

## ABSTRACT

Hydraulic fracturing is a method to extract natural gas from shale rock formations. The fracturing fluid, almost completely water based, is comprised of hydroxypropyl guar (HPG), cross linking agent(s), mineral salts, pH adjusting agents, and other components to regulate rheological behavior. To access the natural gas, the fracturing fluid is pumped at high pressures down into a well to fracture the shale formation. Once the fractures are created, they are held open by proppants, typically crystalline silica, which fills in the cracks created to allow for the appropriate flow of hydrocarbons. Once the proppant is in place, a breaker entity is added to decrease the viscosity of the gel and allow the fluid and the natural gas to flow back up the well for recovery. This method of natural gas extraction is an efficient means of providing natural resources; however, the current fluid components used in industry are hazardous and present health risks upon unanticipated exposure. The ultimate goal of this research is to develop a model of current fracturing fluid behaviors. From these models, a solidified method for fracturing fluid synthesis can be explored using environmentally friendly chemicals.

This work is an examination of the rheological properties of crosslinked HPG solutions with boric acid (BA), current components used in hydraulic fracturing. Two different synthesis methods are analyzed, using steady and dynamic rheological tests on an ARES LS-2 (TA Instruments – Waters LLC) rheometer with couette geometry. The two fluids are tested over a span of four days to examine the longevity and repeatability of the fluid properties desired for fracture use. The results of the tests are evaluated further to determine the appropriate method for synthesizing an environmentally friendly fracturing fluid.

## INTRODUCTION

In the United States, natural gas plays a significant role in energy production. Approximately 85% of the energy demand is fueled by oil, coal, and natural gas, with natural gas supplying 22% of the total.<sup>1,2</sup> Sources estimate that the U.S. alone has 1,744 trillion cubic feet of recoverable natural gas with 211 trillion in reserves.<sup>1</sup> With easily accessible fuel sources running low, evident by the near \$4.00 per gallon of gas, there is a need for these natural gas sources to be accessed by means of hydraulic fracturing.

Though hydraulic fracturing can be beneficial in reducing the gap between supply and demand for fossil fuels, there are environmental concerns surrounding the process that is limiting its implementation in some regions.<sup>3</sup> Though most

of the public concern stems from faulty well construction, blowouts, and above-ground spills,<sup>3</sup> there are concerns with toxicity in some of the fluid components.<sup>4</sup> To alleviate these anxieties, we look to replace currently used toxic components with environmentally friendly entities, while retaining the functionality of the current species.

To begin, a complete understanding of the current nature of fracturing fluids and their rheological properties is essential in order to evaluate what properties are desired in the fracturing process. To obtain the knowledge required, examining the shear and complex viscosities of the fluid with an ARES LS-2 rheometer leads to an understanding of the flow characteristics of the fluid; however, in order for the results to have significant meaning, the fluid has to be synthesized properly; that is, useful results will be obtained when there exists a homogeneous distribution of polymer and acid molecules in order to ensure the fluid is a uniform gel.

By combining formulations and experimental protocols from previous works<sup>5,6</sup> and the use of the ARES LS-2, we look to formulate an efficient and effective method for fracturing fluid synthesis to be used in the development of future experimental testing.

## EXPERIMENTAL

The fluids were both prepared by combining 0.5 wt% HPG, 0.36 g/L BA solution, 2 wt% potassium chloride, and water. The pH was adjusted with a concentrated solution of sodium hydroxide (NaOH) (20 wt%) to make the fluids basic in order to encourage crosslinking; however, each solution was prepared in a different fashion.

Solution A was prepared by mixing water and potassium chloride salt in a 500 mL glass jar for 2-3 minutes with a magnetic stir bar. Once dissolved, the stir bar RPM was set to 550 and the HPG was added and mixed for 2-3 minutes. While still mixing, the BA and NaOH solutions were added and allowed to mix for 5 minutes. Once the 5 minute period had elapsed, the solution was placed on a roller mixer for 24 hours.

Solution B was synthesized similar to Kesavan and Prud'homme's experimental procedure.<sup>5</sup> Water and potassium chloride salt were combined in a blender and once dissolved, the polymer powder was added by a controlled flow rate into the operating blender to ensure optimum dispersion of the polymer molecules. The BA and NaOH solutions were then added drop wise into the functioning blender and the solution was blended for 3-4

minutes. The fluid was distributed to jars in order to be placed on the roller mixer for 24 hours. Solution B was kept on the roller mixer in between testing phases.

## Rheological Characterization

Each fluid was tested over a span of four days. During the testing period, the fluid was loaded into the couette and subjected to steady shear and oscillatory tests. Each test was repeated, with a sufficient amount of time between each trial to allow for the fluid to recover, and averaged in order to account for variability in between runs. Once the tests concluded, the data was collected and analyzed to determine the success of the synthesis method.

## RESULTS AND DISCUSSION

### Shear Viscosity vs. Shear Rate

During regular well operation, the fracturing fluid is pumped down the well in order to break into the shale deposits and extract the natural gas. While it is being pumped, it experiences extensive amounts of shear from the well, which can affect its proppant carrying ability, so a study of the fluid's shear viscosity is crucial to ensure that the fluid will be viscous enough to carry the proppant to the fracture.

On the ARES LS-2, steady shear tests were performed to examine the shear behavior of the fluids as well as the fluid stability over time. In Figures 1 and 2, the shear viscosity of the fluid decreases with an increase in shear rate, better known as a property called shear thinning. This phenomenon was anticipated due to the crosslinked nature of the system. Although both fluids exhibit shear thinning behavior, there were some noticeable differences between the two results. In the lower range of shear rates, solution A had a larger viscosity, but also had a larger amount of variability in values. From previous experiments, the fluid should behave in accordance with the Cross Model, which displays Newtonian behavior at the two extremes of the shear rate spectrum.<sup>7</sup> As it can be seen from the multiple inflection points in the curves in Figure 1, the Cross Model would not accurately describe the characteristics of solution A beyond the first day, but the Cross Model would be applicable to solution B due to its Newtonian-like behavior in the lower range of the shear rate.

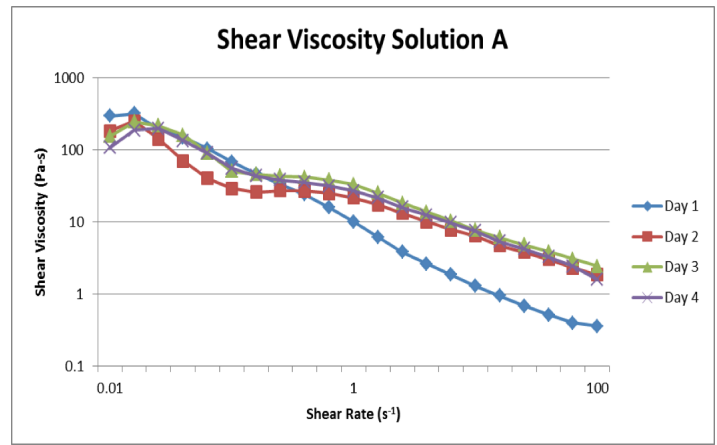


Figure 1: Shear Viscosity vs. Shear Rate for Solution A

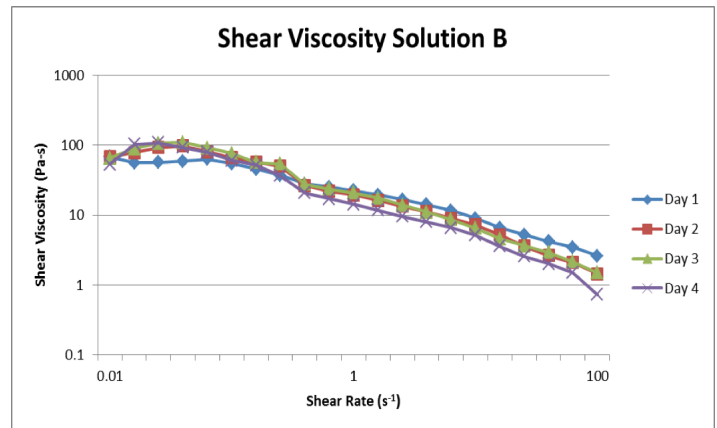


Figure 2: Shear Viscosity vs. Shear Rate for Solution B

### Storage and Loss Moduli vs. Frequency

To better understand the fluid behavior, the storage and loss moduli are studied so that the elastic and viscous behaviors of the fluid may be determined.

Figure 3 depicts the comparison of the storage and loss moduli of the two fluids 24 hours after sample preparation. For solution B, the storage modulus was greater than the loss modulus over the range of frequencies investigated, displaying that solution B behaved more like an elastic solid than a viscous fluid, which is typically characteristic of a strongly-gelled system. Solution A differed in that it contained an intersection point, called the relaxation point, where the fluid switched from behaving like a viscous liquid to an elastic solid. This is characteristic of weaker gel systems, which could potentially lead to premature fallout of proppant sands which would make the fluid insufficient.

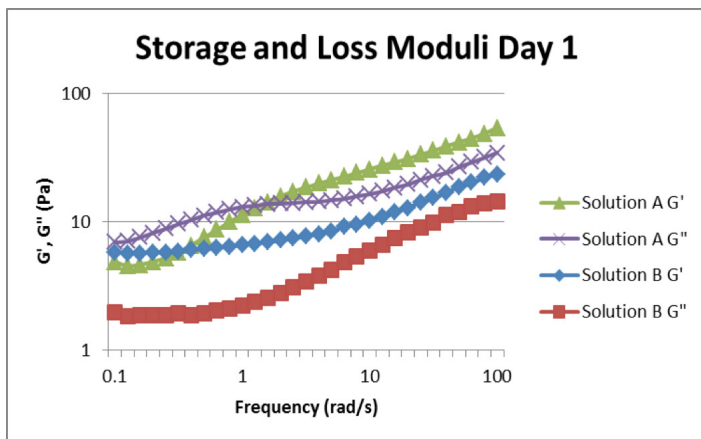


Figure 3: Storage and Loss Moduli vs. Frequency Day 1

In Figure 4, the storage and loss modulus are examined four days after sample preparation. It can be seen that there are slight changes in each of these curves that can be contributed to the time frame of testing. Both sets of curves began to converge on one another at the higher frequency values, which displayed the beginning of the gel network beginning to decay; however, solution A had lost its relaxation time and instead displayed a greater storage modulus over the frequency range. This can be attributed to the phase separation that was observed at the beginning of the testing phase on day 3. The amount of the fluid that was tested was specifically extracted from the gelatinous layer that had formed so that the rheological properties could be measured more accurately, whereas solution B was observed to be homogenous throughout the testing period.

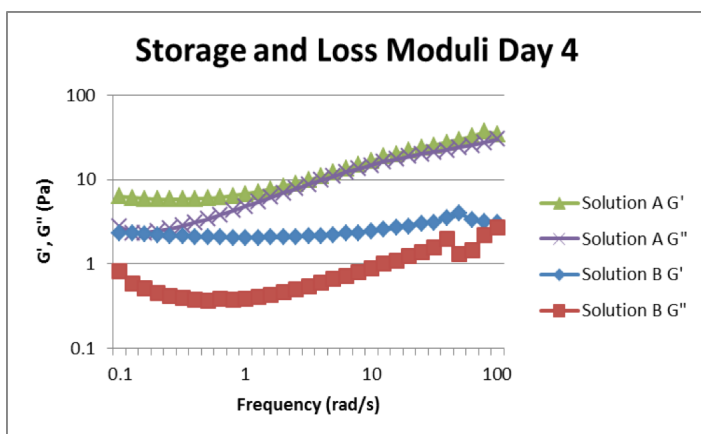


Figure 4: Storage and Loss Moduli vs. Frequency Day 4

## CONCLUSION

In conclusion, because of phase separation, lack of repeatability during steady shear testing, and lack of gel strength in solution A, solution B possesses properties more desirable for a fracture fluid. Solution B had a much stronger gel network over the four-day span than solution A, which would allow it to carry proppant efficiently to the fracture;

whereas, solution A would encounter too much fallout. Although there was a slight reduction in solution B's shear viscosity over the four day span, the solution maintained its homogeneity which allows the fluid to be useable for a longer period of time, whereas solution A's phase separation prohibits any consistent results beyond a two day span.

## ACKNOWLEDGEMENT

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