PROCEEDINGS, 50th Workshop on Geothermal Reservoir Engineering
Stanford University, Stanford, California, February 10-12, 2025
SGP-TR-229

The Rheology and Flow Visualization of Temperature-Responsive Microgels and Their Potential for Geothermal Reservoir Management

Aaron M. Baxter[1], Danni Tang[2], Adam J. Hawkins[3], Ulrich B. Wiesner[2], Jefferson W. Tester[1], Patrick M. Fulton[4], Frederic Blanc[5], Sarah Hormozi[1].

Robert Frederick Smith School of Chemical & Biomolecular Engineering[1], Materials Science & Engineering[2], Earth & Atmospheric Sciences[4], Cornell University, 113 Ho Plaza, Ithaca, NY 14850, USA.

Department of Environmental Engineering & Earth Sciences[3], Clemson University, 137 Rich Lab, Anderson, SC 29625, USA.

Nice Institute of Physics[5], Côte d'Azur University, Parc Valrose, 06108 Nice, France.

amb639@cornell.edu

Keywords: rheology, suspensions, hydrogel, short-circuit.

ABSTRACT

Geothermal energy remains a largely untapped natural resource for nations across the globe to increase their energy security and simultaneously reduce their carbon footprint. Enhanced geothermal systems have particularly amplified the potential for geothermal extraction in previously overlooked regions, but also present significant uncertainty with the inherent risk of premature thermal breakthrough. Previous reservoir simulations within our group have suggested a temperature-responsive change in fracture aperture to redirect flow around flow paths which are prematurely drained of their thermal energy can significantly boost system efficiency and life expectancy. Volume-phase transition microgels present a real-world implementation of this change in aperture through their ability to reversibly swell and shrink in response to temperature changes. A variety of synthesis inputs provide a control framework for particle mechanical properties, swelling ratio, and the volume-phase transition temperature. Here, rheometry combined with visualization techniques are performed to evaluate the potential for microgel usage in geothermal reservoirs by understanding the microstructure, macro-rheological properties, and velocity distribution of these microgel suspensions. In particular, we will demonstrate the ability of these microgel suspensions to reversibly form a yield stress fluid which can effectively plug and redirect flow through a change in the suspension's solid volume fraction, which is inherently coupled with temperature.

1. INTRODUCTION

Nations across the world are working to move towards renewable, low-carbon energy sources, while simultaneously working to improve their energy independence and security. Geothermal energy presents an excellent option for both of these goals, as it provides a low-carbon, baseload, and indigenous energy source. In today's energy markets, geothermal systems have been predominantly located in regions with high thermal heat flux like the Western United States, Iceland, or Indonesia where it is most economically viable. However, if geothermal is to make a meaningful impact on the energy landscape, it needs to be accessible and affordable in less favorable geothermal regions. Fortunately, adequate sub-surface temperatures for at minimum direct-use heating are available at reasonable depths in most parts of the world. Furthermore, enhanced/engineered geothermal systems (EGS) provide a means to artificially increase permeability for a geothermal system where it is not naturally present using highly pressurized fluids to reopen and create new fractures in the rock.

A primary concern with EGS is the risk of premature thermal breakthrough due to the formation of short-circuits within the reservoir. This occurs when a predominant flow path or channel forms during the fracturing or heat extraction process which provides a low impedance path that lowers the effective heat transfer area of the reservoir. These short-circuits cool quickly and contribute heavily to rapidly declining production-well temperatures. Such thermal drawdown of the reservoir substantially lowers the economic favorability of the geothermal system, which is expected to have a lifetime of 10 or more years. Significant previous work has been performed to simulate these effects and the possible improvements which can be realized through a temperature-responsive aperture which can artificially increase the flow resistance in these cold, short-circuited regions (Hawkins et al. 2023). By drastically reducing the aperture size in short-circuited regions, the flow is forced to spread out and accesses a far larger volume of the sub-surface, resulting in higher production temperatures over longer timescales. Reservoir modeling suggests that the gains in thermal efficiency far outweigh the losses suffered through increased reservoir pressure losses that would require higher pumping power. Despite these promising results, a practical implementation of this temperature-responsive change in aperture has yet to be seen. Here we present a rheological study on thermally-responsive, volume-phase transition (VPT) hydrogel suspensions as a means of implementing this approach. The focus of this rheological study is to provide foundational information required to successfully use thermally-responsive hydrogel suspensions as a practical means of flow control in fractured geothermal reservoirs.

Polymerized N-Isopropylacrylamide (NIPAM) hydrogels were pioneered in the 1970s and 1980s by Tanaka and noted for their counter-intuitive VPT properties (Tanaka et al., 1979; Tanaka et al., 1985; Matsuo et al., 1988). When immersed in water, these hydrogels swell at low temperatures and reversibly shrink at high temperatures due to the cross-linked network switching from a hydrophilic to hydrophobic state. This causes the network to collapse in on itself at a critical temperature through a diffusion-controlled process.

Furthermore, **Figure 1** shows that incorporating sodium acrylate into the gel's network enables one to tune the temperature at which this VPT occurs (Tanaka et al., 1993). Beyond this, sodium acrylate can increase the extent to which the hydrogel swells and as a result the overall swelling ratio between swollen and shrunken state.

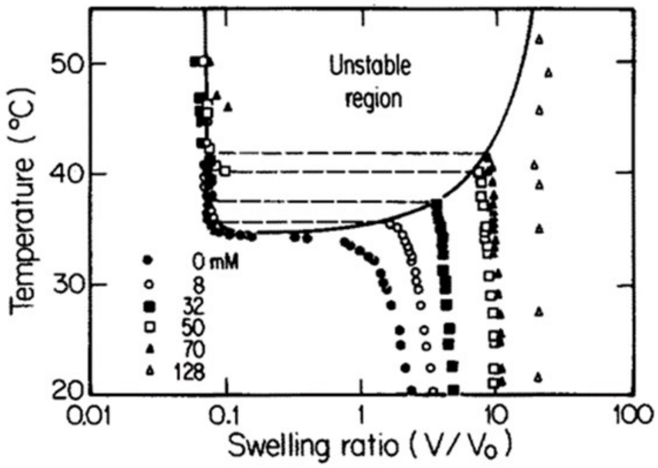

Figure 1: Swelling ratio vs temperature for a variety of NIPAM-SA hydrogel recipes. The legend displays the concentration of sodium acrylate (SA) while the overall monomer concentration of the hydrogels (NIPAM + SA) was held constant at 700 mM. N,N'-Methylenebis(acrylamide) is held at 81 mM (Tanaka et al., 1993).

As a result, the PNIPAM to sodium acrylate ratio is of significant importance and can be tuned or individualized for each unique geothermal reservoir based on design and operating criteria. However, changing this ratio also significantly impacts the hydrogels mechanical properties which can be further tuned with the concentration of organic cross-linker or by introducing clays as a natural cross-linker. Naturally, to function properly in a geothermal system, these particles must be able to withstand large forces and deformations. As such, the mechanical properties of a variety of gel recipes have been investigated as well.

Through pulse injection of concentrated suspensions of micron-scale spherical PNIPAM hydrogels into a geothermal system above the volume-phase transition temperature (shrunken state), we aim to jam the cold, short-circuited paths through the localized swelling of hydrogels in these regions only. Through this swelling, the suspension's particle volume fraction can increase beyond the typical jamming volume fraction due to the particle's deformable nature, generating a yield stress fluid as demonstrated in our previous work (Baxter et al., 2024). **Figure 2**, presents these results for a particular recipe via measurement on a TA Discovery HR30 rheometer using a cross-hatched parallel plate to eliminate slip.

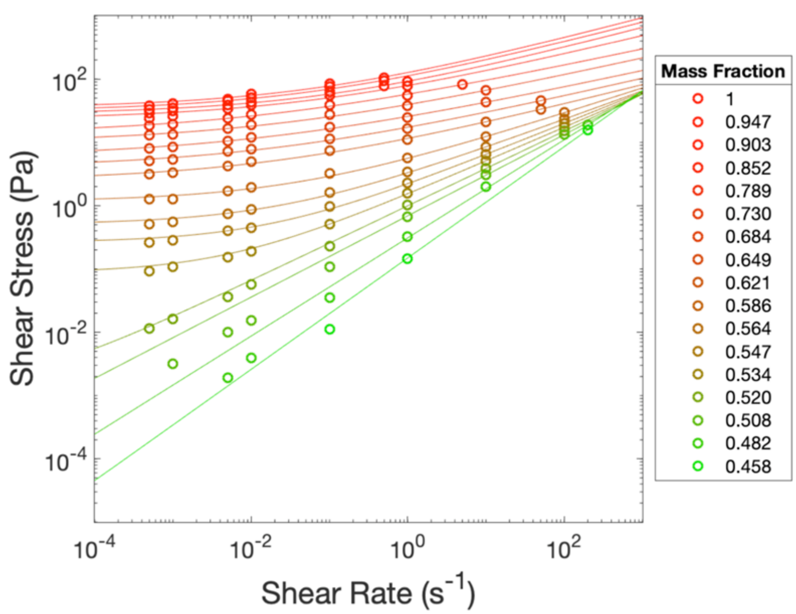

Figure 2: Log-log plot of shear stress vs shear rate at a variety of mass fractions for a pNIPA-SA particle suspension with no clay, 1.29 g/L BIS, and a 90:10 NIPAM to SA ratio.

In **Figure 2**, a mass ratio is used instead of volume fraction due to the difficulty in determining a volume fraction given the particle's high polydispersity, deformability, and readiness to change volume in response to changes in its environmental conditions. Each open circle represents an individual experiment where the shear rate is held constant and the shear stress is monitored until it has reached steady-state. It can clearly be seen that as the sample is diluted, the mass ratio and in turn the volume fraction decreases, leading to a reduction in the yield stress until the point that it drops below the jamming volume fraction and the yield stress is eliminated. Despite the promise shown in these results, macro-rheological experiments such as the one above in a parallel plate geometry presented numerous challenges. Slip was a common issue for particular recipes even with a roughened surface, likely due to the particle's high deformability. More importantly was the challenge of understanding the impact of temperature on the system, as we cannot directly visualize or measure changes in particle size or shape. As a result, in this paper we present a device we have constructed which allows us to couple our rheological measurements with a local flow visualization.

2. MICROGEL SYNTHESIS

The nanocomposite NIPAM-SA microgels were synthesized via surfactant-free inverse suspension polymerization. In this process, an aqueous per-gel solution (containing monomers, crosslinkers, and initiators) was stirred vigorously in paraffin oil to form spherical droplets. Then, an accelerator was added to initiate droplet polymerization. The particle properties (i.e. size, volume phase transition temperature, swelling ratio, and mechanical properties) can be fine-tuned by varying three parameters: ionic comonomer amount, organic crosslinker amount, and physical crosslinker amount. Specifically, sodium acrylate (SA), the ionic comonomer, enables the tuning of particle swelling ratio and volume phase transition temperature by increasing the osmotic pressure and hydrophilicity of the NIPAM polymer network. N,N'-methylenebisacrylamide (BIS) serves as the organic crosslinker, chemically crosslinking the NIPAM-SA polymer and providing mechanical strength to the microgel. However, pure organic crosslinked gels are usually brittle, which significantly limits their application in harsh environments where high shear and pressure are present, such as EGS systems. Hence, Laponite-RDS (Lap-RDS), a synthetic clay nanoparticle, is incorporated as a physical crosslinker to improve the microgel toughness. The prepared microgels were designated as NCn-ORm-SAx, according to the amounts of nanoclay (n mol% per L of H2O), BIS (m mol% against total monomer amount), and SA (x mol % against total monomer amount) added. The synthesis is based on free radical polymerization where an initiator, potassium persulfate (KPS), and an accelerator, tetramethylethylenediamine (TEMED) are combined to generate active radicals. With those tuning knobs, we established methods to tailor particle properties to match the physical demands of reservoir systems. Additionally, a fluorescent dye, acryloxyethyl thiocarbamoyl rhodamine B (ATRhB), is added to enable particle visualization during rheological studies.

For the application in EGS, a large particle swelling ratio, relatively high volume-phase transition temperature, and good mechanical performance are required. Hence, as proof of principle, we selected NC2-OR0.6-SA10 composition with an expected volumetric swelling ratio of 150x, volume phase transition temperature at around 50 ˚C, and enhanced mechanical properties with clay to conduct rheology tests. The exact composition is listed in **Table 1**.

Table 1. Chemical composition used in microgel synthesis for rheology studies

	Monomers			*Crosslinkers*		*Initiator*	*Accelerator*
Chemicals	NIPAM	SA	Dye	BIS	Laponite-RDS	KPS	TEMED
Concentration	**630 mM**	**70 mM**	**0.115 mM**	**4.3 mM**	**20 mM**	**3.5 mM**	**8 mM**

The resulting nanocomposite NIPAM-SA microgels adopt a well-defined spherical shape as shown in **Figure 3**. The particle size distribution was obtained through flow imaging microscopy where flowing particles were imaged and analyzed to give size information. Results show that the particle adopt a left-skewed size distribution ranging from 50 μm to 1000 μm, with predominant sizes between 75-200 μm. It is noteworthy that in fluorescent microscopy, the particle fluorescence signal intensity at the microgel edge was observed to be much stronger than that at the center. This non-uniform dye distribution is likely due to a heterogenous clay distribution caused by the Pickering effect. The Pickering effect is a stabilization phenomenon where small solid particles create a protective layer between two immiscible liquids to lower the interfacial energy (Pickering, 1907). Our microgels are synthesized via inverse suspension polymerization, where the aqueous pre-gel solution is dispersed in an oil phase. During this process, the nano-sized clay discs will likely absorb onto the oil-water interface, resulting in a higher clay abundance at the edge. Consequently, this special clay distribution is manifested by positively charged dyes which preferentially locate near the negatively charged clay discs.

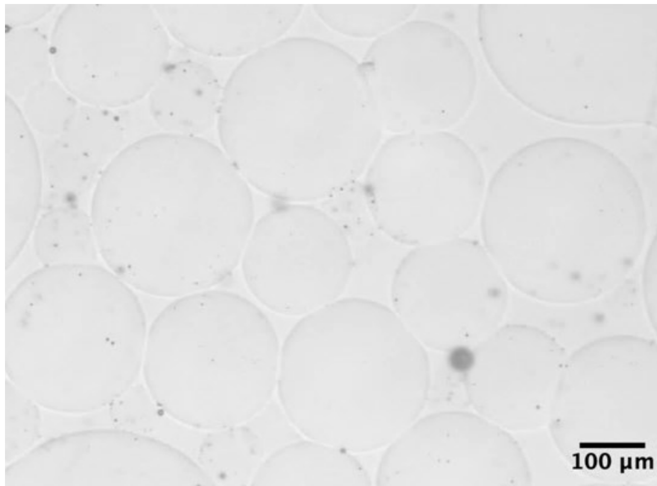

Figure 3: A typical optical image of the resulting particles.

3. FLOW VISUALIZATION

NIPAM hydrogel suspensions benefit from two key features which allow for flow visualization. The first being that the hydrogel suspensions have a near-perfect index match at all temperatures. This being a result of the hydrogel particles being primarily composed of water as well as being dispersed in water. Even in dense regimes when a yield stress exists, the overall system is still a majority water by mass and volume, so the small volume fraction of polymer allows for clear visualization a few millimeters into the sample before scattering becomes too large. The second key feature, as discussed in Section 2, is that the dye used for visualization concentrates on the surface of the particles, such that we can get good contrast and understand the microstructure even in dense regimes.

A dense system with the chemical composition as described in **Table 1** is visualized below in **Figure 4**. The image shows a narrow slice of the suspension produced by shining a 532 nm laser sheet through the system. The laser sheet excites the fluorescent dye and produces light with an emission peak of 566 nm. A high-pass filter is then used to filter out the laser light, such that we see primarily only the light produced by the dye.

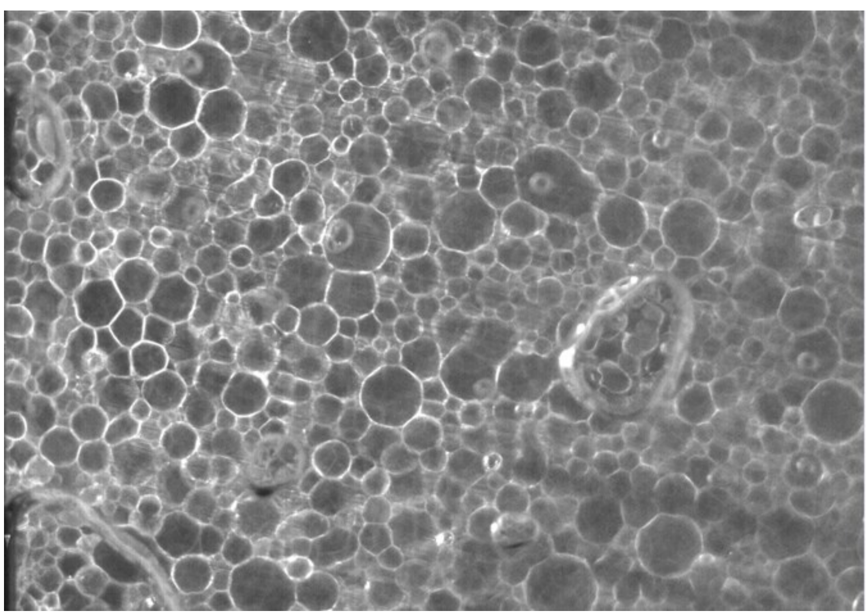

Figure 4: Visualization of a narrow slice of a dense NIPAM-SA suspension with use of a laser sheet and high-pass filter. Laser sheet enters from the left and travels towards the right.

As described, we see excellent contrast at the edge or surface of the particles where the image appears bright. This imaging was performed in a basic rectangular box composed of polymethyl methacrylate (PMMA) commonly known as acrylic. The laser sheet enters from the left side of the image and due to scattering from the imperfect index match the image becomes more blurred as you visualize further to the right. Air bubbles in the system drastically scatter the light and can cast lines of shadows in the system. A few larger air bubbles can also be seen which are not in-plane with the laser sheet but disrupt the visualization nonetheless such as the one in the very bottom-left of the image.

The persistence of these air bubbles in the system, along with the non-spherical shape of the particles is a clear indication of the yield stress within the system. These deformations store elastic energy which defines the energy barrier which must be overcome in order to achieve plastic, yielding flow.

To better understand the rheological properties of our system, we have specially designed an acrylic, temperature-controlled Taylor-Couette device placed in-line with a rheometer which allows us to visualize a slice of our system while under shear. This allows us to gain insight into the flow profile, effect of temperature, as well as macro-rheological properties all in one. Please attend the presentation for further information on the setup as well as results.

4. CONCLUSIONS

This study characterized the rheological properties of micron-scale spherical hydrogel suspensions which change their solid volume fraction in response to changes in temperature. Microgels with these properties present an excellent opportunity to improve the performance of EGS reservoirs by reducing flow short-circuiting in regions with large fracture apertures. Flow can be redirected by tuning the rheology to increase the resistance to flow in cold, short-circuited regions of the reservoir. As a result, the thermal performance and lifespan of an EGS reservoir can be increased.

To better understand the rheology and impact of temperature, we have combined rheological measurements with flow visualization. The developed optical setup allows us to perform visualization easily without the need for difficult techniques such as MRI which is often used for foams or emulsions. We are again able to demonstrate the ability of the suspension to form a yield stress which can be eliminated through increases in temperature which inherently reduces the suspension's solid volume fraction. We have also demonstrated that the compositional and operational conditions in the synthesis of the microgels can be tuned to achieve the desired properties of an individual hydrogel particle, such as its mechanical properties, size, swelling ratio, and temperature at which the volume-phase transition occurs.

ACKNOWLEDGEMENTS

This material is based upon work supported by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) under the Geothermal Technologies Office, Award Number DE-EE0009786. The views expressed herein do not necessarily represent the view of the U.S. Department of Energy or the United States Government. The authors also acknowledge the support provided by Cornell University's College of Engineering, and helpful contributions from other members of Cornell's Earth Source Heat project team.

REFERENCES

A. Baxter et. al. "The Rheology of Temperature-Responsive Volume-Phase Transition Hydrogels…". (2024).

A. Hawkins et. al. "Active Tracers for Hydraulic Control of Cooled Short Circuits". (2023).

B. Goldstein, G. Hiriart, R. Bertani, C. Bromley, L. Gutierrez-Negrin and E. Huenges, et al., Geothermal Energy, in O. Edenhofer, R. Pichs-Madruga, Y. Sokona, K. Seyboth, P. Matschoss and S. Kadner, et al., IPCC Special Report on Renewable Energy Sources and Climate Change Mitigation, Cambridge University Press, Cambridge,United Kingdom and New York, NY, United States, 2011.

d'Ambrosio E, Blanc F, Lemaire E. The characterization of the particle normal stresses of concentrated granular suspensions by local rheometry. Journal of Fluid Mechanics. 2023;967:A34.

DOE report - GeoVision: Harnessing the Heat Beneath Our Feet (2019)

Eriko Sato Matsuo, Toyoichi Tanaka; Kinetics of discontinuous volume–phase transition of gels. J. Chem. Phys. 1 August 1988; 89 (3): 1695–1703.

Fox, D. B., Koch, D.L., and Tester,J. W.: The Effect of Spatial Aperture Variations on the Thermal Performance of Discretely Fractured Geothermal Reservoirs, Geothermal Energy, 3, (2015).

Gilbert, D. Role of Adhesive and Friction Contacts in the Rheology of Non-Brownian suspensions (2021).

Pickering, S.U. (1907) Emulsions. Journal of the Chemical Society, 91, 2001-2021.

Shibayama, M., Nagai, K. (1999). Shrinking Kinetics of Poly(N-isopropylacrylamide) Gels T-Jumped across Their Volume Phase Transition Temperatures. Macromolecules 1999, 32, 7461-7468.

Shibayama, M., Tanaka, T. (1993). Volume phase transition and related phenomena of polymer gels. In: Dusek, K. (eds) Responsive Gels: Volume Transitions I. Advances in Polymer Science, vol 109. Springer, Berlin, Heidelberg.

Tanaka T, Sato E, Hirokawa Y, Hirotsu S, Peetermans J. Critical kinetics of volume phase transition of gels. Phys Rev Lett. 1985 Nov 25;55(22):2455-2458.

Tester, J. W. et al, “The Future of Geothermal Energy: Impact of enhanced geothermal systems (EGS) on the United States in the 21st century,” Massachusetts Institute of Technology and Department of Energy Report, Idaho National Laboratory, INL/EXT-06-11746 (2006).

Tester, J.W., K.F. Beckers, A.J. Hawkins, and M.Z. Lukawski, “The evolving role of geothermal energy for decarbonizing the United States,” Energy & Environmental Science 14, 6211-6241 (December 2021).

Toyoichi Tanaka, David J. Fillmore; Kinetics of swelling of gels. J. Chem. Phys. 1 February 1979; 70 (3): 1214-1218.