

5-2019

Plant-Based Crosslinked Polymers

Jackie Davies

Follow this and additional works at: https://repository.lsu.edu/honors_etd



Part of the [Chemistry Commons](#)

Recommended Citation

Davies, Jackie, "Plant-Based Crosslinked Polymers" (2019). *Honors Theses*. 353.
https://repository.lsu.edu/honors_etd/353

This Thesis is brought to you for free and open access by the Ogden Honors College at LSU Scholarly Repository. It has been accepted for inclusion in Honors Theses by an authorized administrator of LSU Scholarly Repository. For more information, please contact ir@lsu.edu.

Plant-Based Crosslinked Polymers

by

Jackie Davies

Undergraduate honors thesis under the direction of

Dr. John Pojman

Department of Chemistry

Submitted to the LSU Roger Hadfield Ogden Honors College in partial fulfillment of
the Upper Division Honors Program.

May, 2019

Louisiana State University
& Agricultural and Mechanical College
Baton Rouge, Louisiana

Abstract:

This study's purpose is to examine the possibilities of microparticles sourced from natural feedstocks and are degradable in the environment. Here we analyze the properties of a latex made via emulsion polymerization of epoxidized linseed oil and *trans*-aconitic acid. This latex was tested for adhesive strength to examine its applications as a glue. The latex was also tested for particle size to observe the size distribution's effects on adhesive strength, agglomeration, and its properties in different solvents during the progress of the reaction. This was done with the help of Dr. Pojman and graduate student Anthony Mai.

Introduction:

Since the passing of H.R. 1321: the Microbead-Free Waters Act of 2015, polymer companies have been working on improving the biodegradability of microparticles. In fact, growing environmental concerns have pushed "green," sustainable plastics to the forefront of R&D, and finding biodegradable microparticles may help fill the niche of plastics formerly occupied by the materials outlawed by this bill's passing. By utilizing unsaturated natural oils with molecules with several carboxylic acid moieties, one can create highly crosslinked resins and microparticles. Epoxidized linseed oil (Fig. 1) serves the purpose of the oil. The epoxy groups react with carboxylic acids when heated to form an ester linkage (Fig. 3). This ester linkage is readily broken down in the environment by enzymes and bacteria, and water will eventually hydrolyze these bonds over time as well.^[4] The carboxylic-acid-heavy molecule used is *trans*-aconitic acid (Fig. 2). Aconitic acid is found in amounts of around 2-3 kilograms per ton of sugar cane leaf matter^[5]. Such a material would provide a good organic substitute to natural rubber. While being a renewable resource, the use of trees that take years to mature isn't as economically advantageous as faster growing annual crops.

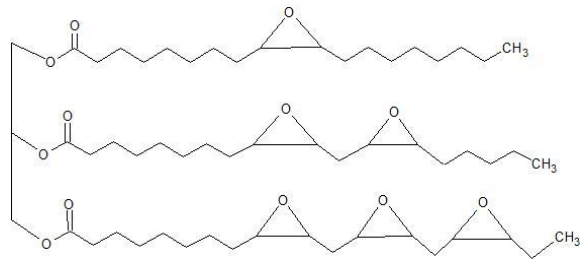


Figure 1: Epoxidized linseed oil. Each of the epoxy groups is a point of initiation of polymerization.

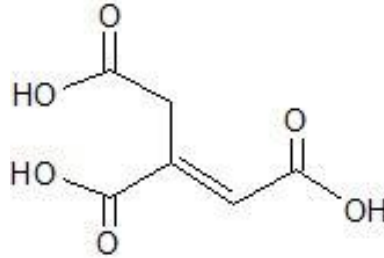


Figure 2: *trans*-Aconitic acid. The epoxy groups react with the hydroxyl groups. The trifunctionality of the carboxylic acid moieties allows for the chains to extend in three directions, making it an effective crosslinker.

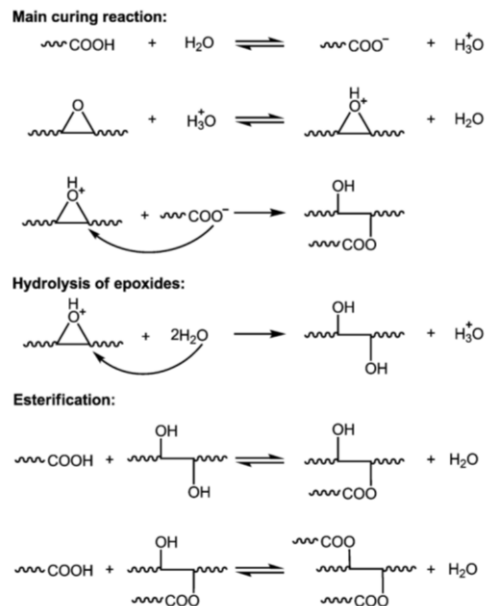


Figure 3: The mechanism of the polymerization reaction. [3]

Aconitic acid is water soluble, and epoxidized linseed oil is immiscible with water. As such, these two monomers are excellent candidates for emulsion polymerization. Emulsion polymerization is a

method of polymerization in which the two phases are reacted in an emulsion such that globules of oil form microparticles of crosslinked polymer to make a latex. The oil phase is kept in suspension by using surfactants. Surfactants, a shortened form of “surface-acting agents,” are molecules that possess both a solvating and non-solvating group. This usually manifests itself as a molecule that has two well-defined groups, a polar, hydrophilic group and non-polar, hydrophobic group for aqueous solutions. This causes each molecule to have two opposing forces acting on it in solution simultaneously and causes these molecules to develop distinct structures. In an aqueous solution, the molecules will migrate to air/water, solid/water, oil/water, or any other interface and orient themselves such that the hydrophilic groups are away from the water. The surfactant molecules may also clump together with the hydrophilic “head” groups exposed to the water and the hydrophobic “tails” packed in the interior. This kind of structure is known as a micelle^[2]. The interior of the micelle makes a favorable environment for the epoxidized linseed oil. By shearing the emulsion of the two phases, we can create increasingly smaller micelles to create a finer, smoother latex. The latex may have applications in coatings and in adhesives. As the latex dries, the chains of interconnected molecules tangle and adhere well to materials like wood.

Initially, experiments were performed to improve the process for preparing the latexes that we would eventually test. The initial aqueous phase was composed of 0.3% by weight (b/w) of METHOCEL, a Dow product composed of cellulose esters, 0.3% b/w of poly(vinyl alcohol) (PVOH), 0.3% b/w of sodium lauryl sulfate (SLS), and 3% b/w of acetic acid, with the remainder being water. METHOCEL, made from cellulose, and PVOH, our only synthetic component but is still biodegradable^[1], act as polymer stabilizers once the micelles form from the surfactant, SLS. METHOCEL has the unique property of gelling above 70°C, which aids stabilization by reducing the dynamic action of SLS molecules in the thickened solution as well as the micelles themselves, thus reducing their ability to break down once in emulsion. The PVOH stabilizes the emulsion by adsorbing to the micelles and helping prevent the individual micelles from colliding and coalescing into larger particles. The organic phase, just composed of epoxidized

linseed oil, would be combined with the completely solubilized aqueous phase at a ratio of 1:3, respectively. The resin was then be sheared at 1500 rpm and heated to a minimum of 73 °C overnight. The latex was then be washed with water such that the polymer microparticles settled and made a thick paste.

The initial latexes we made were quite yellow and would brown when oven-cured at 100 °C. The yellowness can be attributed to the size of the particles being larger than the particles in white industrial latexes. However, I first attributed the browning to unreacted aconitic acid burning during the cuing process. To test this, I titrated a diluted form of the latex to find if there was left-over acid in solution. There was leftover acid, but when I neutralized the latex with sodium hydroxide and again attempted to cure it. This averted some of the browning but not all of it. The solution to this issue came in preparing the resin. Rather than shearing the resin at 1500 rpm overnight, I raised the initial shear rate to 20000 rpm for 30 minutes without heat. Then the resin could be polymerized on a stir plate at 73 °C overnight to produce a fine white latex. This latex retained its color when it was oven-cured. Then, I optimized the ratios of the components of the aqueous phase. Removing the SLS led to the resin coalescing into a ball of polymer. However, removing the METHOCEL suggested that PVOH was sufficient alone as a stabilizer. Our latex was then an aqueous solution composed of 0.5% b/w PVOH, 0.5% SLS, 3% b/w aconitic acid, and the remainder water mixed at the same ratio (1 part organic phase:3 parts aqueous phase). This resin was then sheared at 20000 rpm for 30 minutes, and then polymerized on a stir plate at 73 °C overnight. Modifications of this formula were then tested for particle size and adhesive strength to wood. To measure adhesive strength, we administered a shear compression test to measure the force required to shear two glued-together pieces of wood from each other using an Instron 5582 (Fig. 4). This method of testing was selected for its easy application to testing wood-on-wood adhesion.



Figure 4: An Instron 5582, this machine applied downward force to one of the glued-together blocks while holding the other block in place, thus measuring the force needed to shear the two blocks from each other. Each photograph shows a different side of the machine.

After the initial adhesive strength tests, I tackled another problem. The latex during polymerization would occasionally agglomerate *en masse*. To prevent this, I tried manipulating the surfactant levels, but found that adding antifoam emulsion A1303 prevented the agglomeration. While 1% b/w prevented the polymerization, 0.5% b/w allowed the reaction to progress and prevented agglomeration.

Table 1: Final Latex Contents	
Ingredient	Concentration in Aqueous Phase (% b/w)
Aconitic Acid	3%
Sodium Lauryl Sulfate	0.5%
Poly(vinyl alcohol)	0.5%
Antifoam emulsion A1303 (including poly(dimethyl siloxane))	0.5% (not included in latex for strength testing)
Epoxidized Linseed Oil	Bulk, emulsified with aqueous phase at ratio of 1:3 oil to water

Then I furthered our inquiries into the progress of the reaction. Initially I had trouble finding ways to analyze our particles. The first proposed method of analysis was a washing test. I tried different solvents, like ethanol and hexane, but found that methanol performed best. After centrifuging and decanting the water from the latex, I washed the residual paste with methanol. The idea was that the methanol would draw unreacted oil from the latex into solution. The methanol could then be centrifuged and decanted from the latex and dried to find residual oil. I found that 8.2% of the initial oil remained unreacted. However, this test cannot be called particularly conclusive because methanol was found to have 57% effectiveness of drawing oil from an oil-water emulsion.

Samples were taken of a batch of latex at intervals throughout the reaction. The particle size of each of these samples was then measured in excess water, acetone, and methanol using light scattering from 0.3 to 2000 micrometers (Fig. 5). Acetone was chosen because of its exceptional ability to swell the size of the latex's particles. Methanol was selected for its anti-agglomerative properties.

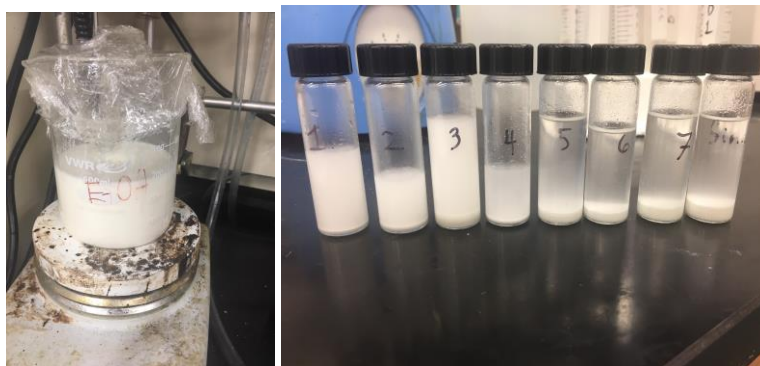


Figure 5: The Latex from which samples 1-7 (see key #1) were taken.

Particle Size Analysis Data:

The tables 2-4 and graphs 1-30 each refer to a series of samples saturated in acetone (A), methanol (M), or water (W). Each sample was taken from a latex in the process of polymerizing. The timing of each sample's withdrawal is as follows (Key 1):

Key 1							
-------	--	--	--	--	--	--	--

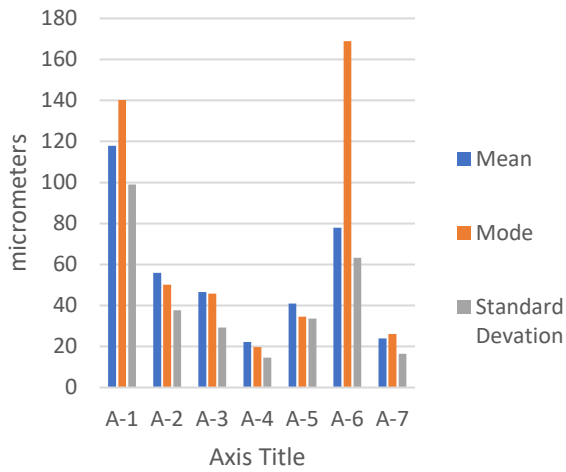
#	1	2	3	4	5	6	7
Time (Hours:Minutes)	0:05	0:37	1:34	2:36	3:37	4:30	5:24

Table 2	Statistical Analysis of Acetone saturated latex						
(units in 10^{-6} m)	A-1	A-2	A-3	A-4	A-5	A-6	A-7
Mean	117.89	55.95	46.53	22.16	41.00	77.99	24.00
Mode	140.25	50.22	45.75	19.76	34.58	168.86	26.14
Standard Deviation	99.06	37.61	29.25	14.65	33.56	63.23	16.51

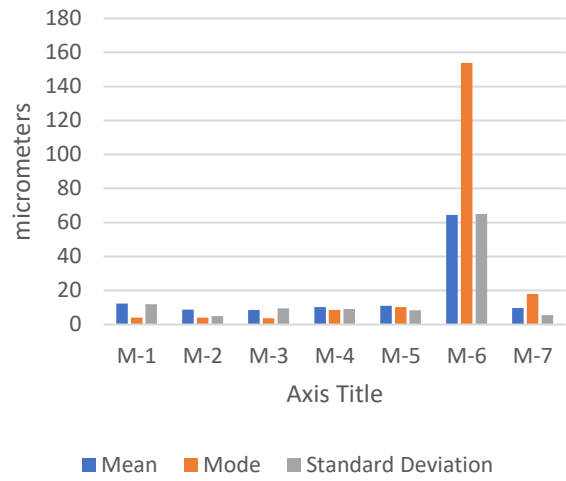
Table 3	Statistical analysis of methanol saturated latex						
(units in 10^{-6} m)	M-1	M-2	M-3	M-4	M-5	M-6	M-7
Mean	12.36	8.83	8.62	10.21	11.1	64.54	9.73
Mode	4.05	4.05	3.69	8.54	10.29	153.82	18
Standard Deviation	11.89	5.03	9.54	9.09	8.38	65.08	5.49

Table 4	Statistical Analysis of water saturated latex						
(units in 10^{-6} m)	W-1	W-2	W-3	W-4	W-5	W-6	W-7
Mean	9.98	11.37	9.24	109.18	134.11	14.71	14.75
Mode	2.31	2.53	9.37	153.82	185.37	11.29	11.04
Standard Deviation	11.94	15.54	9.33	70.94	62.05	12.29	12.48

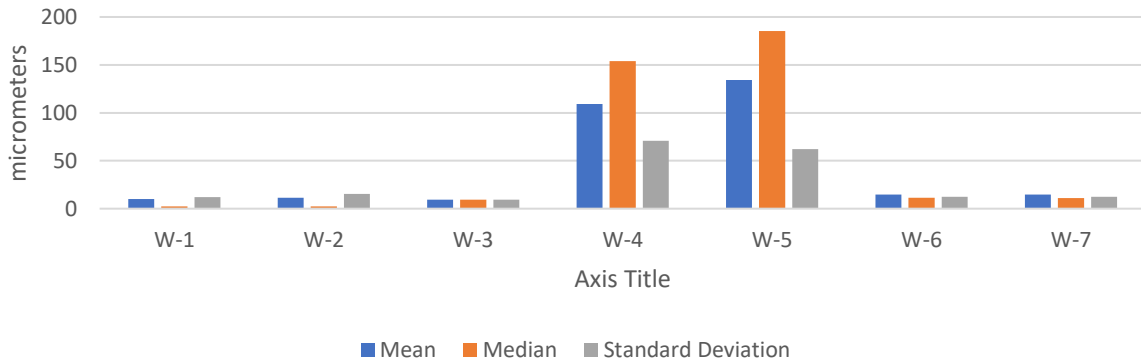
Graph 1: Statistical Analysis of Acetone Saturated Latex



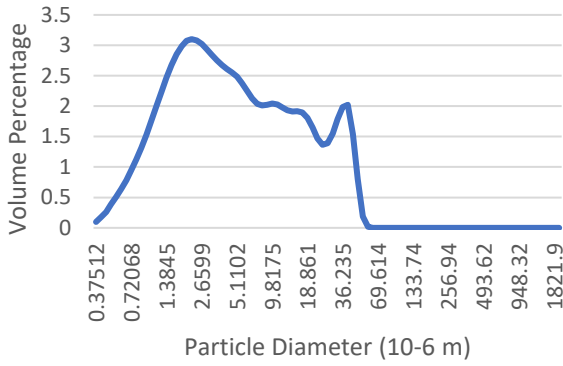
Graph 2: Statistical Analysis of Methanol Saturated Latex



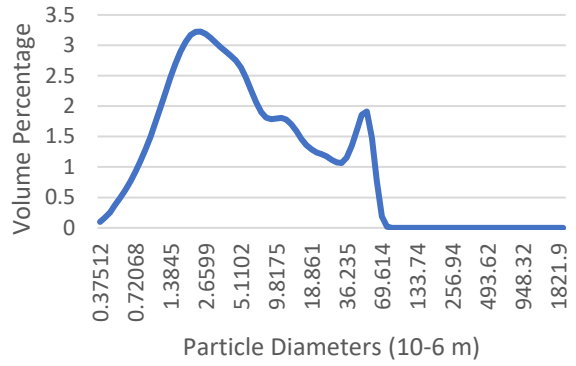
Graph 3: Statistical Analysis of Water Saturated Latex



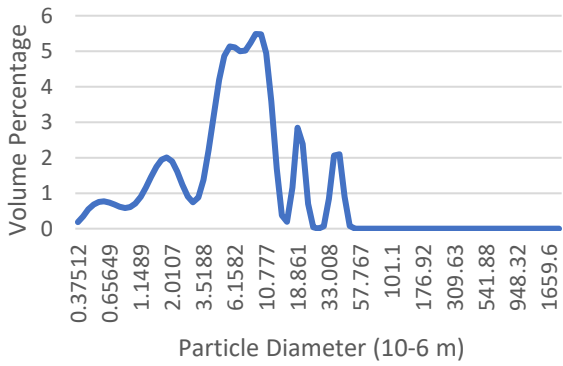
Graph 4: Water-1



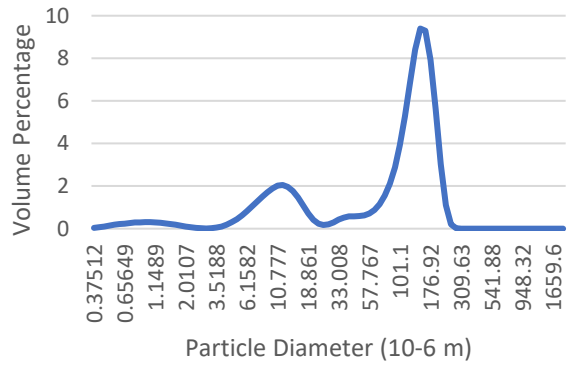
Graph 5: Water-2



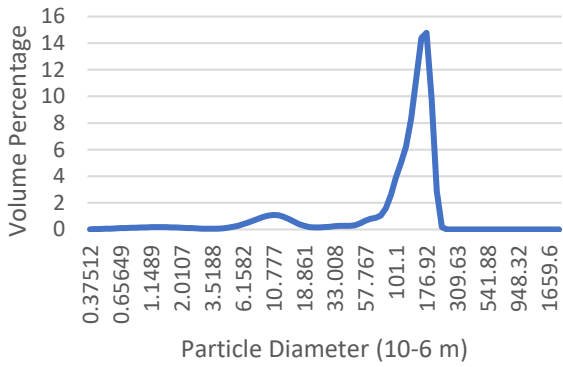
Graph 6: Water-3



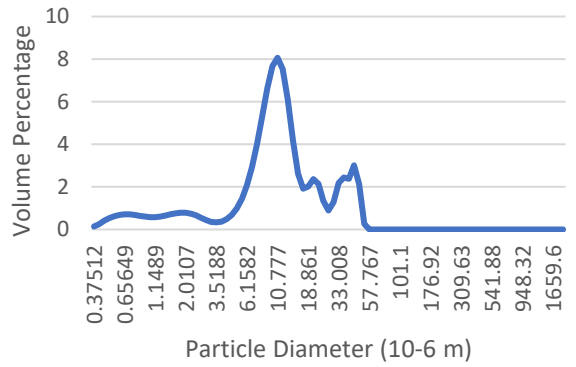
Graph 7: Water-4



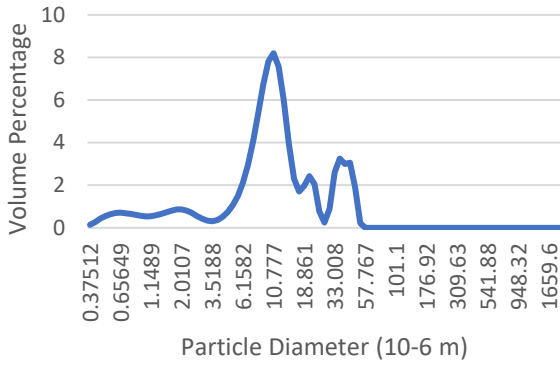
Graph 8: Water-5



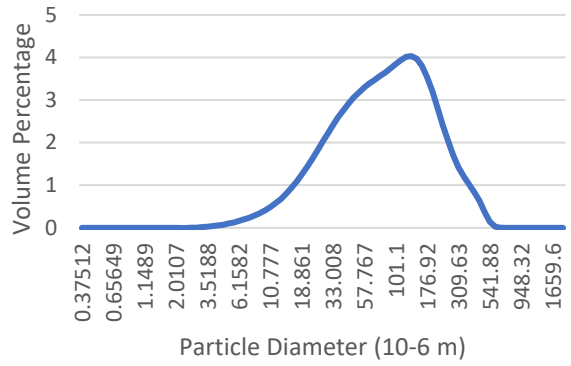
Graph 9: Water-6



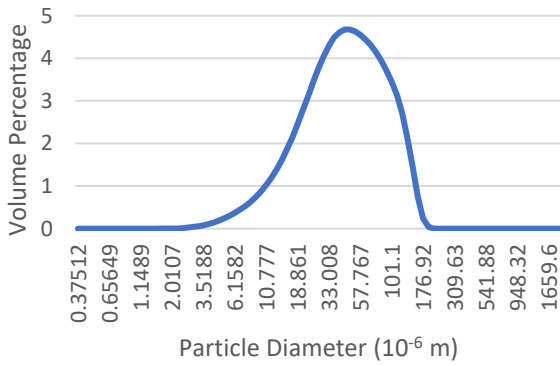
Graph 10: Water-7



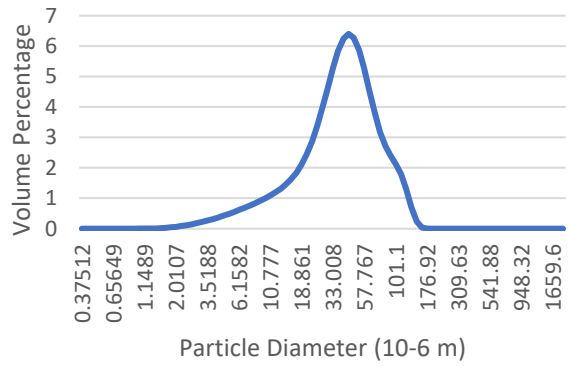
Graph 11: Acetone-1



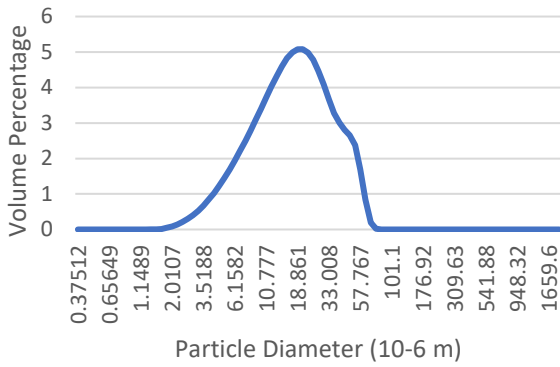
Graph 12: Acetone-2



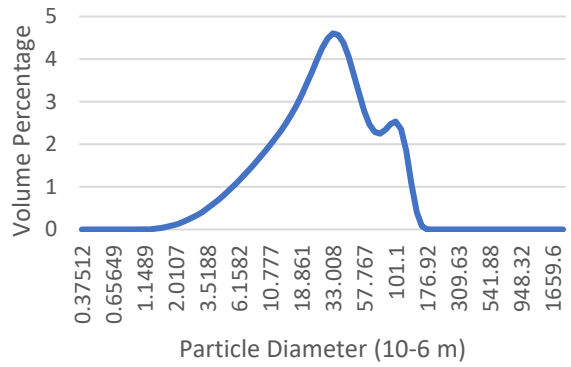
Graph 13: Acetone-3



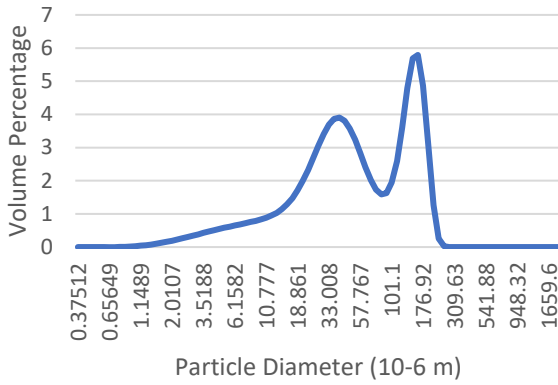
Graph 14: Acetone-4



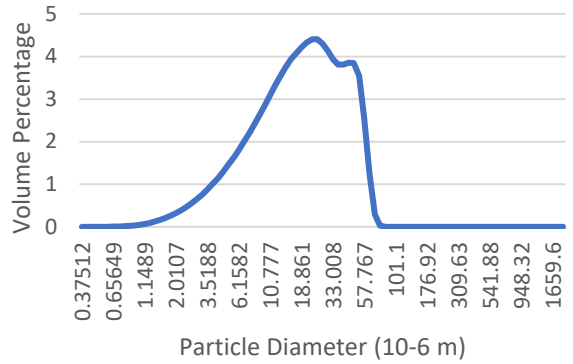
Graph 15: Acetone-5



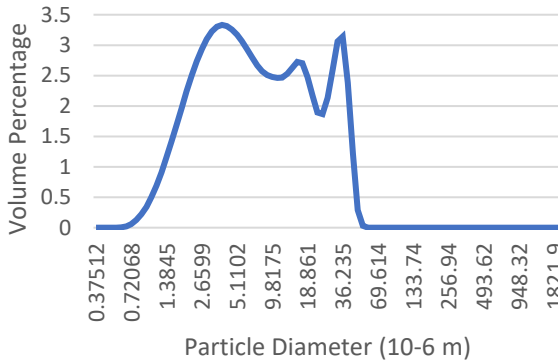
Graph 16: Acetone-6



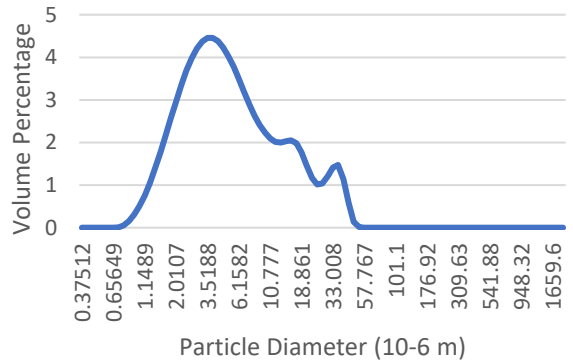
Graph 17: Acetone-7



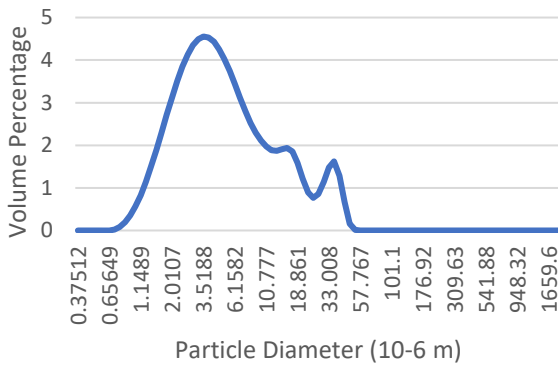
Graph 18: Methanol-1



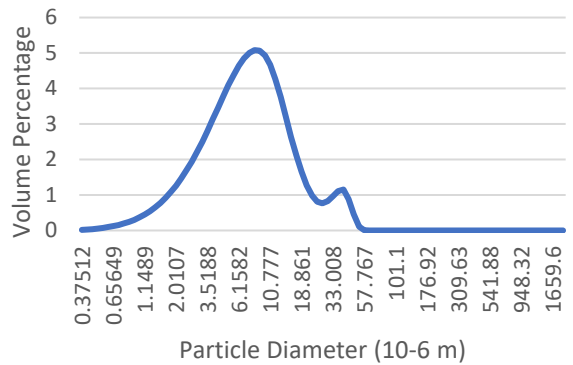
Graph 19: Methanol-2

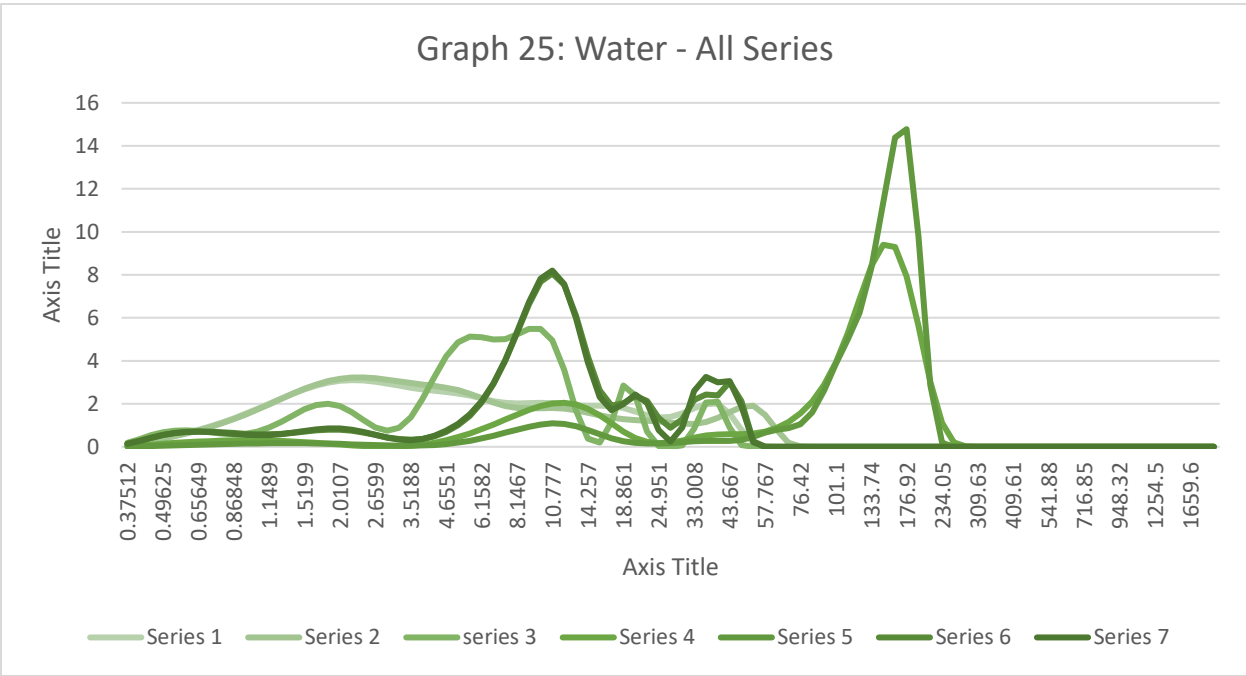
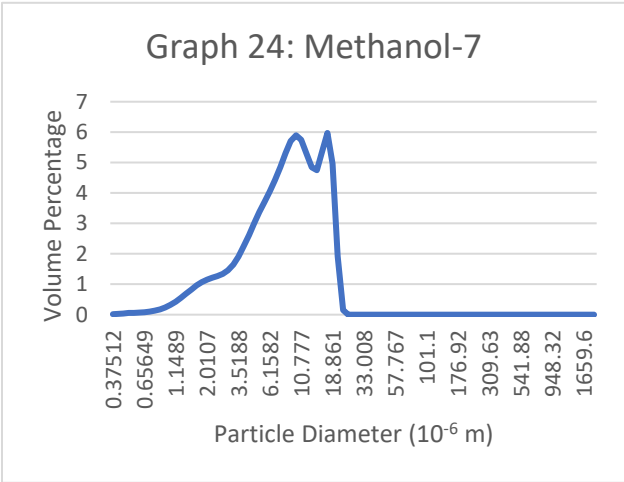
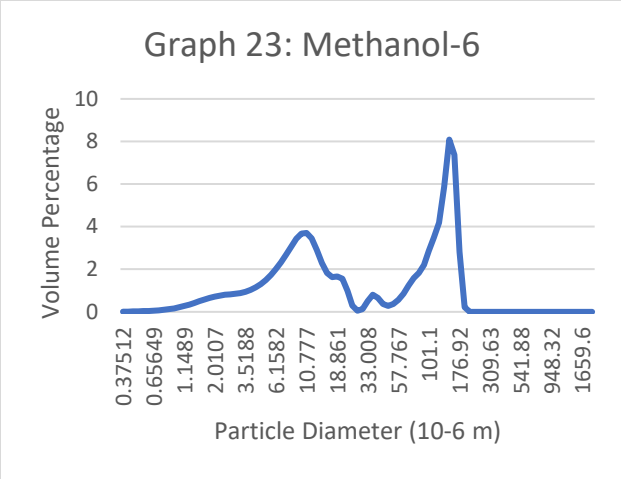
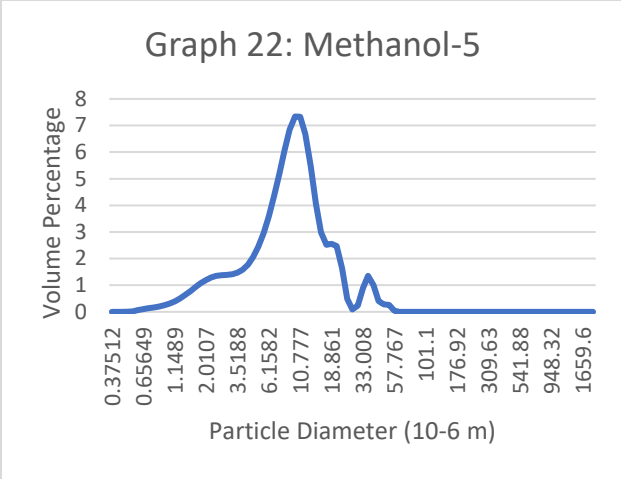


Graph 20: Methanol-3

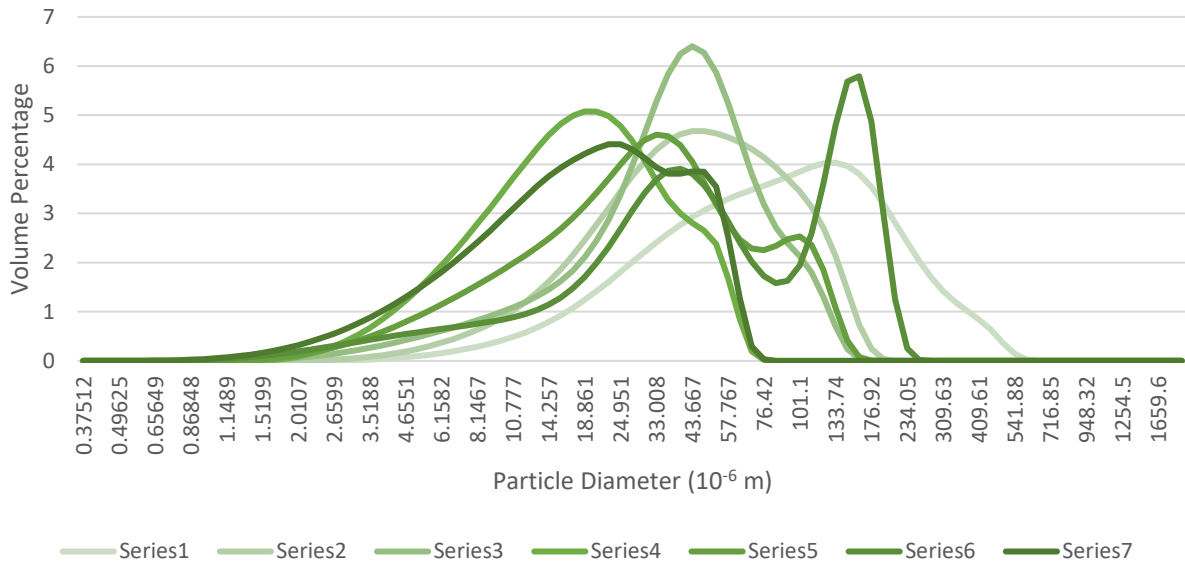


Graph 21: Methanol-4

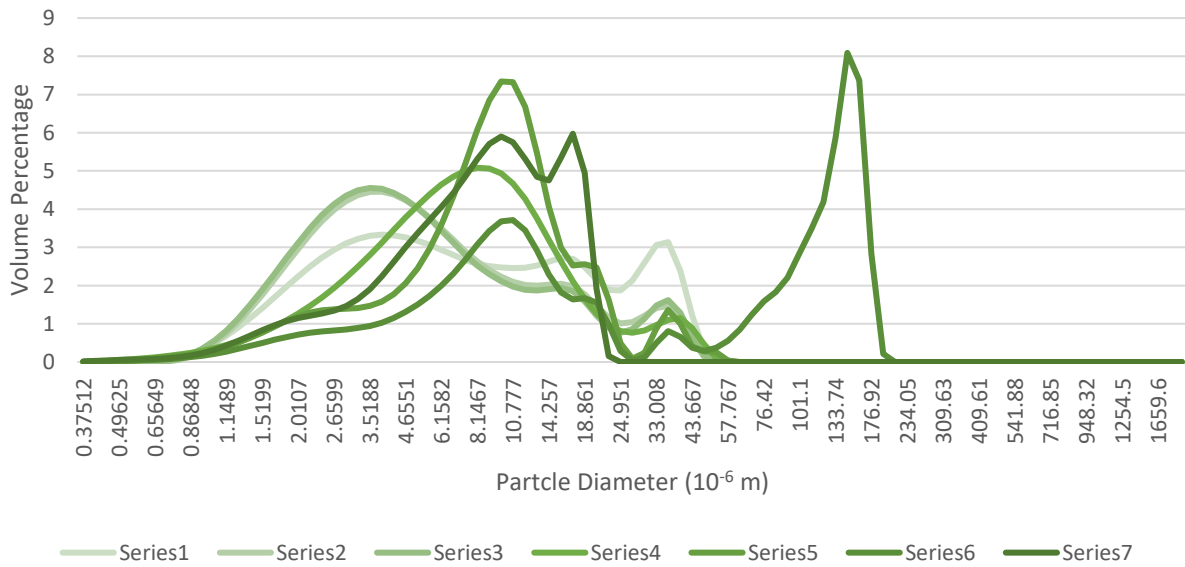




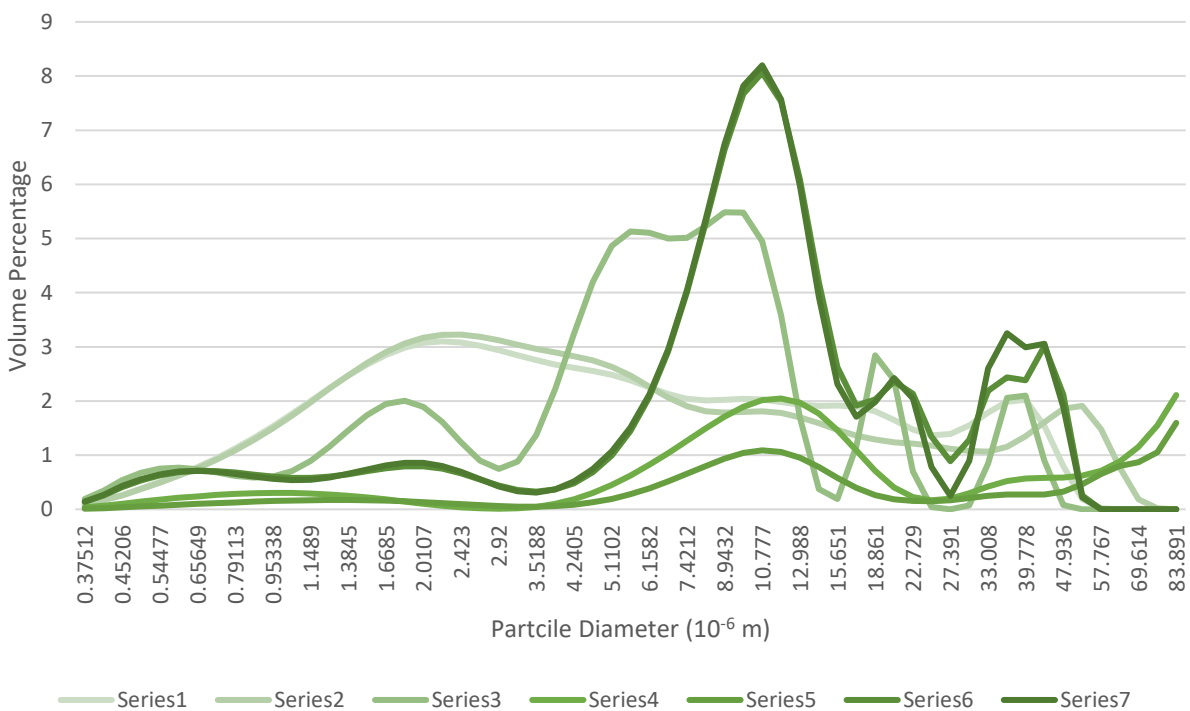
Graph 26: Acetone - All Series



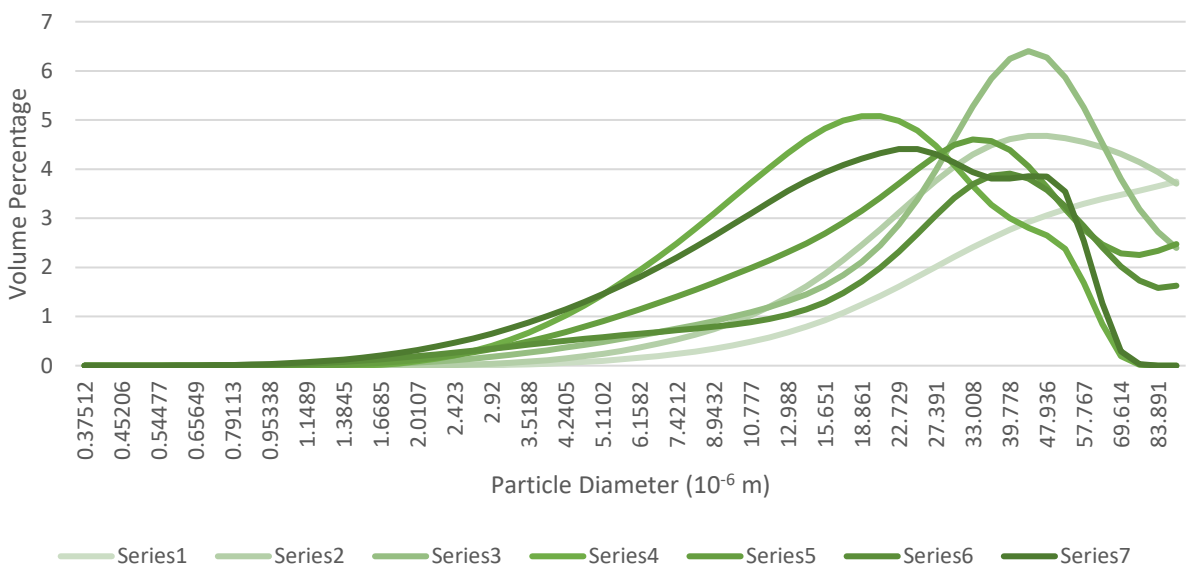
Graph 27: Methanol - All Series

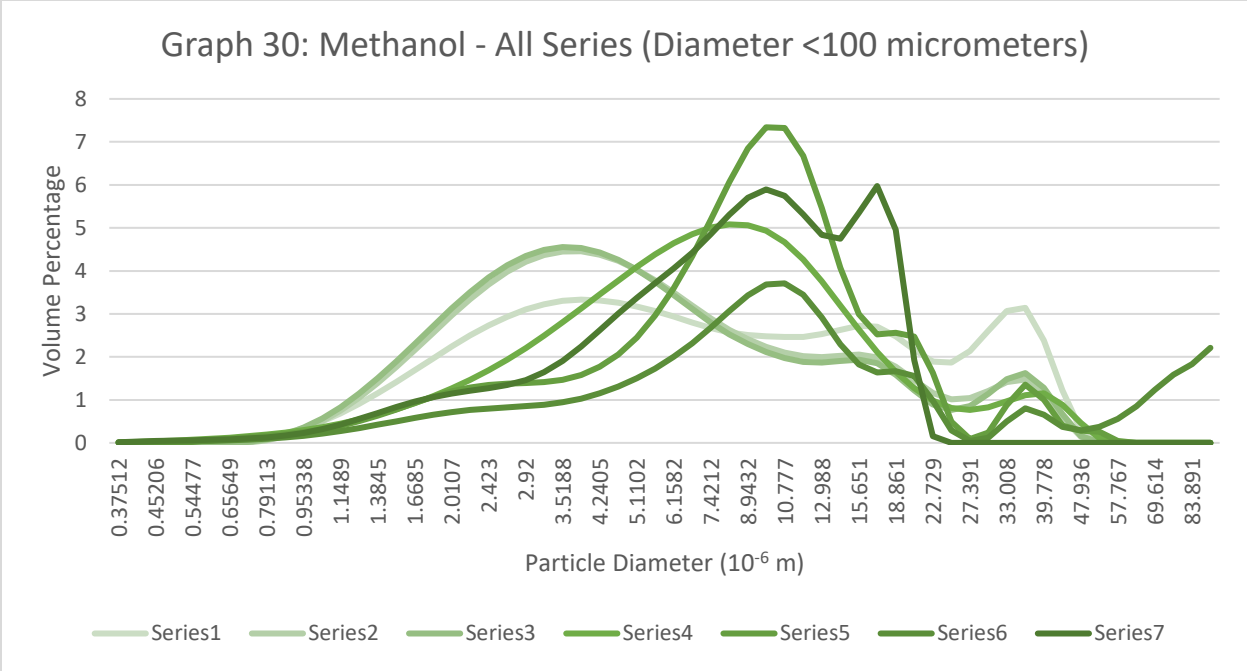


Graph 28: Water- All Series (Diameter <100 micrometers)



Graph 29: Acetone - All Series (Diameter <100 micrometers)





Application Test Data:

Test number	Latex tested	Mean Particle Size (µm)	10 th percentile (µm)	SD of mean (µm)
1	Base latex	148.3	34.75	94.58
2	Double PVOH and SLS	8.716	0.941	10.77
3	Half PVOH and SLS	281.6	5.141	146.9
4	Shear increased to 23000 rpm	190.9	68.59	109.6

	Table 6	Adhesive strength test	
Test Number	Latex tested	Max load (lbf)	bond strength (psi)
1	Original latex recipe, with 5 minutes 11800 rpm shear, and 1200 rpm overnight. Air dried.	538.0	179.3
2	Above latex, oven cured	Fell apart to the touch, not tested	
3	Base, with SLS increased to 0.75% and 0.5% methocel, air dried	496.5. (Wood broke before glue sheared)	165.5
4	Above latex, oven cured	168.8	56.2
5	Above latex, air dried, let sit for 60 days	345.6	115.2
6	Base, oven dried	414.7	138.2
7	Base, sheared for 20000 rpm for 9 minutes and raised to 23000 for one minute, oven dried	322.0	107.3
8	Base, PVOH and SLS doubled, oven dried	254.5	84.8

Discussion:

The above results brought to rise some interesting and unexpected information. Most surprising was that when a latex was cured at room temperature it was superior to the same latex cured in an oven. This was surprising because the wood blocks, composed of southern pine, would quickly and firmly adhere in the oven, whereas the blocks allowed to cure at room temperature took a long time, around a day, to cure and the seal seemed quite loose to the touch. However, the testing revealed that this suspected looseness was elasticity in the bond. This leads me to believe that if the base latex were air dried, it would produce the strongest glue. It appears a wider distribution of particle sizes may produce the best glue, as long as they are not too big, as could be seen by the middling results of test 1 in table 5.

Looking at the particle sizes analyses from the latex throughout its reaction one can make several observations. In water (Graph 25), the mean particle size of the initial monomer suspension (taken to be sample #1) and end-latex were quite near. However mid-reaction (Graphs 7 and 8) large peaks of high diameter can be seen. I attribute this to the loosely-crosslinked particles in the suspension at these points tangling and agglomerating. Methanol (Graph 27) alleviated this problem the best, but M-6 still exhibited this peak. Because of this, graphs 28-30 display the particle size distribution at diameters of less than 100 micrometers. Here the peak location movement should be observed more than the peak's height due to the high-volume percentage that may have been taken up by agglomerates.

The progress of the crosslinking can best be observed in the acetone tests (Graph 29). Acetone solvates the latex better than any solvent tested. The lower the degree of crosslinking, I posit, the greater the ability of a good solvent to permeate the particle, swelling its size. The opposite effect is observed in "bad" solvents. For example, hexane causes the latex to contract into essentially a single

particle. In graphs 11-17, note how the peak particle size contracts as the reaction goes along (also noting the formation of agglomerates separating the spectrum as the peak begins to shoulder in graph 13, is its completely own entity in graph 16, but collapsing into the left peak again in graph 17).

Conclusion:

In future testing air curing will be the go-to for testing adhesive strength. Different methods of polymerization and curing, like using a shaker table and vacuum oven, can also be tested. I'm also curious to see if leftover surfactant may be interfering with the curing, because while increasing the surfactant didn't help much with adhesive strength, see test 8 table 6, this latex did demonstrate some interesting properties. It was our smallest particle size latex by a wide margin and the after the glued blocks were sheared from each other, this latex also was the only one to remain tact enough to re-stick the blocks to each other. Analyzing what it was about this particular latex that gave it these re-adhesive properties will be appoint of interest in the future. Also finding a way to substitute PVOH with a "greener" material would be optimal.

From the particle size analyses, it can be concluded that the particle finishes crosslinking as the polymer particles approach the initial monomer size, after around 5-6 hours. After this point, the latex's adhesive ability should reach its maximum. It also shows the formation of agglomerates part-way through the reaction which needs to be suppressed such that the particles may stay succinct and properly crosslink.

Sources and References:

- 1) Chiellini, Emo et. al. "Biodegradation of Poly (vinyl alcohol) Based Materials." *Progress in Polymer Science* **2003**, 28, 963-1014.
- 2) Farn, Richard J. *Chemistry and Technology of Surfactants*; Blackwell. 2006
- 3) Mai, Anthony Q.Q. "A New Gereation of Polymer Particles." *Dissertation Proposal*. 2018.

- 4) Shogren, Randal L., Zoran Petrovic, Zengshe Liu, and Sevim Z. Erhan. "Biodegradation Behavior of Some Vegetable Oil-based Polymers." *Journal of Polymers and the Environment* **2004**, 12, 3, 173-178.
- 5) Zapata, Nicolas. "Aconitic Acid from Sugarcane: Production and Industrial Application." *Dissertation*. December 2007.