PEPTIDE HYDROGELS FROM TWISTED RIBBON AGGREGATES

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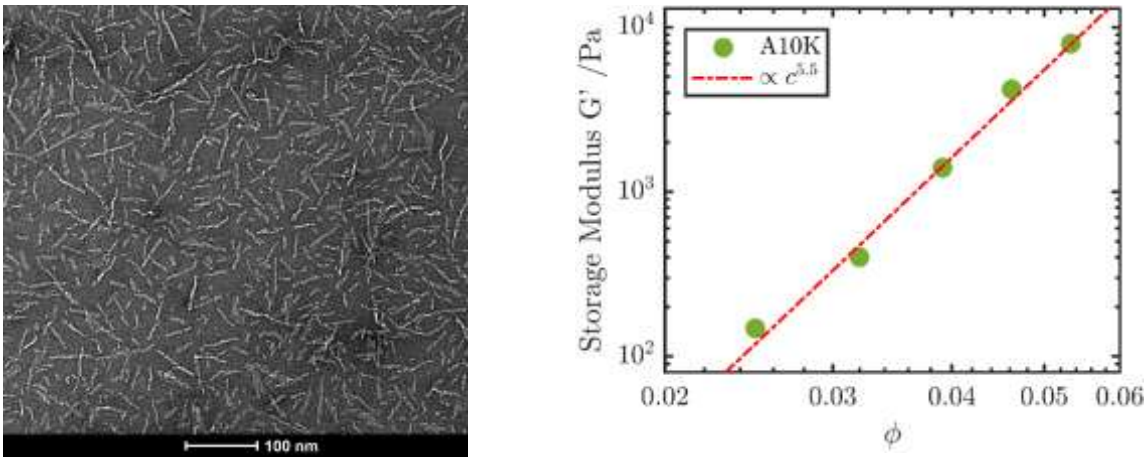
Key Words: Model peptides, hydrogel, self-assembly.

We have studied the rheology of an aqueous solution phase formed in the model peptide system $A_{10}K$ (A=alanine, K=lysine), where the short hydrophobic peptides self-assemble into twisted ribbon structures consisting of laminated beta-sheets. The ribbons are crystalline in 2 dimensions, therefore rigid, and they are weakly charged. The average ribbon lengths, $\langle L \rangle \approx 60$ nm, corresponding to an aspect ratio, $L/d \approx 10$. With increasing concentration a transition from a viscous liquid into a gel-like solid occurs around a volume fraction $f \approx 0.02$, that we identify as the overlap concentration f^*. Coinciding with the overlap concentration is also a phase transition, from the low concentration isotropic liquid phase to a nematic phase. This concentration is significantly lower than what is predicted for hard rods by Onsager theory for this given aspect ratio. We attribute this to the ribbon charge and long range electrostatic interactions, stabilizing the nematic phase. In this nematic phase, the storage modulus G' increases strongly with increasing f.



a) ***b)***

Figure 1- a) Negatively stained TEM image of $A_{10}K$ twisted ribbons. The average length $\langle L \rangle \approx 60$ nm, with a significant polydispersity. b) The storage modulus, G', at a constant strain, γ=1%, as a function of volume fraction above f, where the dashed line is a guide to the eye.*

LARGE-AREA ALGINATE/PEO-PPO-PEO HYDROGELS WITH THERMOREVERSIBLE RHEOLOGY AT PHYSIOLOGICAL TEMPERATURES

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Key Words: alginate, injectable, thermoresponisve, biomaterials, drug delivery

Alginate hydrogels have shown great promise for applications in wound dressings, drug delivery, and tissue engineering. Here, we report the fabrication, rheological properties, and dynamics of a multicomponent hydrogel consisting of alginate and poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) triblock copolymers, and the achievement of thick, castable gels with tunable, thermoreversible behavior at physiological temperatures (Figure 1). PEO-PPO-PEO triblock copolymers can form temperature-sensitive hydrogels that exist as liquids at low temperatures and soft solids at high temperatures. In this work, we have employed PEO-PPO-PEO triblock copolymers to impart thermoresponsive properties to alginate hydrogels in the form of a multicomponent hydrogel. These systems can transition between a weak gel and a stiff gel, with a corresponding increase in the viscoelastic moduli of approximately two orders of magnitude as temperature is increased. The temperatures corresponding to the upper and lower boundaries of the stiff gel region, as well as the storage modulus at physiological temperatures (e.g., 36 – 40 C), can be controlled through the PEO-PPO-PEO concentration. Additionally, we explore the properties of these materials under compression and large deformations, and describe how alginate and F127 concentration can be used to control the fracture stress and strain. Finally, we compare the results from bulk rheology to the structure and dynamics of the gels measured via small-angle X-ray scattering (SAXS) and X-ray photon correlation spectroscopy (XPCS) experiments. Optically clear gels that are homogeneous on the microscale can be fabricated in a scalable manner to create flat, large-area thick films, making these systems favorable for applications in wound healing, soft tissue repair, and biomedical device coatings.

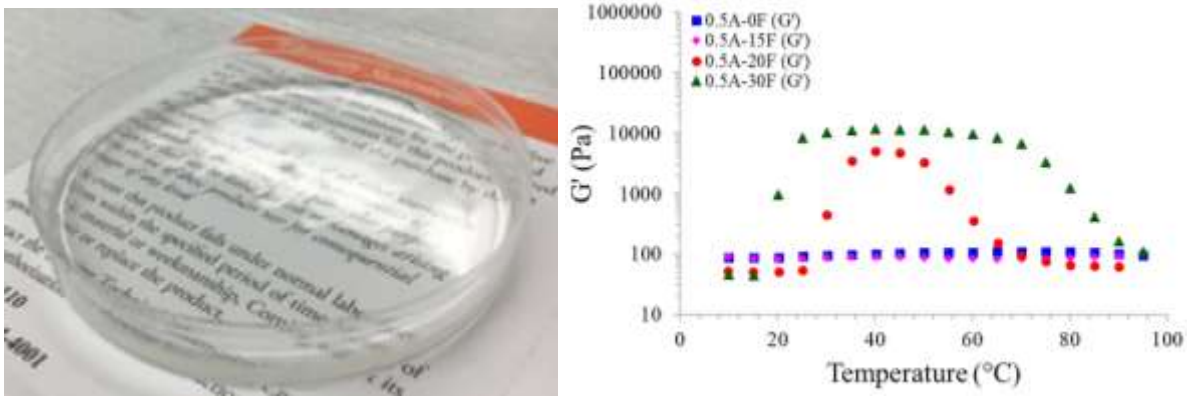

Figure 1. Left: Photograph of large, homogeneous gels. Right: Storage modulus of gels as a function of temperature for varying amounts of F127. From Quah et al., Polymer, 2018.

CLUSTER FORMATION DURING AGING OF COLLOID-POLYMER DISPERSIONS AND RE-ENTRANT RHEOLOGICAL BEHAVIOR AT INTERFACES AND THE MICROSCALE

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Key Words: colloidal glass, colloidal gel, polymer-clay, nanocomposite

We report the dynamics of aqueous dispersions of the disk-shaped colloidal clay laponite® with poly(ethylene oxide) (PEO) chains of moderate molecular weight, explored via angle-dependent dynamic light scattering (DLS), bulk rheology, passive microrheology, and interfacial rheology. The PEO chains adsorb onto the laponite® surfaces, causing interesting dynamic behavior, including transitions from arrested states to liquid states as the concentration and molecular weight of PEO is increased. This re-entrant behavior has been attributed to formation of particle clusters induced free PEO chains. Our DLS results are consistent with a slow diffusive dynamic process, suggesting the formation of large particle clusters, in samples at aging times < 75 days (Figure 1). By contrast to behavior observed in laponite® dispersions with a non-adsorbing polymer, poly(acrylic acid) (PAA), diffusion coefficients of these clusters in the laponite®-PEO systems continue to decrease with aging time until samples reach an arrested state. Finally, interfacial rheology and passive microrheology also show some evidence of re-entrant behavior, although the polymer concentrations at which this occurs do not exactly correspond to the conditions under which re-entrant behavior is observed in bulk rheology.

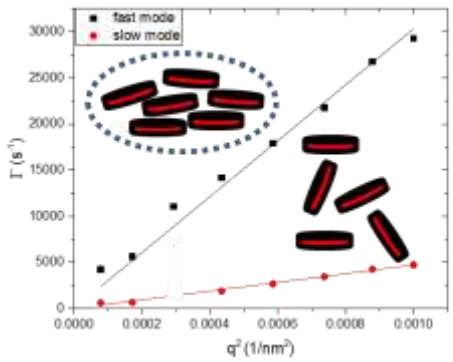

Figure 1. Evidence of large particle clusters in colloidal glasses containing polymers. From Zheng et al., Colloids and Surfaces A, 2017.

UNDERSTANDING AFFINITY-DRIVEN PROTEIN UPTAKE INTO IONICALLY CROSSLINKED CHITOSAN MICRO- AND NANOGELS

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Key Words: Chitosan, microgels, nanogels, ionotropic gelation, protein uptake.

Colloidal particles formed through the ionotropic gelation of chitosan with tripolyphosphate (TPP) have attracted widespread interest as protein drug and vaccine delivery vehicles. Yet, aside from the consensus that efficient protein uptake into these particles requires particle/protein affinity, factors affecting uptake performance of colloidal chitosan/TPP particles have, until recently, remained poorly understood, with many seemingly conflicting reports appearing in the literature. To this end, we have recently hypothesized that some of these differences in uptake might have stemmed from variations in the particle yield, which are frequently ignored and, for the purpose of this study, were quantified as fractions of the chitosan molecules assembled into particles (X_{Agg}). Spectroscopic analysis revealed that X_{Agg} increased sharply with both TPP:glucosamine molar ratio and pH until reaching 100%, whereupon further TPP addition coagulated the particles into macroscopic precipitates. Likewise, when particles were prepared from solutions at pH-values above the protein pI, X_{Agg} increased with the protein concentration. Thus, the efficiency of particle formation depended strongly on chitosan/TPP mixture compositions. A corresponding analysis of the association efficiency (*AE*), defined as the fraction of the added protein taken up by the particles, revealed that the uptake of the model, bovine serum albumin (BSA; pI ≈ 4.7 – 4.9) and α-lactalbumin (α-LA; pI ≈ 4.2 – 4.5) proteins was also highly composition-dependent. When particle formation and protein uptake, for instance, were performed using parent chitosan and TPP solutions at pH 4.0 (i.e., below the protein pI), the chitosan/protein binding was weak and the *AE* was below 10%. Raising the parent solution pH to 5.5 (above the protein pI), however, strengthened the chitosan/protein binding and enabled efficient protein uptake (where at optimized TPP:glucosamine ratios the *AE* reached 90%). Hence, consistent with prior reports, significant chitosan/protein affinity was needed to achieve high *AE*. Conversely, TPP:glucosamine molar ratio effect was nonmonotonic. Regardless of the protein composition, the *AE* first increased with the TPP:glucosamine ratio (up to the ratio where X_{Agg} first reached 100%), and then decreased with the TPP:glucosamine ratio. Additionally, *AE* often (albeit not always) increased with the protein concentration.

Despite this variable uptake, however, when *AE*-values obtained at pH > pI was plotted against X_{Agg}, all the data collected for each model protein (at variable TPP:glucosamine ratios and protein concentrations) up to the TPP:glucosamine ratio where X_{Agg} first reaches 100% collapsed onto a single line, indicating that, as long as there was substantial chitosan/protein affinity, X_{Agg} was the primary determinant of protein uptake. Further, replotting the *AE* vs. X_{Agg} data as binding isotherms (where the uptake was normalized by particulate chitosan mass) revealed that the apparent particle/protein association strength also increased sharply with X_{Agg}, suggesting that soluble chitosan inhibited protein association with chitosan/TPP particles. This soluble chitosan effect was inferred to reflect the formation of soluble chitosan/protein complexes, which prevented protein molecules from binding to the chitosan/TPP particles (and whose presence was confirmed through dynamic light scattering). When the TPP content, however, exceeded that needed to maximize X_{Agg}, its further addition eliminated the cationic chitosan/TPP particle binding sites, and thus weakened particle/protein association. Moreover, the *AE* vs. X_{Agg} and binding isotherm curves agreed well with a simple competitive binding model (derived based on linear chitosan/protein binding isotherms), where the binding constants for protein/particulate chitosan and protein/soluble chitosan association were the only adjustable parameters and had remarkably similar values. These experimental and model analyses indicate two reasons for the *AE* vs. X_{Agg} scaling: (1) that, not surprisingly, higher X_{Agg}-values increase the number of particulate binding sites; and (2) that higher X_{Agg}-values reduce the formation of uptake-inhibiting soluble chitosan/protein complexes. Collectively, these findings provide essential guidelines for optimizing protein uptake into chitosan/TPP micro- and nanogels, and likely (at least in part) extend to other related drug carriers, such as micro- and nanogels prepared through the ionotropic gelation of alginate or complexation of oppositely charged polyelectrolytes.

References:
Cai, Y.; Lapitsky, Y. Analysis of chitosan/tripolyphosphate micro- and nanogel yields is key to understanding their protein uptake performance. *J. Colloid Interface Sci.* 494, 242-254 (2017).

DESALINATION USING POLYELECTROLYTE HYDROGELS

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Key Words: polyelectrolyte hydrogel, swelling, salt partitioning, desalination, water treatment

When the gel is put into contact with aqueous salt solution, it absorbs a solution with the ion composition different from the original one. The absorbed solution can be easily squeezed out from the gel by means of sieve or microfiltration membrane. In our previous work we proposed a fully reversible desalination cycle made of compression and swelling steps, which can in principle work on ideal thermodynamic efficiency.
In this work we simulate the desalination process using theoretical and coarse-grained models of gel and prove the concept by experiment.

We used Monte Carlo and molecular dynamics molecular simulations in the reaction ensemble to predict the degree of ionization of the weak polyelectrolyte hydrogel when it is put in contact with salt solution, and calculate the salt partitioning between the gel and bulk salt solution.

We constructed laboratory apparatus based on swelling and pressing cycles of the gel. First, we let the polyelectrolyte gel swell with salt solution of defined concentration. Then we press the gel and the liquid is released. Due to the ion exchange in polyelectrolyte hydrogel, this released liquid has lower salt concentration than the initial one. We measure the salinity of the solution before and after this procedure and we compare the results with theoretically obtained salt partitioning. We also measure the pressure applied on the gel and corresponding gel volume and compare these results with respective computational results.

SHEAR-DEPENDENT STRUCTURES OF MICROFIBRILLATED GELS

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Key Words: nanocellulose, gels, flocculation

Cellulosic nanomaterials have recently gained increased attention due to their potential for use as an environmentally friendly replacement conventional materials in many diverse applications. Understanding the rheology of these resources is critical to properly tailor their properties and processing conditions. Aqueous suspensions of microfibrillated cellulose form weak physical gels at low concentrations due to extensive entanglement and hydrogen bonding. These gels are shown to have complex structural properties that are directly dependent on their recent shear history. In this work we discuss the effects of “slow quench” and “fast quench” shear conditions on the suspension properties, including yield stress, viscosity, and structure elasticity. We also assess the recovery of the network structure itself as a function of the applied breakdown conditions. These observations give detailed insight to the morphology of the floc-based network structure and help to quantify critical conditions that characterize the floc dynamics.

ELECTROSPINNING COMPLEX COACERVATES

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Key Words: Complex coacervate; rheology; electrospinning; phase separation; polymers

As polymer-based materials become ever more integrated into our daily lives, there is an increasing need to develop both materials that are safe for the consumer, and manufacturing strategies that have a minimal impact on the environment. However, the vast majority of polymers require either organic solvents for dissolution, or the use of potentially cytotoxic cross-linking agents to prevent material dissolution. Additionally, many of the chemistries and solution conditions necessary for processing can damage cargo molecules and create biocompatibility issues for subsequent use. Complex coacervation is an associative, liquid-liquid phase separation that has the potential to circumvent many of the challenges associated with processing traditional polymers and encapsulating actives. Complex coacervation is driven by the electrostatic and entropic interactions between oppositely-charged polymers in water. For many coacervating systems, the solid or liquid nature of the complex can be tuned via the concentration of salt present. Additionally, the strength of the electrostatic interactions within the complex are such that in the absence of salt, solid complexes are highly resistant to thermal melting and/or solvent dissolution. Furthermore, complex coacervation has a strong history of use for the encapsulation of a range of cargo. We have taken advantage of this salt-driven plasticity to enable fabrication of ultra-stable electrospun fibers directly from aqueous solutions. These efforts have required the simultaneous characterization of coacervation, as well as the effect of cargo molecules on the phase behavior and rheology of the resulting coacervates/precursor solutions. Furthermore, these materials show tremendous promise for the use of electrospun coacervate-based nanofiber meshes across a range of applications.

ONE-POT SYNTHESIS OF SURFACE ANCHORED NETWORK COATINGS

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