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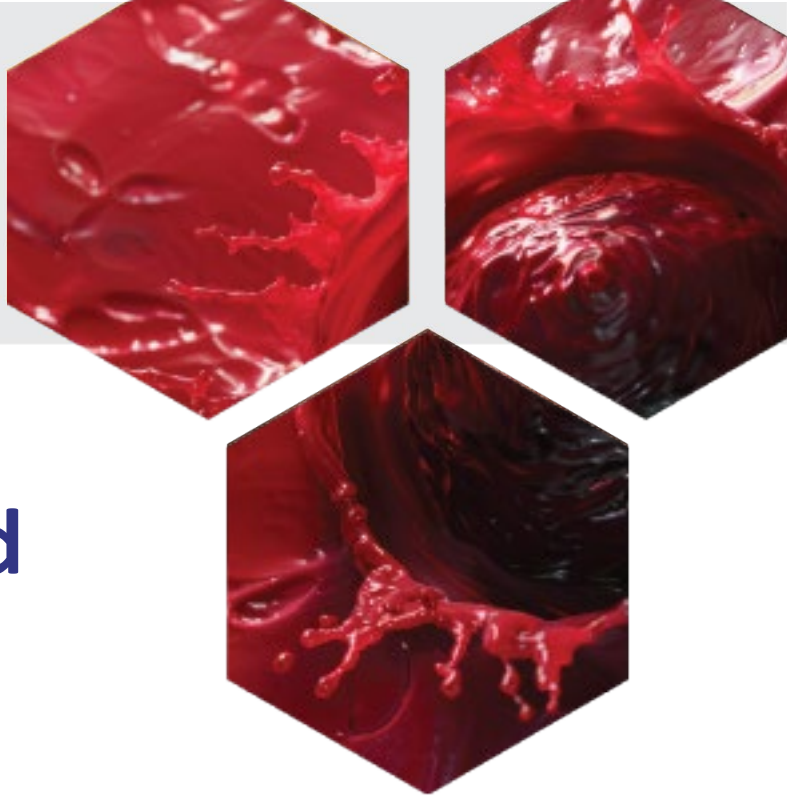


Rheology of Rapid Kinetics

By Joseph White, Research Scientist

Summary

Quantifying changes in rheological properties of fluids undergoing rapid physical change is a non-trivial feat. Certain stimuli (like UV-light, electrical fields, magnetic fields, chemical species interaction, or heat) can initiate rapid changes in rheological properties (viscosity, modulus, etc.). Example systems could include hemostatic agents intended to rapidly coagulate blood, or curing hydrogels for use in medical applications. CPG has the capability to quantify rapid rheological changes of various fluids—even develop non-standard test methods for uncommon requests. This note describes the rheological characterization to quantify soak-up time for a highly absorbent material.

Introduction

Measuring the kinetics of a rapid rheological transition plays a vital role in material and product design. Common examples of systems that can exhibit a rapid rheology transition (e.g., crosslinking, curing, particle aggregation/agglomeration, molecular alignment, etc.) include electrorheological systems, magnetorheological systems, ultra-violet (UV) curing systems, and stimulus-responsive systems. In some cases, being able to tune short time-scale phenomenon can have a large impact

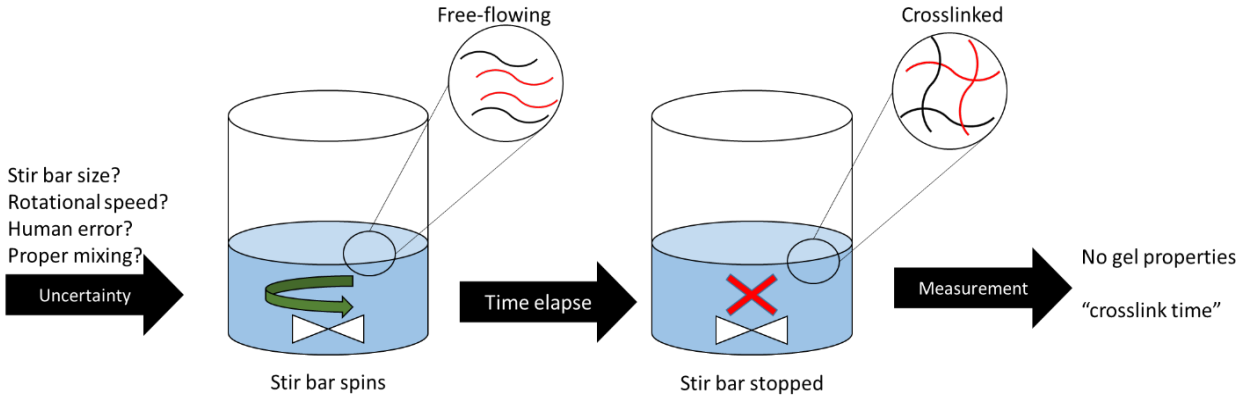


Figure 1. Stir bar stop method typically used as a qualitative metric to measure near rapid rheological transitions. Example shown for crosslinking. Time accuracy is only as good as the human pressing the start/stop button on a stopwatch.

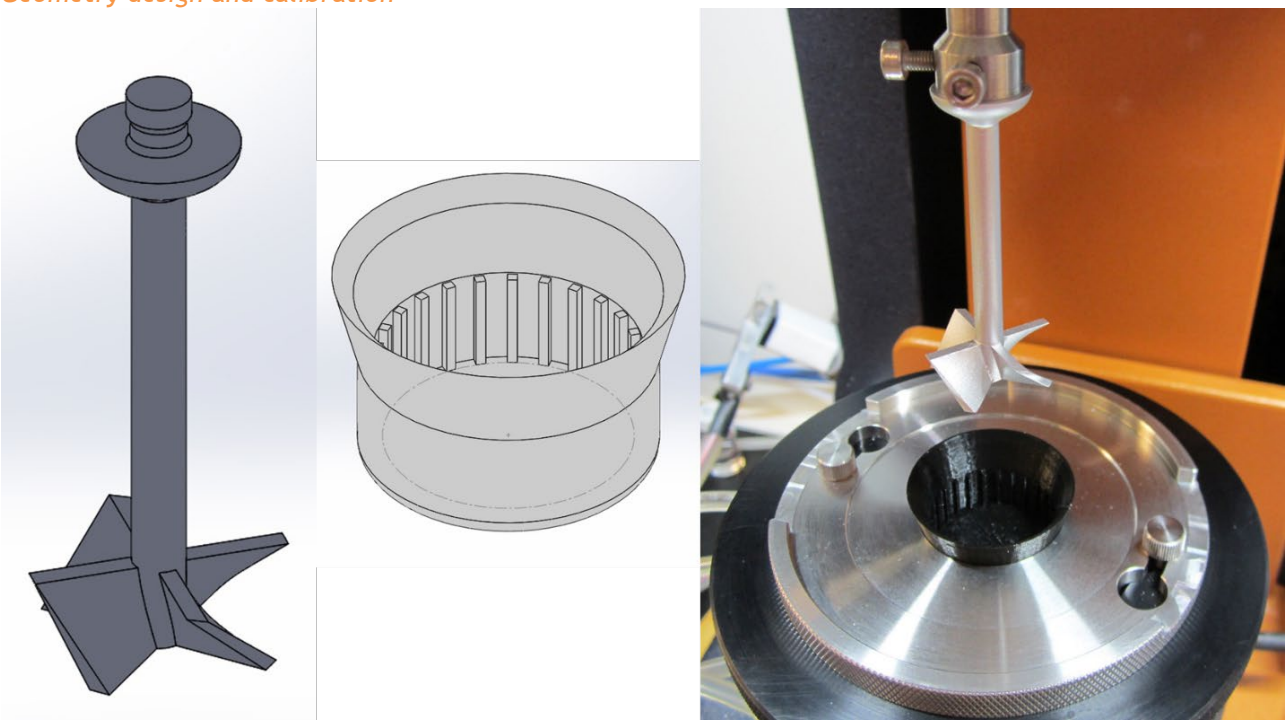
on material/product performance. For example, in 3D printing (a.k.a., additive manufacturing), optimizing the cure or crosslinking time for the filament material—either thermoplastic or gel-based—is necessary to ensure a clean print, dimensional conformity, and minimization of printer clogging. Rheological testing of the cure behavior can help to optimize formulations for a 3D printer.

Rheometer suppliers provide some accessory lines to measure some rheological systems. The vane and cup accessory is advertised to measure rheological properties of slurries but typically requires a large sample volume, ~20 mL. For some formulations, this large volume requirement is cost-prohibitive, and these users are obliged to resort to more qualitative approaches such as the stir bar stop method (see Figure 1). The stir bar stop method can require very small sample volumes and consists simply of a stir bar rotating in a fluid sample. Upon the required stimulus, be it thermal, chemical, electrical, etc., a stopwatch is used to measure how long it takes for the stir bar to stop rotating. This method can be useful on a qualitative level for a ranking of performance but is usually not accurate enough to capture rapid transitions faster than a second. Therefore, capturing rapid rheological transitions while using minimal sample volumes is not straightforward.

Below, we describe an example of the characterization of the swelling and gelation kinetics of a rapidly-absorbing material. These materials are often used for spillage cleanup, hemostatic agents, and other applications. Rapid swell kinetics is an import design parameter for spillage cleanups by determining the minimum time the absorbent material needs to soak up a 'mess' before the user cleans it up, which is a diffusion-limited process. As shown below, rheological characterization can be used to measuring swelling kinetics.

Experimental

Geometry design and calibration



A TA Figure 2. CAD sketch of custom vane (left) and custom baffled cup (middle). Machined vane and 3D printed baffled cup assembly (right).

Instruments DHR-2 rheometer was equipped with a custom-made vane and baffled cup geometry (see Figure 2). The baffled cup was designed to fit into the jacketed Peltier fixture for concentric cylinder geometries. The vane was designed to reduce the required sample volume to 6 mL (standard vane accessory requires ~20 mL sample volume). The custom geometries were designed using SolidWorks; the baffled cup was 3D printed from PLA and the vane fixture was machined from aluminum. For standard vanes, a concentric cylinder analogy is typically used to determine stress and strain constants, and with a sufficiently large gap the end effects (contributions from a parallel plate analogy) are not significant. Here, in order to reduce the sample volume requirements, a smaller than recommended gap was used therefore stress and strain factors contained concentric cylinder components as well as parallel plate components [1], (see Figure 3). The vane geometry was calibrated using a model fluid to determine stress and strain coefficients (see Figure 4).

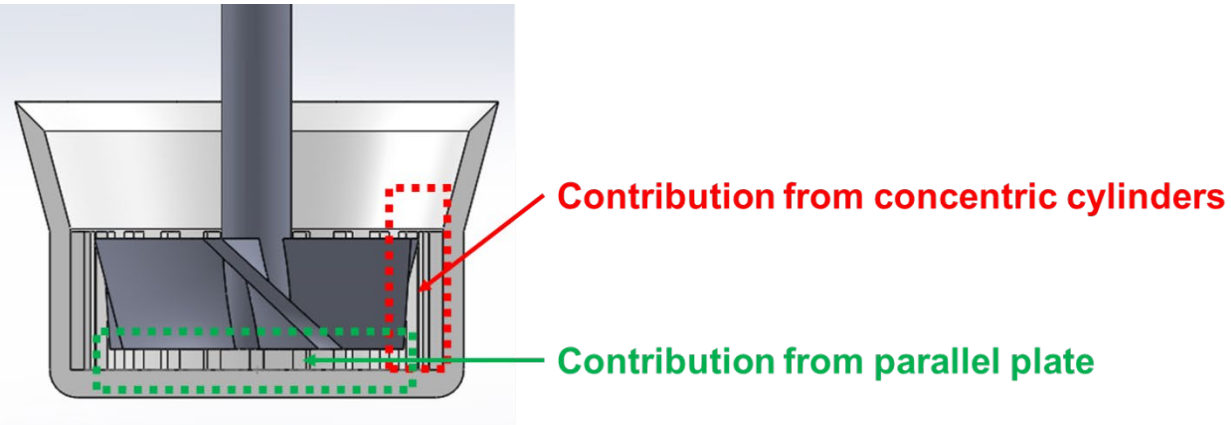


Figure 3. Schematic of custom vane/baffled cup fixture. Due to narrow gap at cup wall and at cup floor, torque/deformation contributions from concentric cylinders and parallel plate analogies must be used.

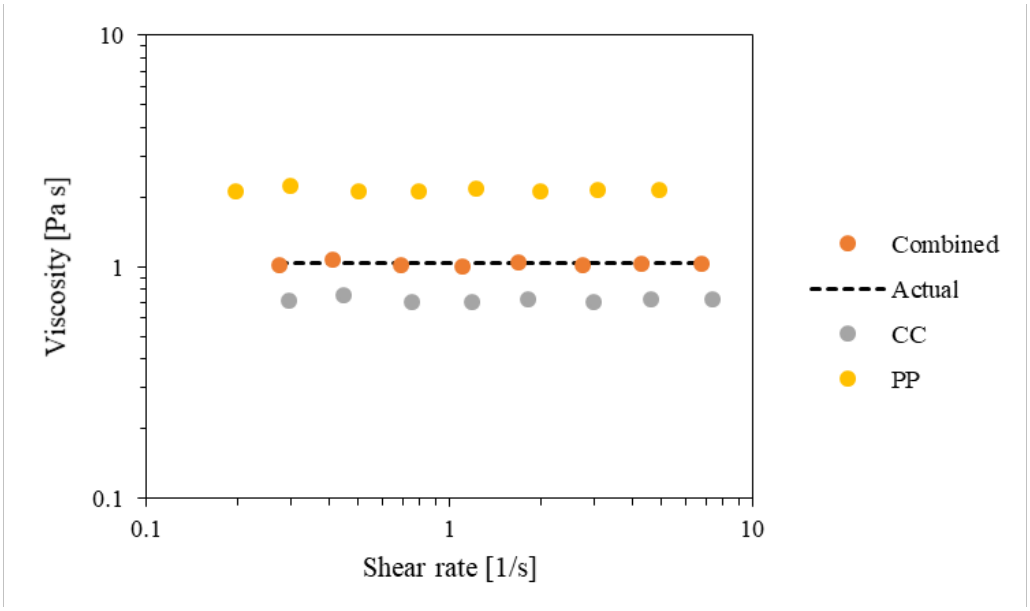


Figure 4. Sketch of test method: Powder absorbent added to cup with scoop while vane rapidly rotates within the baffled cup containing model "spilled fluid."

Capturing rapid absorption of liquid by powder absorbents

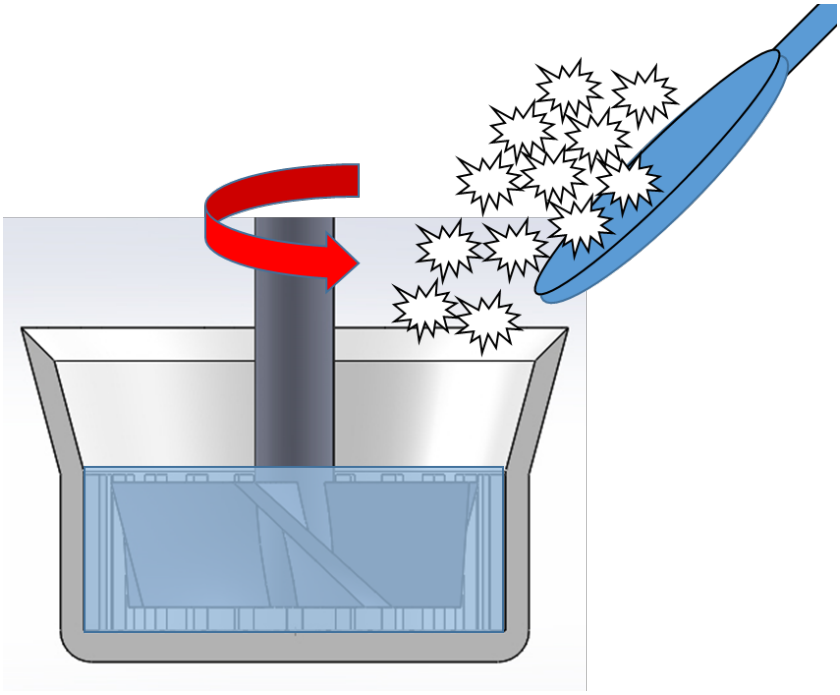


Figure 5. Sketch of test method: Powder absorbent added to cup with scoop while vane rapidly rotates within the baffled cup containing model "spilled fluid."

A sketch of the test initiation is shown in Figure 5. To measure rapid kinetics of a liquid/powder absorbent system, the vane/baffled cup geometry was utilized by initially rotating the vane rapidly while submerged in the liquid. At a specified time, powder was placed in the cup while spinning the vane continuously at a fixed speed. The torque required to maintain the rotation speed is then monitored until a torque threshold was surpassed. At this point the test method was switched to an oscillatory test in order to measure the modulus of the resultant slurry. The moment of powder addition is signified by an abrupt change in torque.

Results

Sufficient mixing is key for producing meaningful, reproducible results for rapidly absorbing systems. By initially rotating the vane at very high speed, 50 rad/sec (not fast enough to expel fluid, however), the powder absorbent was almost instantaneously mixed with the fluid because the vane acts more like a mixing blade than a rheological fixture. Figure 6 shows a typical result from a rapid absorbent powder and model spilled fluid system. The moment the powder was added to the liquid is signified by the abrupt increase in torque starting at 3.69 seconds; this is time zero when calculating crossover time and time for modulus to reach a plateau. The data shows a crossover time within 1.79 seconds of addition of the powder. The stress and strain coefficients discussed above allowed direct transformation of raw torque and displacement data to calculate stress, strain, and modulus. The modulus of the slurry plateaued within 17.85 seconds from the addition of the powder to liquid, indicating that the powder is fully swollen in the water.

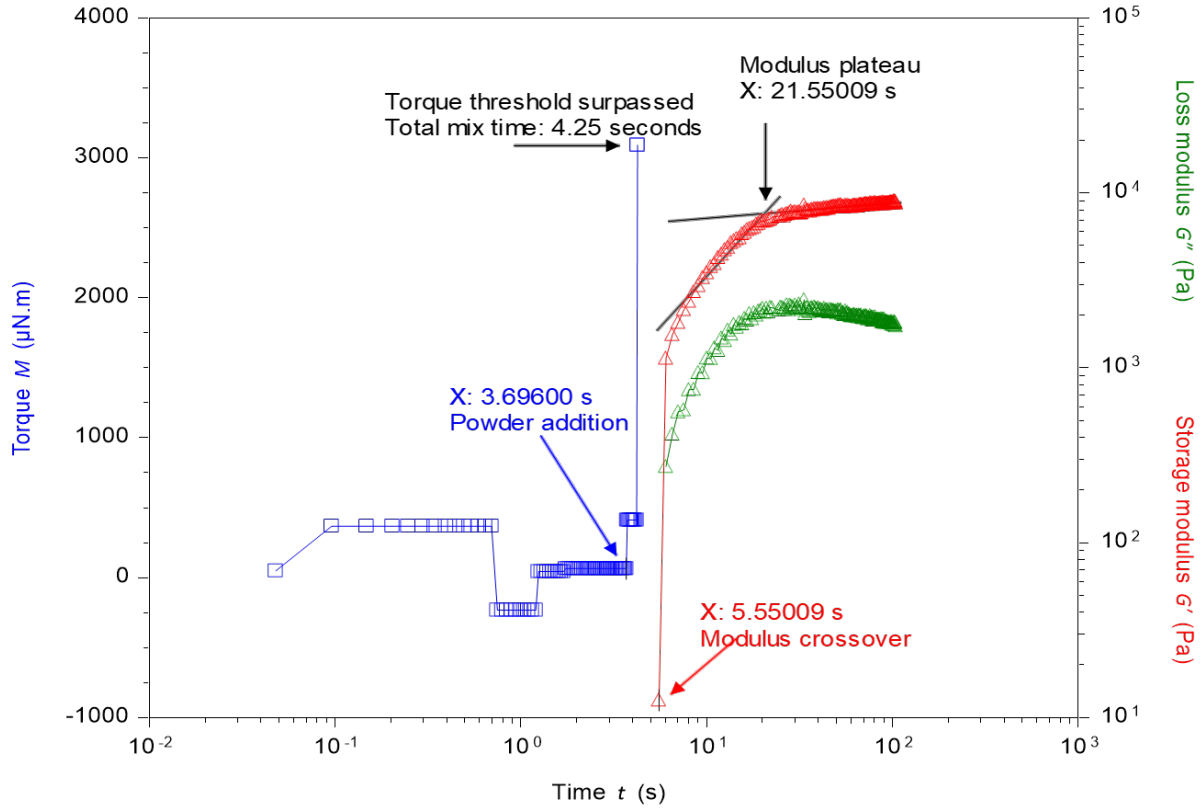


Figure 6. Powder absorbent added to liquid "spill." Blue curve from the initial mix step: powder added at ~3.7 seconds, mixed rapidly for ~0.5 seconds until a predetermined torque threshold was surpassed indicating the slurry was sufficiently mixed. Red (G') and green (G") curves: modulus growth kinetics shows crossover within ~1.8 seconds after addition of powder and full absorbency within 17.9 seconds from addition of powder.

Conclusions

CPG leverages its extensive hydrogel expertise to assist medical device developers and synthetic tissue model designers in creating custom tissue model formulations development and lab-scale manufacturing. Our expertise in testing, and particularly the adaptation of standardized tests for unusual needs, gives us a unique experience in test design and development. Coupling that experience with a deep understanding of materials science and hydrogel chemistry allows us to assist in the construction.

References

[1] Zhang, XD, et al. Measurement of foam modulus via a vane rheometer. *J Rheol.* 42(4). July/August 1998.

About Joseph White, Ph.D.

Joseph White, Ph.D. is a Cambridge Polymer Group Research Scientist II, specializing in biomaterials, including hydrogels for medical applications. He has co-authored numerous publications, including studies on oxygen transport enhancement and the development of composite hydrogels with improved mechanical properties. Joe has presented his work at major scientific conferences and contributed to several SBIR projects focused on innovative biomedical solutions. He holds a patent for a thermo-reversible amphiphilic gel device, reflecting his commitment to advancing biomaterial technologies.

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