropylacrylamide-co-Ru(bpy)$_3$ are synthesized in order to elucidate chemical and mechanical (chemomechanical) coupling in synthetic, stimuli-responsive materials, and to design mechanically induced, oscillatory signaling systems.

N-isopropylacrylamide-co-Ru(bpy)$_3$ gels represent a unique class of polymeric materials known as BZ gels, that are capable of undergoing the Belousov-Zhabotinsky (BZ) self-oscillating reaction. When submerged in stagnant solution containing chemical reactants, and in the absence of continuously applied external perturbation, the BZ gels exhibit sustained, colorful oscillations due to the changing oxidation state of Ru(bpy)$_3$ transition metal complex. By measuring temperature profiles of the BZ gel, we showed that the swelling behavior and hydrophobicity of the gel depend on the oxidation state of covalently bound Ru(bpy)$_3$. Using timelapse microscopy, we recorded the BZ oscillations and tracked the far from equilibrium chemical behavior exhibited by the gels. At constant system temperature, the BZ reaction induced cyclic changes in the osmotic pressure of the gel, resulting in periodic gel swelling and shrinking. Such volumetric changes, driven by the BZ reaction, are largest (22 %) when the edge length of the gel is relatively short (0.6 mm), and pattern formation is dominated by slow kinetics. Therefore, by quantifying the chemomechanical behavior of BZ gels, we demonstrated that the gels convert chemical oscillations into mechanical actuation.

Next, we sought to design novel stimuli-responsive behavior in BZ gels by devising methods for mechanically triggering oscillations in quiescent gels. When sufficient macroscopic compressive stress was applied to submerged, non-oscillating gels, BZ oscillations were triggered and persisted until the stress was removed. To our knowledge, BZ gels represent the first synthetic hydrogel capable of producing oscillations in response to mechanical stimuli. To establish the conditions conducive to mechanical triggering, we quantified the chemical regimes for which BZ gels spontaneously oscillate or fail to oscillate. In doing so, we demonstrated that such regimes are governed...
by the ratio of inhibitor to activator species, which are both intermediate species that are produced throughout the reaction, providing negative and positive chemical feedback, respectively. Mechanically triggerable conditions corresponded to an intermediate ratio of reactant to inhibitor species, such that mechanical compression enabled transitions near the boundary dividing the non-oscillatory and oscillatory regimes. By varying the crosslinking density of the material, we also showed that both the required stress and strain for inducing oscillations in BZ gels increased with decreasing polymer volume fraction. Application of macroscopic, compressive stress to BZ gels caused a decrease in overall gel volume and an increase in the concentration of \text{Ru(bpy)}_3\textsuperscript{3+}, and oscillations were triggered at a critical concentration of \text{Ru(bpy)}_3\textsuperscript{3+}. In demonstrating that BZ gels can sense mechanical pressure and respond by transducing such energy into chemical oscillations, we have opened up new avenues of research based on mechanical sensing in BZ gels.

Finally, we explore the mechanisms of synthetic “communication” in which discrete BZ gels sense mechanical stress and transmit chemical signals to neighboring gels. Specifically, we designed arrays of closely spaced gels (0.2 mm gap distance) that communicate via diffusion of activator species. We demonstrated that mechanical triggering can induce wave directionality to a set of gels that would otherwise exhibit disorder, and can propagate signals that change directions by migrating around bends without decay in signal amplitude. By introducing a node to a set of BZ gels, we showed that the BZ signal can split without attenuation, effectively doubling the system output. Last, we quantified the collision of two mechanically induced signals to show that wave collision occurs without amplification, and results in signal extinction. Taken altogether, these studies of signal propagation in BZ gels demonstrate that the underlying mechanism of BZ gel communication is governed by the diffusion of activator species. In addition to demonstrating for the first time a synthetic hydrogel that is capable of generating oscillations in response to mechanical compression, we have shown that BZ gels can propagate mechanically induced signals over long ranges and complex trajectories. Our results can be used to facilitate understanding of complex biological phenomena involving chemomechanical coupling and mechanotransduction, or to design advanced, functional materials that act as pulsating chemical or pressure sensors.

Thesis Supervisor: Krystyn J. Van Vliet
Title: Paul M. Cook Career Development Associate Professor

Thesis Supervisor: Paula Hammond
Title: David H. Koch Professor