

Polymer Gels: Fracture, Friction, Healing and Superabsorbency

K. A. Erk^{*^}, T. L. Thornell*, Q. Zhu*, and M. J. Krafcik*

* School of Materials Engineering, Purdue University, West Lafayette, IN, USA
[^] erk@purdue.edu

ABSTRACT

This proceeding describes a series of experimental investigations performed to better understand and ultimately control the nonlinear mechanical behavior of soft polymeric gels. In the first part, shear rheophysical experiments are described in which the shear-induced flow instability formation of fracture planes and shear bands is studied for a model physically associating polymer gel. When the fractured gel was allowed to rest for a given time period, the mechanical strength of the gel progressively increased as the internal macromolecular network structure healed. In the second part, a specific application of polymer gels as internal curing agents in high performance concrete is described. The swelling performance of model chemically crosslinked polymer gels was found to be strongly affected by the ionic nature of the aqueous environment, ultimately leading to reductions in absorption capacity that could be detrimental to the internal curing of concrete.

Keywords: self-healing, injectable, infrastructure, concrete, soft materials

1 INTRODUCTION

Polymeric gels are used in a variety of industrial and biological applications. Taking advantage of their tunable chemical structures and physical properties, polymer gels have been widely employed from drug delivery aids in the human body [1–3] to internal curing agents for pavement concrete. [4–6] More recently, many research studies have focused on optimizing their properties for use as injectable materials for regenerative medical applications. [7–9]

In these applications, it is important to understand the mechanical properties of the gels, including their fracture toughness, self-healing ability, and swelling response. However, characterizing the properties of these mechanically soft materials using traditional techniques is difficult as the materials will deform or deswell with only slight changes in applied pressure or environment. For example, many soft materials can be nearly impossible to grip during traditional tensile tests and solvent evaporation can be significant during compression testing. Some soft materials are also viscoelastic and can thus deform and relax due to gravity and are thus impossible to mold into a well-defined, isolated shape for mechanical testing.

One solution to these characterization limitations is to employ *shear rheometry* to probe the fracture, friction, and healing properties of soft materials. By using shear

rheometry, experiments have been designed to successfully quantify the strain stiffening behavior of gels [10], the onset and evolution of fracture and shear banding flow instabilities [11], the sliding friction response [12] and, more recently, the healing kinetics of fractured gels. [13] Additionally, traditional swelling studies have also been performed on hydrogels for specific application as internal curing agents in high performance concrete. [14] In this proceeding, the results of these studies on the properties and applications of polymer gels are summarized. For more details, refer to Refs. 10-14.

2 EXPERIMENTAL METHODS

The model gels described here are polyacrylic-based macromolecular networks immersed in solvent. For the stiffening, fracture, friction, and healing experiments, a triblock copolymer consisting of 8.9 kg/mol poly(methyl methacrylate) endblocks connected by a 53 kg/mol poly(*n*-butyl acrylate) midblock was dissolved at different concentrations in 2-ethyl hexanol. At the temperature range of interest (20-28 °C), the copolymer self assembles to form a macromolecular network composed of physically associated endblock aggregates interconnected by flexible midblock bridges, resulting in a physically crosslinked gel. Rheological characterization was performed in a shear rheometer (Anton Paar MCR 302) using a concentric cylinder fixture. Rheophysical experiments were performed to correlate rheometry data with the macroscale response of the sample, as quantified by optical tracking of micron-scale inert tracer particles within the gel during the rheometry experiments. [12,13] For the hydrogel swelling experiments, random poly(acrylic acid-acrylamide) copolymer with varying acrylic acid and acrylamide ratios were custom synthesized and chemically crosslinked to form a strong hydrogel for use as a concrete internal curing agent. Gels were immersed in different aqueous environments and the tea bag test was used to quantify the overall swelling capacity and swelling kinetics. [14]

3 RESULTS AND DISCUSSION

3.1 Shear-Induced Strain Stiffening

When the model physically associating polymer gels are deformed in shear in a rheometer cell, strain-stiffening behavior is observed at relatively low values of strain (see upturn in stress-strain data of Figure 1A). The observed

stiffening was accurately described by a constitutive model with a single fitting parameter related to the dimensions of the internal polymer network:

$$\tau = G_0 \gamma \exp \left[\left(\frac{\gamma}{\gamma^*} \right)^2 \right], \quad (1)$$

where τ is the measured shear stress, G_0 is the small-strain (elastic) shear modulus, γ is the applied shear strain, and γ^* is the critical value of shear strain at which stiffening becomes significant. The same model is also effective for describing the stiffening of actin, collagen, and other biopolymer networks. [10]

3.2 Flow Instabilities and Sliding Friction

If shear deformation is applied at relatively high shear rates, the physical crosslinks within the gel's network structure are disrupted, and the gel displays a corresponding overshoot in the measured stress response (see overshoot in Figure 1A). This behavior was found to be due to cohesive fracture, which was confirmed by particle tracking flow visualization techniques. [11,12] Once shear-induced fracture or shear banding interfaces were created in the gel, the resulting stress response was found to be related to sliding friction forces at that interface by applying theories from polymer physics. [12] The rheological response following the instability formation within the gel was power-law shear thinning with a fixed slope, regardless of the type of instability – *i.e.*, high-rate fracture or low-rate shear banding. Thus, at the molecular level, fracture can be considered to be a special case of shear banding within these physical gels. [12]

3.3 Fracture and Healing Behavior

When the fractured gel was heated above a critical temperature ($T_{crit} \sim 33\text{-}36^\circ\text{C}$) and then cooled to $T < T_{crit}$, the physically crosslinked network was re-formed and the gel was found to recover its original elasticity. A shear rheometry protocol was designed to study the fracture-healing behavior in a controlled way. [13] First, the shear stress response measured from applying a fixed shear rate (e.g., 1 s^{-1}) to the gel was recorded as the 'primary fracture' (see Figure 1A). Fracture was confirmed by simultaneous optical particle tracking analysis. Second, the shear rate was reduced to zero and the fractured gel was allowed to wait in the rheometer undisturbed for a desired 'resting time' of 5 minutes to several hours. Third, the shear rate was re-applied at the same magnitude (e.g., 1 s^{-1}) and the gel was subsequently re-fractured to determine the 'recovery fracture' stress response (see Figure 1A). The ratio of the maximum stress of the 'recovery fracture' to the maximum stress of the 'primary fracture' was used to determine the percentage of strength recovery for each resting time.

Figure 1 displays examples of the collected results. Figure 1A represents the primary and recovery shear stress responses of a 25°C , 5.5 vol.% gel for various resting times.

The maximum stress of the recovery fracture increased at greater resting times as shown in Figure 1B. At a resting time of 5 minutes, 45% of the primary strength was recovered while after a resting time of 45 minutes, the strength recovered was 79%. The magnitude of strength recovered for a given resting time was also dependent on the temperature of the gel, as shown in Figure 1B.

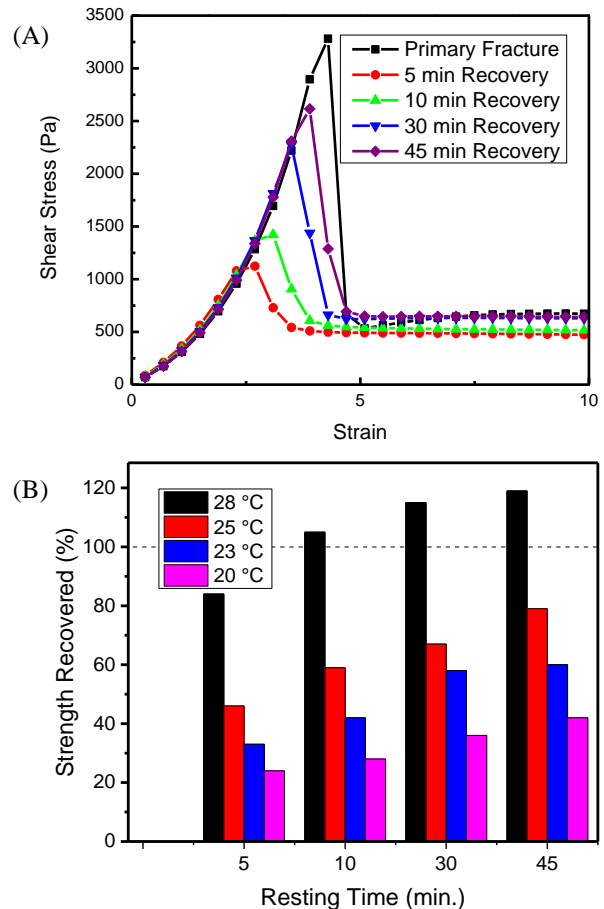


Figure 1. (A) Primary and 5-45 min. recovery stress-strain curves of 5.5 vol.% gel at 25°C . (B) Recovery kinetics for a 5.5 vol.% gel at different temperatures. Adapted from Ref. [13].

The time to achieve 100% strength recovery was determined from power law fitting of experimental data. These 'full recovery' times were determined for concentrations of 5, 5.5, and 6 vol.% gel and temperatures of 20, 23, 25, and 28°C . These values are presented in Figure 2 in comparison with the small-strain, characteristic relaxation time values of the different gels as determined from stress relaxation experiments. In addition to the similar Arrhenius behavior and activations energies in the range of 300-500 kJ/mol, the most important observation from the experimental data was the complete separation of timescales, with the characteristic relaxation time of the gels ranging from a few seconds to a few minutes and the full recovery times ranging from tens of minutes to tens of hours. The

mechanism by which the gel heals and recovers its elastic strength was endblock re-association and re-formation of the endblock aggregates, which act as the physical crosslinks of the macromolecular network.

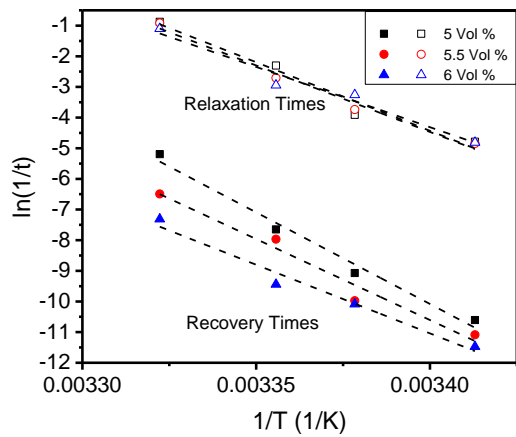


Figure 2. Arrhenius relationships of small-strain characteristic relaxation times and full recovery times at various temperatures and gel concentrations. Adapted from Ref. [13].

3.4 Hydrogel Superabsorbency

When superabsorbent polymer (SAP) hydrogels are used as internal curing agents in concrete, their role is to adsorb water during cement mixing and subsequently release the water within the concrete after placement. [15,16] As the concrete cures, the mixture water is consumed during the hydration reaction with unreacted portland cement, forming the hardened aggregate-cement composite material commonly known as concrete. Incorporation of hydrogel-based internal curing agents within the mixture ensures that water is available for the hydration reaction and is dispersed evenly throughout the volume of the concrete, promoting even curing. The incorporation of SAP also leads to a reduction in autogenous shrinkage of the cement and the reduced formation of shrinkage-induced microcracks within the system, thus creating a stronger, more durable final product. [4] Therefore, similar to how injectable gels can be used as drug delivery agents in medicine, hydrogels used as internal curing agents can be thought of as similarly beneficial transport agents in concrete, delivering the water that is required to fuel the curing reaction.

SAP hydrogels are comprised of a chemically crosslinked polyelectrolyte network that is swollen with water during immersion. The overall anion concentration within the network, controlled by the chemical composition of the polymer, directly controls the driving force for swelling. In applications involving concrete, the absorbed water will typically contain a variety of ions derived from the cement hydration reaction. Unfortunately, these ions can deleteriously affect the swelling behavior of the polymer hydrogel. [17] The research summarized here employed

model SAP hydrogels with varying anionic concentrations to systematically quantify the magnitude of SAP-ion interactions. [14]

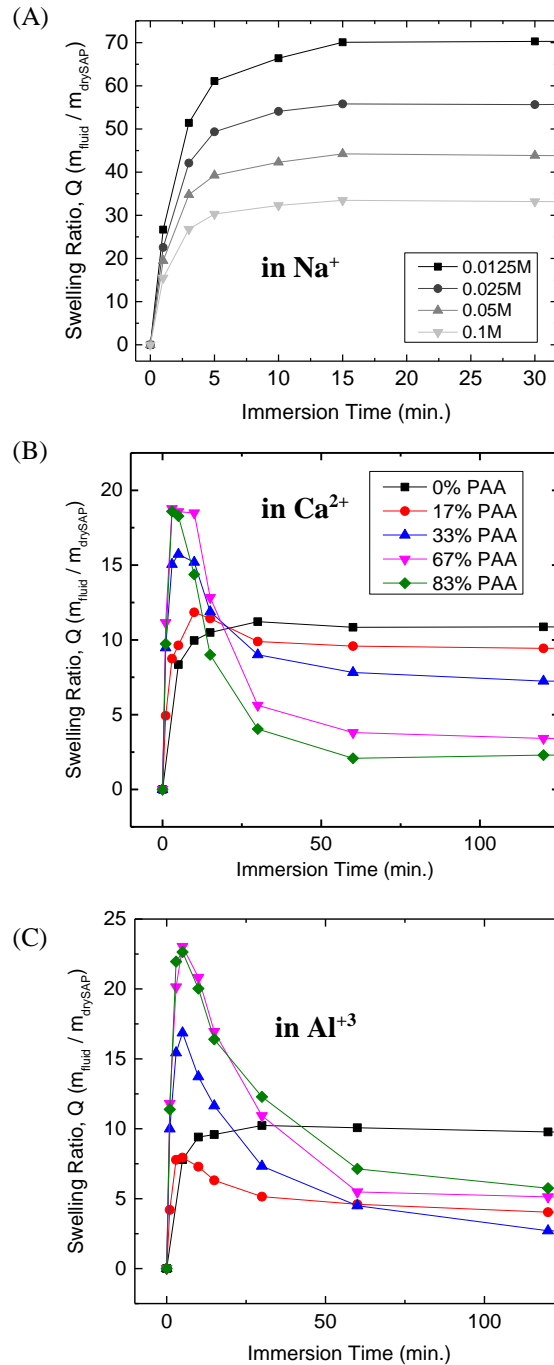


Figure 3. (A) Swelling response of 33% PAA SAP hydrogels immersed in different concentration solutions of Na^+ . Swelling and rapid deswelling response of SAP hydrogels immersed in (B) Ca^{2+} solution and (C) Al^{3+} solutions. Adapted from Ref. [14]

In the experiments, chemically crosslinked gels created from neutralized poly(acrylic acid-polyacrylamide) copolymer were swollen in different aqueous environments. As shown in Figure 3, the overall equilibrium swelling capacity and the swelling kinetics were strongly dependent on the concentration and type of salt ions in solution. In the presence of multivalent cations, such as calcium (Ca^{2+}) and aluminum (Al^{3+}), the swelling capacity was strongly reduced and a strong deswelling behavior was observed after only 5–10 minutes of immersion. Additionally, the presence of Al^{3+} resulted in the unexpected formation of a mechanically stiff barrier layer at the hydrogel's surface, which hindered the release of fluid and caused the overall elastic modulus of the hydrogel to increase from ~10 kPa for hydrogels immersed in Ca^{2+} solutions to ~100 kPa for hydrogels immersed in Al^{3+} solutions.

The impact of ions on the SAP behavior was found to be stronger for SAP hydrogels which contained the highest concentration of anions in their polymer network (which resulted from deprotonation of the acrylic acid monomer during immersion). [14] It was believed that the reduced swelling capacity and fast deswelling was due to ionic crosslinking taking place within the hydrogels due to complexation of neighboring anionic groups in the polymer network by the multivalent cations in the absorbed fluid. This observed ionic sensitivity of SAP would most likely lead to an overall performance reduction when SAP-based hydrogels are used as internal curing agents in concrete. Current work at Purdue is focusing on the bottom-up synthetic design of SAP hydrogel systems that are more ionically resistant and incorporate additional inorganic phases within the network that will act to further enhance the cement curing reaction and lead to the formation of stronger, more durable concrete.

4 CONCLUSIONS

Controlled rheometry and swelling experiments of model physically and chemically crosslinked polymeric gels are useful to accurately and consistently quantify the nonlinear properties of these soft materials, including the gel's strain-stiffening response, fracture toughness, internal sliding friction, self-healing abilities, mechanical strength, and equilibrium swelling capacity and kinetics. By studying gels that are custom synthesized in house, complete control can be had over the physical and chemical parameters of the polymeric network, which can allow for the gel's properties and performance in specific applications (e.g., cement curing) to be directly linked to the synthetic structure of the gel. In the future, this will allow for the bottom-up design and development of synthetic strategies to create gel systems with properties that are fully optimized for their required applications.

REFERENCES

- [1] A. S. Hoffman, *Adv. Drug Deliv. Rev.* **64**, 18 (2012).
- [2] N. A. Peppas, K. B. Keys, M. Torres-Lugo, and a M. Lowman, *J. Control. Release* **62**, 81 (1999).
- [3] L. Zha, B. Banik, and F. Alexis, *Soft Matter* **7**, 5908 (2011).
- [4] V. Mechtcherine, M. Gorges, C. Schroefl, A. Assmann, W. Brameshuber, A. B. Ribeiro, D. Cusson, J. Custódio, E. F. Silva, K. Ichimiya, S. Igarashi, A. Klemm, K. Kovler, A. N. Mendonça Lopes, P. Lura, V. T. Nguyen, H.-W. Reinhardt, R. D. T. Filho, J. Weiss, M. Wyrzykowski, G. Ye, and S. Zhutovsky, *Mater. Struct.* **47**, 541 (2013).
- [5] O. M. Jensen and P. F. Hansen, *Cem. Concr. Res.* **32**, 973 (2002).
- [6] O. M. Jensen, *Concr. Int.* **35**, 48 (2013).
- [7] D. J. Overstreet, D. Dutta, S. E. Stabenfeldt, and B. L. Vernon, *J. Polym. Sci. Part B Polym. Phys.* **50**, 881 (2012).
- [8] C. Yan, A. Altunbas, T. Yucel, R. P. Nagarkar, and P. Schneiderk, *Soft Matter* **6**, 5143 (2010).
- [9] B. D. Olsen, J. A. Kornfield, and D. A. Tirrell, *Macromolecules* **43**, 9094 (2010).
- [10] K. A. Erk, K. J. Henderson, and K. R. Shull, *Biomacromolecules* **11**, 1358 (2010).
- [11] K. A. Erk and K. R. Shull, *Macromolecules* **44**, 932 (2011).
- [12] K. A. Erk, J. D. Martin, Y. T. Hu, and K. R. Shull, *Langmuir* **28**, 4472 (2012).
- [13] T. Thornell, B. Helfrect, S. Mullen, A. Bawiskar, and K. A. Erk, *ACS Macro Lett.* **3**, 1069 (2014).
- [14] Q. Zhu, C. W. Barney, and K. A. Erk, *Mater. Struct.* **In Press**, doi: 10.1617/s11527 (2014).
- [15] S. Friedrich, in *Appl. Superabsorbent Polym. Concr. Constr.*, edited by V. Mechtcherine and H.-W. Reinhardt (RILEM State of the Art Reports 2, 2012), pp. 13–19.
- [16] H. W. Reinhardt, A. Assman, and S. Monning, in *Int. Conf. Microstruct. Relat. Durab. Cem. Compos.*, edited by W. Sun, K. van Breugel, C. Miao, G. Ye, and H. Chen (2008), pp. 313–322.
- [17] C. Schröfl, V. Mechtcherine, and M. Gorges, *Cem. Concr. Res.* **42**, 865 (2012).