Rheological Characterization of Cementitious Mixtures with Free Polyethylene Oxide

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Abstract:

The effects of free polyethylene oxide (PEO) chains on cementitious magnesium oxide (MgO) suspensions were examined through shear start up tests, creep tests and flow curves. Previous experiments used varied amounts of ADVA, a superplasticizer found in commercial cements. Samples with greater amounts of the superplasticizer experienced higher overshoot peaks during shear start up tests, due to particle jamming. Because its side chains are composed of PEO, free PEO chains were introduced from 0-50 wt% into new samples with constant ADVA concentration to investigate particle aggregation. Over-dosage of an admixture such as this can alter the workability of the cement and previous studies of ADVA-adsorbed suspensions only contained 5% non-adsorbed chains. MgO and free PEO suspensions without the superplasticizer were also tested. To reduce wall slip and sedimentation, a vane fixture and sandblasted cup were used along with preshearing of the samples.

ADVA was found to increase the workability of MgO suspensions. While creep tests showed that ADVA-adsorbed samples required a greater stress to flow (5 Pa for unadsorbed vs. 20 Pa for adsorbed), some of the unadsorbed MgO particles settled to the bottom of the sandblasted cup making the suspension appear thinner. Superplasticizers such as ADVA are used in industry to disperse particles, so without it the suspensions do not easily retain a uniform consistency. Flow curves support the presence of depletion flocculation and depletion stabilization in the suspensions. As the particles flocculate, shear stresses increase from 10-30 wt% PEO. Particles then stop coming together and stabilize, which decreases the shear stresses for 40 and 50 wt% PEO. Because the viscosity is also lowered, the 40 and 50 wt% PEO suspensions become more workable and better candidates for cement processing.

1.0 Introduction

Cements today commonly use polymer additives to prevent the shear thickening of particles, which can impact the product while pouring but before curing. Comb polymers, like the ADVA 190 polymer seen in Figure 1, are used because of their ability to adsorb to particles and because their side chains help repel other particles enough to lower viscosity. [1]

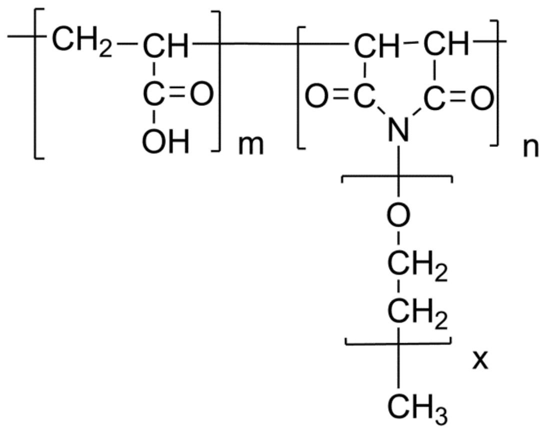

Figure 1: Molecular structure of ADVA. The vertical portion of the molecule depicts a polyethylene oxide side chain, and the backbone is comprised of poly(acrylic-acid). [1]

Jamming occurs when neighboring particles in a suspension lock together and create a barrier to flow because of the shear forces induced on the sample. This is common in colloidal suspensions such as cement, and can cause issues when mixing and processing these cements. [1]

After analysis of model cement samples containing MgO particles and either 0 mg/g, 0.06 mg/g, 0.6 mg/g, or 6.0 mg/g ADVA, it was found through UV-vis that the 6.0 mg/g sample had a small amount of free, unadsorbed ADVA. [1] This sample required higher shear stresses than others and a question was posed as to whether this excess comb-polymer affected the microstructure of the cement suspension by entangling more particles and forming networks. It was also unknown whether the polymer chains were aggregating. Because of this, model cement samples comprised of MgO particles, constant amounts of ADVA, and varying amounts of free polyethylene oxide (PEO) chains were investigated using rheological tests. Free PEO chains were used because the ADVA side-chains are comprised of PEO. This causes the molecule to behave like a PEO chain when it isn't adsorbed.

Previous samples were tested in a Couette cell, however it was found that the flow was affected by wall slip. Wall slip causes suspensions to appear to yield at a lower shear stress, when it is actually sliding against the wall [2]. To account for this, a cup with a rough geometry on the inside surface and a vane fixture was used. Vane fixtures also help test materials that have large particles and exhibit slip. The vane geometry acts like a cylindrical bob because some of the suspension gets trapped between the blades of the vane [3].

2.0 Experimental Methods

2.1 Samples

Samples in these tests consist of 150 g narrow distribution magnesium oxide (MgO) powder, 50 g deionized water, either 0.9 g dialyzed ADVA or no ADVA, and varying weight percentages of 1,000 g/mol PEO. Table 1 shows the different amounts used for each sample. The ADVA and PEO were first added to a clean bottle, then the water was added. The MgO was added as a powder to the sample about 10-15 g at a time, then shaken after each addition to ensure that no sedimentation occurs. The sample is sonicated for 5 minutes, then left to stir overnight. The next day, the sample is sonicated again and tests are run at 25°C.

Table 1: Weight percentages of excess PEO added to each sample. These percentages are based on the amount of ADVA in the sample

Sample	Weight % of PEO	Amount of PEO (g)
1	10	0.09
2	20	0.18
3	30	0.27
4	40	0.36
5	50	0.45

2.2 Testing Conditions

The samples are loaded into a 27 mm diameter sandblasted Couette cup with a vane fixture as well as a solvent trap and presheared for 30 seconds. After the preshear, a 10 second wait period passes to ensure that the vane fixture is no longer moving, then the tests are performed. Figure 2 shows the two types of fixtures used during testing.

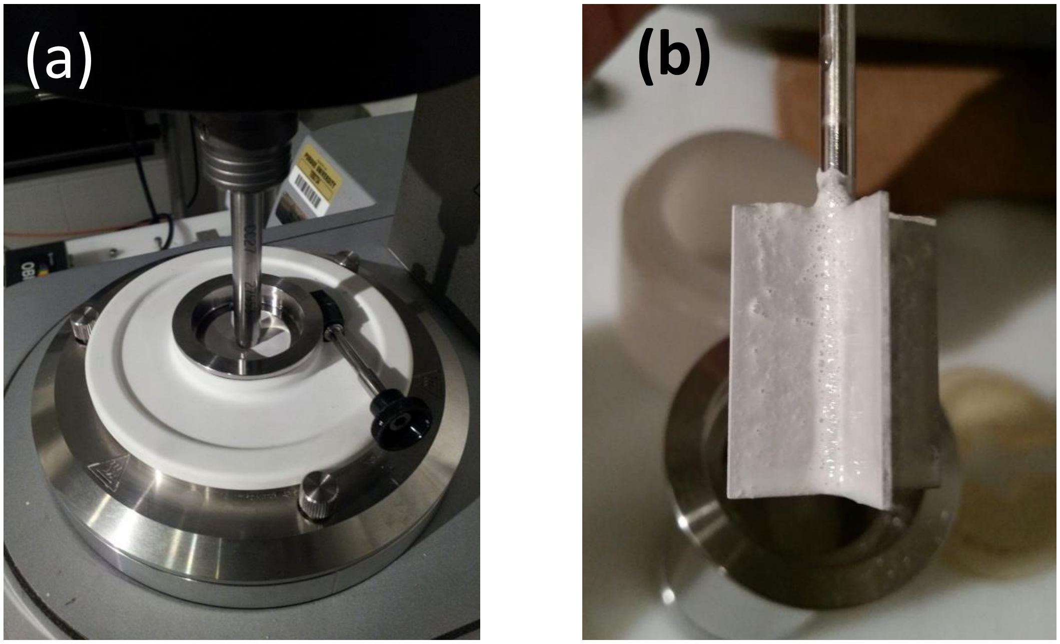

Figure 2: Close-up photo of a 30 wt% PEO sample loaded into the (a) CC27 Couette cell with cylindrical bob and of the (b) vane fixture after a test.

For the shear start up tests, the shear rate was held constant and the shear stress was analyzed versus time. The sample was loaded into the sandblasted CC27 Couette cup, presheared for 30 seconds, and a shear rate of either 0.1 s^{-1} or 0.01 s^{-1} was applied with the vane fixture for 500 data points. Both fixtures were cleaned after each test, and a fresh sample was used for the next test.

For the creep tests, the shear stress is held constant, and the shear rate is analyzed over time. When this data is plotted, one can see how resistant the sample is to flow. If a greater shear rate is recorded, then the sample flows much more easily. For these creep tests, the sample was loaded into the sandblasted CC27 Couette cup with vane fixture again. A shear stress of either 10, 15, 20 or 25 Pa was applied to the sample for 500 data points after preshearing it for 30 seconds. These values were determined by using the lowest shear stresses possible (usually 10 or 15 Pa) until the sample was able to flow. Both fixtures were cleaned after each test, and a fresh sample was used for the next test.

Flow curves were also obtained by logarithmically increasing the shear rate from 0.1 s^{-1} to 100 s^{-1} in 400 data points and analyzing the shear stress. These samples were presheared for 30 seconds in the sandblasted CC27 Couette cup with the vane fixture and then the flow curve was run. Both fixtures were cleaned after each test, and a fresh sample was used for the next test.

3.0 Results

3.1 Shear Start up

Shear start up tests for samples containing both ADVA and PEO with a Couette cell in Figure 3 displayed overshoot peaks, which indicate shear-induced jamming. These samples were tested at 0.1 s^{-1} and 0.01 s^{-1}. Samples with and without ADVA were then tested in a vane fixture at only 0.1 s^{-1}, due to time constraints. There are still slight overshoots in the ADVA adsorbed suspensions in Figure 4a, but one can see how the vane fixture and sandblasted Couette cup has caused them to occur at later times (around 20 seconds for the new tests, and between 0.5-1 seconds for the older tests). The samples without ADVA in Figure 4a did not show any overshoot peaks.

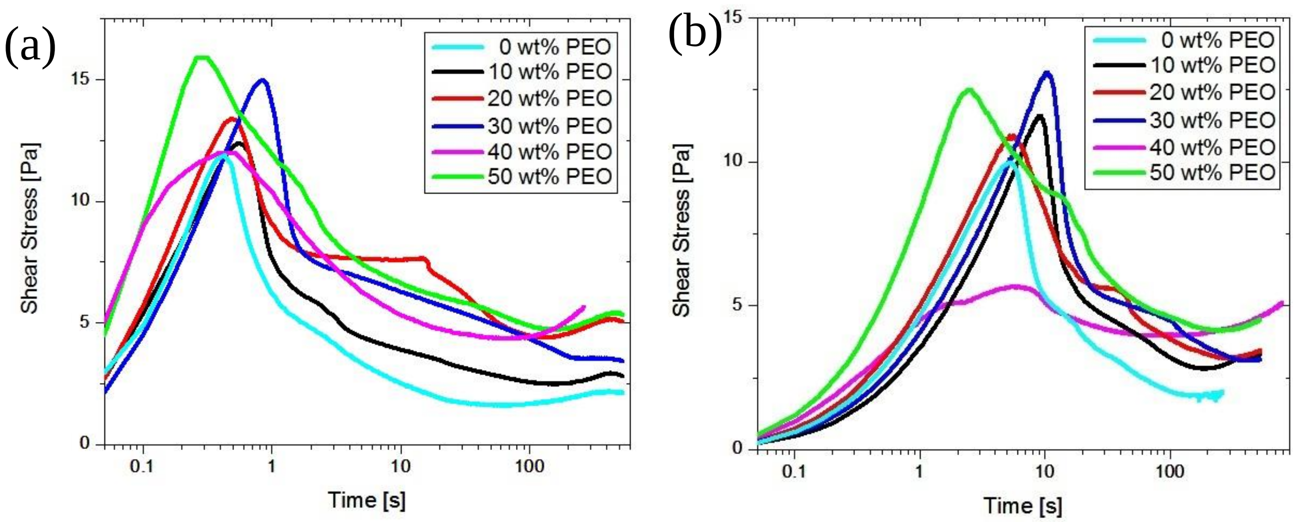

Figure 3: Shear start up tests performed in the Couette cell at (a) 0.1 s^{-1} and (b) 0.01 s^{-1} of samples with ADVA and excess PEO [1]

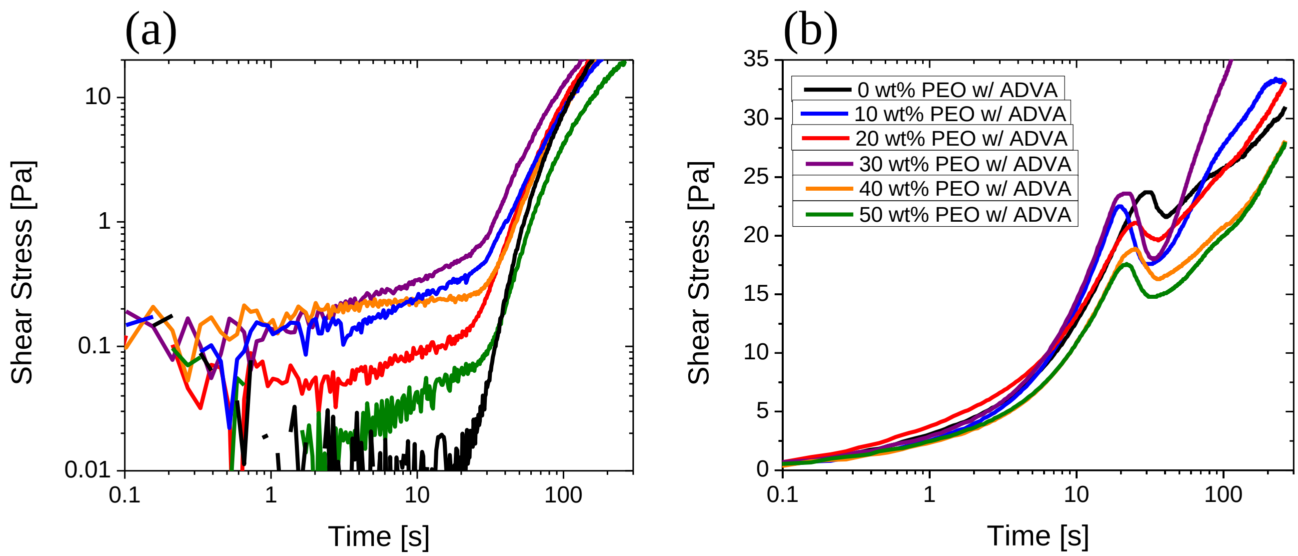

Figure 4: Shear start up tests performed in the vane fixture for samples (a) without ADVA and (b) with ADVA run at 0.1 s^{-1}

3.2 Creep Tests

Creep tests are a way to simulate how a material moves through a pipe. Creep tests conducted in the Couette cell can be seen in Figure 5. The 40 wt% PEO sample in Figure 4b was the first creep test out of all the samples, and it was determined from that data that the others could be tested at a higher shear stress. A new 40 wt% PEO sample was not able to be tested at 20 Pa due to time constraints. More creep tests with the vane fixture were performed on the samples with shear stresses of 10, 15, 20, and 25 Pa, seen in Figure 6. The shear stresses increased as weight percentages of PEO increased because the PEO made it harder for the suspensions to flow. Suspensions without ADVA were also tested in Figure 7 at only 5 Pa with the vane fixture, due to sedimentation of the samples.

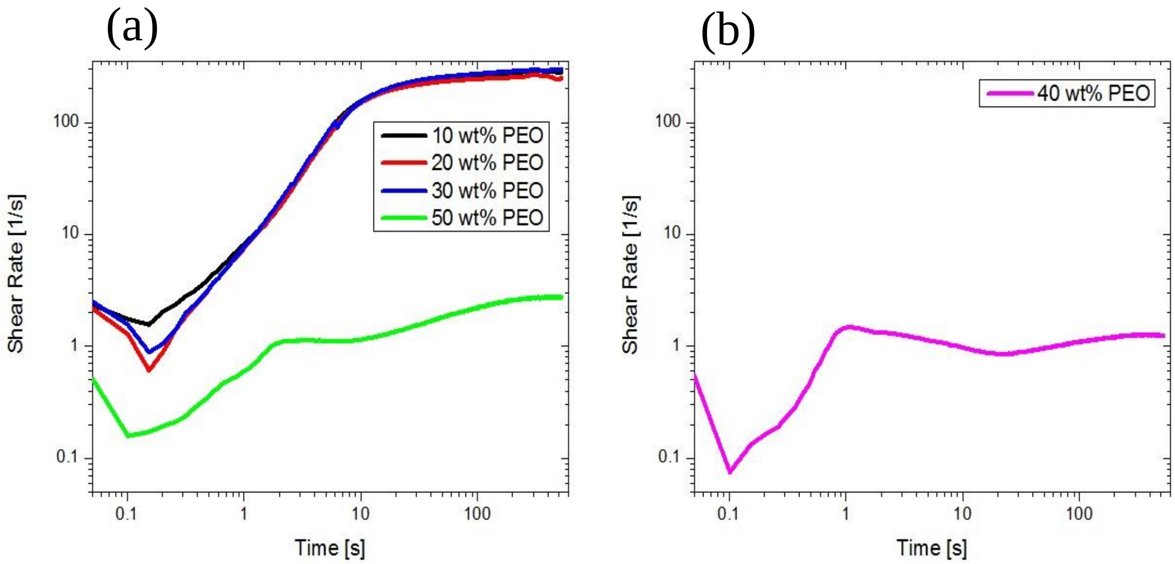

Figure 5: Results of creep tests performed in a Couette cell at (a) 20 Pa and (b) 10 Pa. Note that the y-axis is identical in both plots so that the data can be more easily compared.

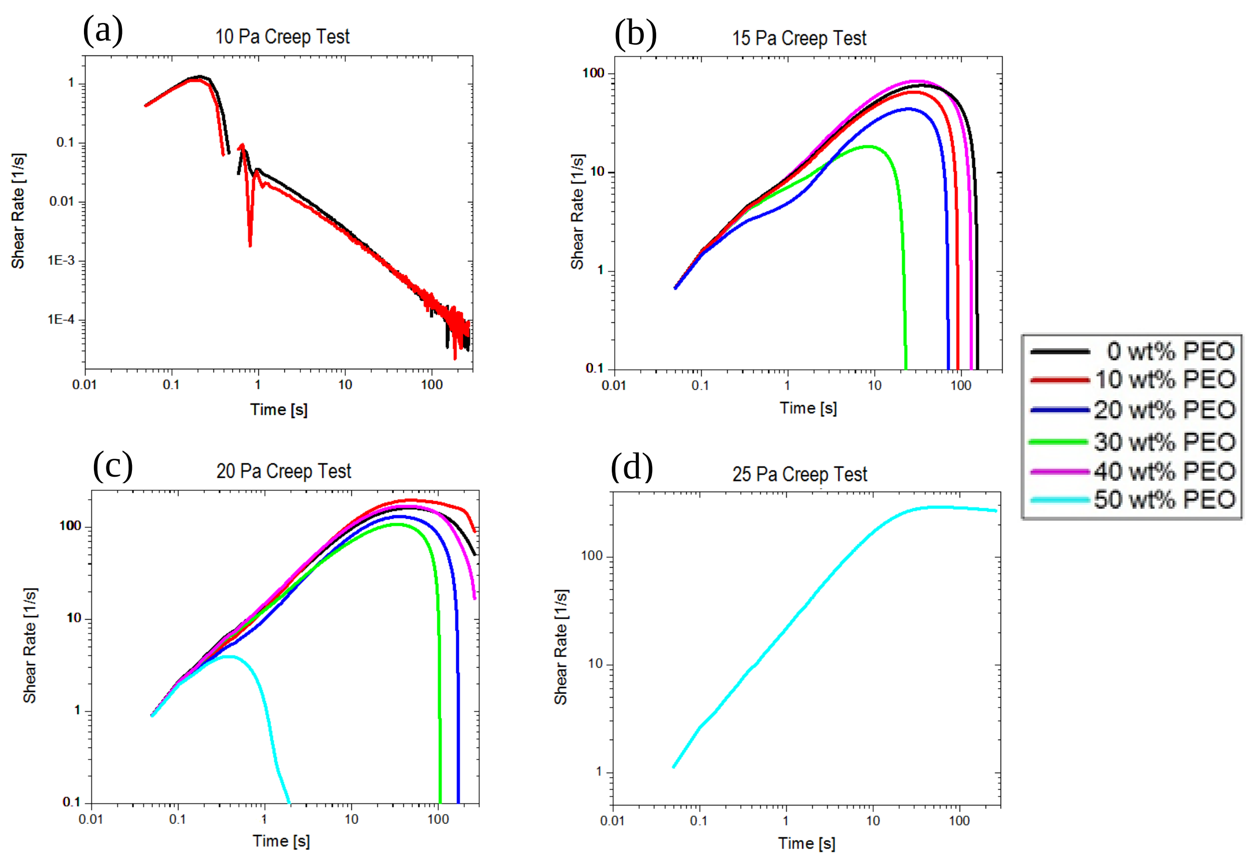

Figure 6: Results of creep test data for ADVA adsorbed suspensions performed in a vane fixture for (a) 10 Pa, (b) 15 Pa, (c) 20 Pa, and (d) 25 Pa. An MgO control suspension was also tested at 10 Pa, however its peak maximum was at 81.6 s^{-1}

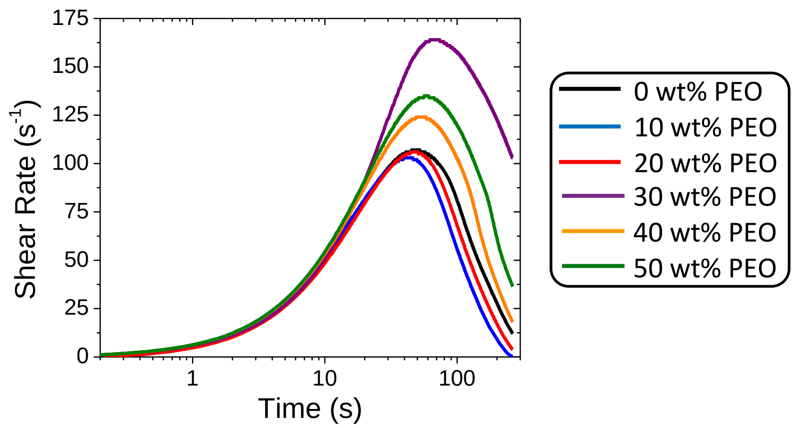

Figure 7: 5 Pa creep test results of suspensions without ADVA in a vane fixture

3.3 Flow Curves

Flow curves simulate the mixing of a material and were only tested with the vane fixture. The results from these flow curves are plotted by viscosity in Figure 5.

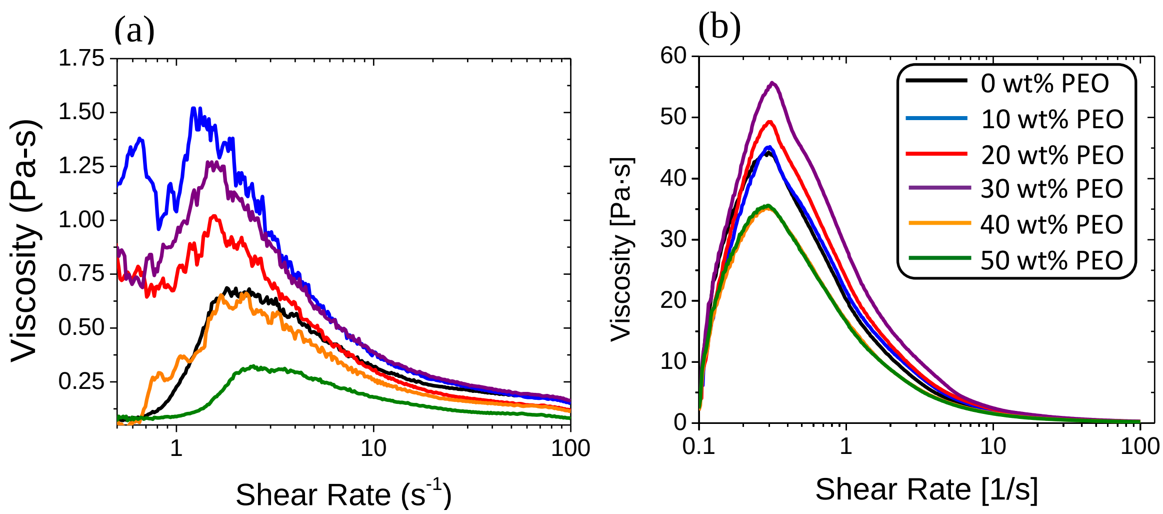

Figure 8: Results of flow curves of samples (a) without ADVA and (b) with ADVA

4.0 Discussion

4.1 Testing Differences

One of the main differences between earlier tests with the Couette cell and later tests with the vane fixture is the change in fixtures to account for wall slip. Figure 3a and Figure 4b both depict 0.1 s^{-1} shear start up tests of ADVA-adsorbed samples, but were tested in either a Couette cell or with a vane fixture and sandblasted cup respectively. There are still overshoot peaks, however the tests run with the vane fixture have later peaks than the tests run with the Couette fixture. The maxima of these peaks also differ. For example, the 30 wt% PEO sample in the Couette cell shear start up had a 15 Pa peak, while the 30 wt% PEO sample with the vane fixture had a peak at around 23.6 Pa. The first sample began to slide along the walls of the smooth Couette cell, which gave the appearance of lower shear stresses. The sandblasted cell used with the vane fixture gripped the suspension better and allowed for more accurate results. The vane fixture catches material in between its blades, causing it to act like a cylinder when spun. [2] This allows it to act like a cylindrical bob, but with the smaller surface area of the vane fixture's blades so the suspension doesn't slip as much.

Another difference is the addition of a preshear before the tests are run in the vane fixture to improve the uniformity of testing. Each sample was subjected to 30 seconds of preshear, then a 10 second wait time before the test, so the particles in suspension had no time to settle beforehand. The higher weight PEO samples were noticeably more resistant to flow when loading and cleaning the fixtures, so they could have settled out slightly during the 5 minute wait before previous tests in the Couette cell.

4.2 Shear Start up

From the shear start up tests, it is shown that the samples containing ADVA undergo jamming as indicated by the presence of the overshoot peaks in Figure 3 and 4b. However the behavior of these peaks changes as the amount of PEO in the suspension changes. In the 0.1 s^{-1} tests depicted in Figure 3a, the overshoots occurred around the same times but at different maxima. The 50 wt% PEO suspension had the highest peak, which would be logical as one would expect the greatest amount of PEO chains to interfere with the flow of particles the most. The 40 wt% sample, however, had the lowest peak at 12.4 instead of the 10 wt% sample. The reason for this is because of the constant ADVA amount. When one analyzes the peaks of these shear start up tests compared to tests with variable amounts of ADVA, the change in peak size is much more noticeable. An MgO suspension in a 0.1 s^{-1} shear start up test with no ADVA has a peak around 3 Pa, while an MgO suspension with 6mg/g ADVA and the same testing conditions changes to about 13 Pa [1] which is more drastic than the range seen in Figure 3. The PEO chains may contribute to the fluctuation of these peaks, however their maxima are more dependent on the amount of ADVA in the suspension.

More important, however, is the shape of the peaks. When comparing the shape as PEO increases in both Figure 3a and 3b, one can see that the peaks broaden. This means that the PEO chains seem to be causing aggregation of the particles and extending the jamming time. This is easily seen when comparing the 50 and 10 wt% PEO samples in Figure 3b. The 10 wt% PEO peak is much narrower than the 50 wt%, which means that the jam occurs in the sample, then quickly starts to flow again. The 50 wt% sample jams, then resists flow for a longer amount of time, even developing a slight shoulder. In Figure 4b, the shapes differ by their height. The 30 wt% sample doesn't have the highest peak, but the height of the peak compared to the others is largest. This means it experiences more jamming than the others at that time. Jamming does not occur, however, in excess PEO samples without ADVA, as shown in Figure 4a. The side chains of the ADVA helps bring the particles together, so without it the particles do not jam.

4.3 Flow Curve

From the vane fixture flow curves in Figure 8, it was found that the 40 and 50 wt% samples reached lower viscosities than the 10–30 wt% samples. The samples without ADVA in Figure 8a follow a decreasing trend, while the samples with ADVA in Figure 8b increase until the 30 wt% mark. Here, the peaks jump from 49.3 Pa·s for 20 wt% to 55.7 Pa·s for 30 wt% then down to 35.3 Pa·s for 40 wt%. It is possible that there is some transition point between 30 and 40 wt% PEO as the 40 and 50 wt% samples decrease drastically and behave the same way. This is representative of depletion flocculation and stabilization, which will be discussed later. The 50 wt% sample may behave like the 40 wt% sample because there are so many free chains in suspension that any higher amounts of PEO will behave like 40 wt%.

The viscosities also differ greatly between the ADVA adsorbed and unadsorbed samples. This is due to the fact that ADVA is a dispersant for the MgO particles. Without the superplasticizer keeping the particles in the suspension, they settled quickly to the bottom of the cup during tests. The settling was discovered during the cleaning of the cup, seen in Figure 9. Sedimentation skews the results to make the suspensions look thinner than they truly are during testing, because not as many particles are being tested.

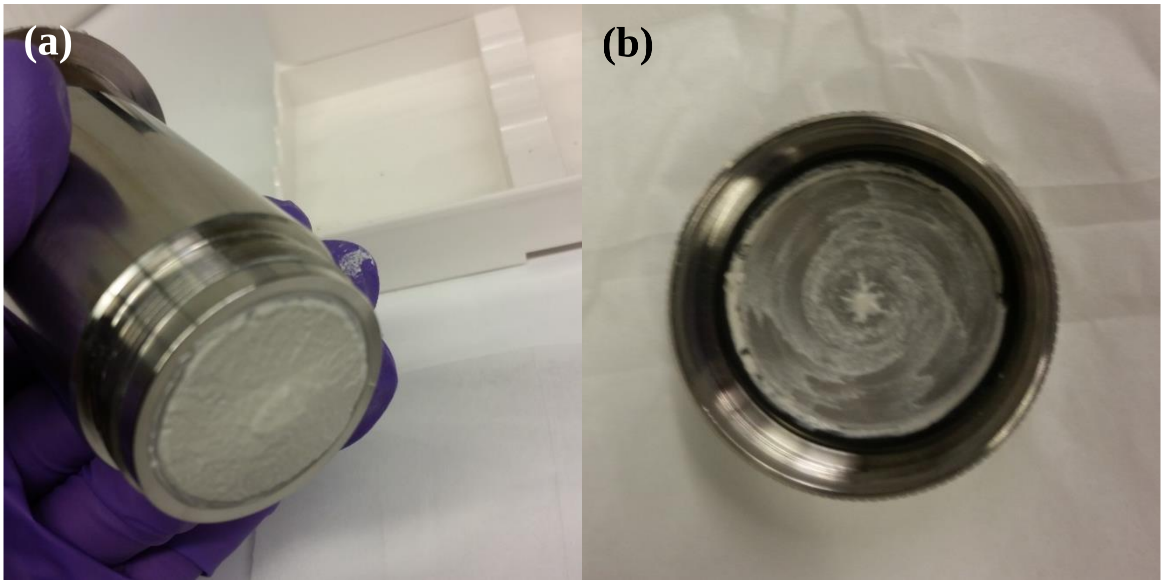

Figure 9: Samples without ADVA settled out of suspension and (a) formed a viscous "plug" that did not stick to the (b) bottom of the cup when twisted off.

4.4 Creep Test

It was found through the vane fixture creep tests in Figure 6 that most of the ADVA adsorbed samples started to flow around 15-20 Pa. Both the 0 and 10 wt% samples did not flow during the 10 Pa test, so the shear stress was increased for samples with more PEO. At 20 Pa, the 50 wt% samples were more resistant to flow, but were successfully run at 25 Pa. The MgO control suspension (no excess PEO or ADVA) was not included in these plots because it was only tested at 10 Pa and had a peak of $81.6 s^{-1}$, which means that it flowed much more readily than its PEO counterparts.

Because the suspensions settled out, samples without ADVA in Figure 7 were able to be tested at much lower rates. This could lead to problems if extrapolated to actual pipe flow, as extra pressure will be necessary to push the sediment through the pipe. To remedy this, a vane fixture that spans more of the cup could be used to test the bottom section as well as the middle and top sections.

4.5 Depletion Flocculation and Stabilization

The trends seen in all three tests point to both depletion flocculation and depletion stabilization occurring in the suspensions. When a suspension undergoes depletion flocculation, shear stress increases while shear rate decreases. This can be seen in the 10-30 wt% samples in the flow curves and creep tests. The particles in the suspension are still coming together because of osmotic pressure and the excess PEO chains are pushed away from these particle agglomerations. However, the suspensions then undergo depletion stabilization in the 40-50 wt% samples. The shear stresses decrease, while the shear rates increase because the excess PEO chains help keep the particles from coming together. This keeps the viscosity lower because the particles stay dispersed throughout the suspension.

5.0 Conclusions and Future Work

By reducing wall slip and adding a preshear to optimize the uniformity of tests, it was found that free PEO chains in a suspension with ADVA-adsorbed particles increase the shear stress until the 30 wt% sample, then decreases according to flow curves. This trend is reversed with the shear rate as shown by the creep tests performed. These trends support the presence of depletion flocculation and depletion stabilization within the sample. In application, the 30 wt% sample would be best for mixing, while the 40 wt% sample would be better suited for pumping through a pipe. There were slight overshoot peaks in the shear start ups indicating that there still is some jamming occurring, however no overshoot peaks occurred in samples containing excess PEO and no ADVA. The biggest improvement from previous testing, however, was the reduction of wall slip through the use of a new vane fixture and sandblasted cup. This allowed for more accurate and higher yield stress values because the samples were not sliding along the walls of the fixture.

It would be beneficial to run more tests with the 30 and 40 wt% PEO samples to further investigate their behavior and any possible transition points. It is possible that lubrication could be affecting the samples as well. Because 40 and 50 wt% PEO samples also proved to have lower viscosities, they are more suited for cement processing. With the addition of ADVA, these two samples – especially the 40 wt% – are more workable and well-suited for the pumping and mixing in the cement industry.

6.0 References

1. Murray, L.; Erk, K.; *J. Appl. Polym. Sci.* **2014,** DOI:10.1002/app.40429

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