AN ABSTRACT OF THE THESIS OF

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Title: Synthesis, Degradation and Practical Application of a Glycerol/Citric Acid Condensation Polymer

Abstract approved:

Willie E. Rochefort

This study looks at the properties of glycerol/citric acid as they are affected by the length and temperature of the bake used to facilitate the condensation reaction that creates the polymer. In particular, the length of time required for the polymer to break down in the presence of water, both humidity and submersion, was examined. Given the degradable nature of the glycerol/citric acid it was examined for suitability as a replacement for Bitusize (emulsified asphalt) in the making of degradable flower pots. It was found that the Bitusize did not act as a binder in the flower pots, but as a water repellant, thus the glycerol/citric acid polymer was not a suitable replacement material.

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Synthesis, Degradation and Practical Applications of a Glycerol/Citric Acid Condensation Polymer

by
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APPROVED:

Major Professor, representing Material Science

Director of the Material Science Program

Dean of the Graduate School

I understand that my thesis will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my thesis to any reader upon request.

Jan Trenkel-Amoroso, Author

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I'd like to express my appreciation to Dr. Skip Rochefort. Whenever I've found myself at a dead end, he's always helped me figure out how to see it as a surmountable roadblock, in both my research and in career planning. Thanks Skip.

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TABLE OF CONTENTS

Page

Introduction……1

Background……4

Green Polymers……4

Uses for Degradable Polymers……6

Synthesis: Glycerol/Citric Acid Polymers……7

Effect of Bake Temperature and Time on Polymer Properties……7

Moles of H_2O Lost During Polymer Formation……9

Rheology……10

Synthesis with Impure Glycerol……16

Degradation: Glycerol/Citric Acid vs Glycerol/Tartaric Acid……18

Degradation of Short Bake, Low Temperature Glycerol/Citric Acid……18

Degradation of Long Bake, High Temperature Glycerol/Tartaric Acid……20

Degradation of Polymer Cubes……22

Degradation at Elevated Temperature and Humidity……28

Application: Potential for Glycerol/Citric Acid Polymer as a Replacement for Bitusize in Degradable Flower Pots……34

Paper Mache Pots……34

Coupons……35

Coupon Making Procedure……36

Glycerol/Citric Acid Polymer Preparations……37

Dry Burst Testing……38

Absorbance Testing……38

TABLE OF CONTENTS (Continued)

Page

Wet Burst Testing……39

Results: Baseline Coupons……39

Results: Glycerol/Citric Acid Coupons……40

White Water Analysis……42

Viscometry……43

Evaporation Test……43

Amount of Binder……45

Conclusions……51

Bibliography……53

LIST OF FIGURES

Figure Page

1. Glycerol……7
2. Citric Acid……7
3. Tartaric Acid……7
4. Moles of H_2O lost in comparison to the time the polymer was baked for the glycerol/citric acid polymer……9
5. Steady shear data for glycerol, glycerol/citric acid mixed in the absence of heat and glycerol/citric acid made by the 'Hot-Plate' method……11
6. Dynamic oscillation data for glycerol, glycerol/citric acid mixed in the absence of heat and glycerol/citric acid made by the 'Hot-Plate' method……11
7. Steady shear data for glycerol/citric acid baked at 85°C for varying times under vacuum……12
8. Dynamic oscillation data for glycerol/citric acid baked at 85°C for varying times under vacuum……12
9. Steady shear data for glycerol/citric acid baked at 90°C for varying times under vacuum……13
10. Dynamic oscillation data for glycerol/citric acid baked at 90°C for varying times under vacuum……13
11. Steady shear data for glycerol/citric acid baked at 95°C for varying times under vacuum……14
12. Dynamic oscillation data for glycerol/citric acid baked at 95°C for varying times under vacuum……14

LIST OF FIGURES (Continued)

Figure Page

13. Steady shear data for glycerol/citric acid baked at 105°C under vacuum……15

14. Dynamic oscillation data for glycerol/citric acid baked at 105°C under vacuum……15

15. Foams produced from glycerol cut with 15, 50, 75 & 90 wt% DI water……..17

16. Degradation of low bake time/temp glycerol/citric acid polymer in water; relative viscosity vs. time……19

17. Glycerol/tartaric acid polymer slab degradation after two months at room temperature and humidity……21

18. % surface area change of glycerol/citric acid cubes vs. time submerged in water……24

19. % mass change of glycerol/tartaric acid and glycerol/citric acid cubes vs. time submerged in water……25

20. DSC first run……26

21. DSC second run……26

22. DSC third run……27

23. Left G/CA, Right G/TA, Time: 0 days……28

24. Left G/TA, Right G/CA, Time: 2 days……29

25. Left: G/CA, Right G/TA, Time: 7 days……29

26. Left G/CA, Right G/TA, Time: 14 days……30

27. Close up of G/CA at 14 days……31

28. Left G/CA, Right G/TA, Time: 29 days……31

29. Left G/CA, Right G/TA, Time: 36 days……32

30. Left G/CA, Right G/TA, Time: 43 days……32

31. Paper Mache Pots……35

32. Coupon making apparatus……36

LIST OF FIGURES (Continued)

Figure Page

33. Dry burst strength vs. sample mass of coupons……40

34. Wet burst strength vs. sample mass of coupons……..41

35. % absorbance vs. sample mass of coupons……..41

36. Magnification of Bitusize particles……45

37. Wet burst strength vs dry mass for coupons made with a range of binder……46

38. % absorbance vs dry mass for coupons made with a range of binder……..47

39. No Binder, 50x Mag……48

40. Low Bitz, 50x Mag……48

41. Med Bitz, 50x Mag……48

42. High Bitz, 50x Mag……48

43. Low Polymer, 50x Mag……48

44. High Polymer, 50x Mag……48

LIST OF TABLES

Table Page

1. Glycerol/citric acid polymers formed at varying bake times and temperatures.....8
2. Foam masses for polymers made from glycerol diluted with DI water……..…..16
3. Relative viscosity of glycerol/citric acid vs time in solution with water……..……20
4. 15hr/100°C polymer dissolution after 30hrs in DI water…….……23
5. 16hr/170°C polymer dissolution vs. time in DI water……..23
6. Baseline coupon data……..39
7. Glycerol/citric acid coupon data……40
8. Analysis of difference for 'Liquid' glycerol/citric acid coupons……42
9. Analysis of difference for 'Ground' glycerol/citric acid coupons……42
10. Analysis of difference for 'Fine' glycerol/citric acid coupons……42
11. Viscosities of glycerol and 'Hot-Plate' glycerol/citric acid or glycerol/tartaric acid in DI water solution……43
12. White water analysis……44
13. Results for range of binder data……..46
14. Analysis of difference for range of binder……47

Synthesis, Degradation and Practical Applications of a Glycerol/Citric Acid Condensation Polymer

Introduction

Polymers are nearly omnipresent in today's world, but they aren't without drawbacks. Two of these drawbacks are that many polymers are derived from petro-chemicals, a non-renewable resource which has become increasingly costly, and most polymers don't degrade in a reasonable time-frame. Thus there is an increasing interest in creating degradable polymers which are derived from renewable resources. [Freemantle, 2005; Sperling, et al.1984]

Glycerol has several promising characteristics for use as a reactant for a polymer chain. One source of glycerol is that it is a bi-product from the production of biodiesel. The current demand for alternative fuel sources has resulted in a surplus of glycerol as more biodiesel is being produced. Glycerol is a highly functional compound with a molecular structure that lends itself to the creation of polymeric networks [Holser et al. 2008]. It's widely available, non-toxic and inexpensive.

Glycerol can be converted to a polyester through condensation reactions with a variety of multi-functional acids such as adipic, sebacic, suberic, tartaric or citric acids [Brioude et al, 2006; Holser et al 2008; Pramanick et al 1988]. The latter two acids were selected for this investigation because of their cost, non-toxicity, local availability and because tartaric acid, like glycerol, is a bi-product in need of an application; tartaric acid is produced during the making of wine. Glycerol/Citric Acid is already being researched for use in foods. The USDA Agricultural Research Service is doing research on combining citric acid with glycerol to produce non-toxic polymer coatings for use as food preservatives [Barone, 2005].

Experiments in this investigation break down into three general categories: 1) synthesis of the glycerol/citric acid polymer, 2) degradation of the glycerol/citric acid and glycerol/tartaric acid polymers and 3) practical applications for the glycerol/citric acid polymer. As other groups in the same lab were working on synthesis and applications for the glycerol/tartaric acid polymer [Warner-Tuhy, et al 2007; Coolman et al 2008], this investigation only looked at the glycerol/tartaric acid polymer's behavior during degradation experiments.

The physical characteristics of the glycerol/acid condensation polymers were found to be dependant on the processing conditions during synthesis. The condensation reaction between glycerol and acid produces a molecule of water for every bond formed. In these experiments the reaction took place under conditions of elevated temperature and reduced pressure, which result in the water turning into steam and becoming a natural foaming agent in the polymer. The molecule length and possibly the degree of cross-linking are influenced by the bake time and the bake temperature used in the polymer synthesis. Much of the experimentation done around the synthesis of the polymer simply looked at mapping out what sort of material was created at specific bake conditions.

The degradation of the glycerol/citric acid and glycerol/tartaric acid polymers were also examined. The ASTM standards for biodegradable polymers were investigated, but it was determined that there were more basic questions that needed answering first. The ASTM standards look at the rate of degradation of a polymer under very specific conditions, and with microbial assistance. The glycerol/acid polymer comes from a reversible condensation reaction. In the presence of water the bonds will eventually hydrolyze [Pramanick et al, 1988]. During the course of this investigation it was noted that the polymer foams will begin breaking down in a few months

simply due to atmospheric humidity. The question became not “What would happen under controlled degradation conditions?” but “What happens to the polymer if it falls in a ditch, is left out in the rain or sits on a shelf in an office?”

Synthesis and degradation experiments looked at answering the question of “What have we got?” which led to the question “What is it good for?” Applications which are being considered include food containers, soap, fuels, fuel additives, insulation material, drug delivery, agricultural uses and adhesives. This study specifically focused on the possibility of using some form of the glycerol/citric acid polymer as a replacement for Bitusize (emulsified asphalt) in Western Pulp’s degradable flower pots. The pots degrade through the process of the fibrous material, recycled cardboard and newspaper, rotting and leaving behind the small amount of asphalt which is used to prevent the early degradation of the pots by making them more water-resistant. The asphalt does not degrade so the glycerol/citric acid polymer was considered as a degradable alternative.

Background

Green Polymers

There is currently considerable interest in 'green' polymers due to increasing awareness of environmental concerns and decreasing petroleum supplies. However there are wide verities of ways in which a polymer can lay claim to being 'green'.

According to the "Guides for the use of Environmental Marketing Claims" environmental claims may apply to improvements in the processes used to make the product or its packaging. Products may be degradable, biodegradable, photodegradable, compostable, recyclable, made with some percentage of recycled material, or reusable. Improvements in processing may include composition of the packaging or product, how much of a harmful chemical is used in the making of the product or packaging, or simply to a reduction in the amount of packaging material used.

The ASTM standards [D6002-96] define a degradable plastic as one where "the plastic is designed to undergo a significant change in its chemical structure under specific environmental conditions, resulting in a loss of some properties that may be measured by standard methods appropriate to the plastic and the application in a period of time that determines its classification." Biodegradable indicates that degradation results from the action of naturally occurring microorganisms such as bacteria, fungi and algae, while photodegrabable indicates that light is necessary for degradation to occur. For the purpose of marketing claims the FTC clarifies that the entire product or package should decompose into elements found in nature within a reasonably short period of time after customary disposal, i.e. not just that it will

decompose under *some* set of conditions, but that it will decompose under the conditions found in the environment where it is customarily disposed.

Compostability is defined as "capable of undergoing biological decomposition in a compost site as part of an available program, such that the material is not visually distinguishable and breaks down into carbon dioxide, water, inorganic compounds and biomass at a rate consistent with known compostable materials." [ASTM D6002-96] The "Standard Specification for Compostable Plastics" [ASTM D6400-04] further specifies that a compostable plastic must meet the following requirements: no more than 10% of the original dry weight should remain on a 2.0mm sieve after a twelve week period in a controlled composting test. The plastic must also demonstrate a satisfactory ratio of conversion to carbon dioxide. The specific ratio depends on the type of polymer. For a homopolymer, such as the one being studied here, it's 60% of the organic carbon converted to CO_2 in less than 180 days. For marketing considerations before something can be labeled compostable, it must be clarified whether that means compostable in a backyard compost heap or if municipal or institutional composting facilities are needed, and if so, is one available to the likely consumers.

The glycerol/acid polymer is 'green' in that it's made from renewable resources rather than the petrochemicals which it may replace. Also it breaks down into its non-toxic constituent monomers through exposure to water.

Uses for Degradable Polymers

Agricultural Uses - Mulching films, nursery containers [Barone et al, 2007], drip irrigation tape and other polymers which are intended to be used for a single growing season and which would be inconvenient to retrieve at the end of their use are all possible applications for degradable polymers. Degradable polymers are also useful for seed coating and in timed release of herbicides, pesticides and nutrients.

Medical Uses - Biodegradable polymers can be used to trap drugs within the polymer matrix for timed release as the polymer degrades. Manipulation of the rate of degradation through controlling cross-link density and solubility can be used to control the rate of drug delivery. [Pramanick et al, 1988; Pramanick et al, 2003; Stumbe et al, 2003]. Some samples of the glycerol/citric acid and glycerol/tartaric acid polymers were provided to Bend Research for testing, but the solubility was determined to be too low for their purposes.

Single Use Items - Disposable packaging, plastic dining-ware and packing peanuts are examples of product that would be improved if they degraded in a reasonable period of time rather than remaining in a dump indefinitely [Nanda et al. 2005].

Synthesis: Glycerol/Citric Acid Polymers

The polymers used in this experiment were created through a condensation reaction between glycerol and either citric acid or tartaric acid (fig 1-3). Removal of the H_2O molecule produced was facilitated by making the polymer in a vacuum oven.

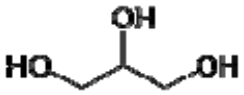

Figure 1) Glycerol

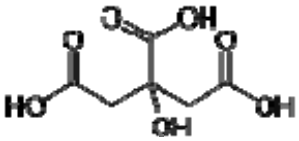

Figure 2) Citric Acid

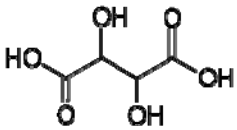

Figure 3) Tartaric Acid

The properties of the polymer created during these experiments were strongly influenced by the length and temperature of the bake used to catalyze the reaction. Longer, higher temperature bakes resulted in harder, longer lasting polymers, presumably because the polymer chains were longer or the chains had become cross-linked.

Most of the data collected with regards to the synthesis of the polymers was done solely on the glycerol/citric acid polymer as earlier work on the polymer had focused primarily on the glycerol/tartaric acid polymer [Warner-Tuhy et al, 2007; Coolman et al, 2008]. With both glycerol/citric acid and glycerol/tartaric acid a 1:1 molar ratio was used. A few glycerol/citric acid polymers were made using a 1.33:1 ratio of citric acid to glycerol due to an error in calculating the mole ratio. This ratio resulted in a grainy layer of unused reactants left under the polymer.

<u>Effect of Bake Temperature and Time on Polymer Properties</u>

A range of polymers were made at different bake times and temperatures to determine, roughly, what sort of polymer could be expected. Observations about the polymer's physical

appearance were recorded when the polymer was hot and after it cooled. Samples of the polymer were submerged in water then heated to 37°C while being subjected to gentle agitation. The length of time it took for the polymer to dissolve was recorded (tab 1).

Table 1) Glycerol/citric acid polymers formed at varying bake times and temperatures.

Bake Time / Bake Temp	3 hours	5 hours	8 hours	12 hours	24 hours
85°C	Hot-Watery Cold-Molasses Dissolve-2.5 hr		Hot - Watery Cold - Taffy Dissolve- 2.5 hr	Hot - Watery Cold - Taffy Dissolve- 2.5 hr	Hot - Watery Cold - Rigid Solid Dissolve- 2.5 hr
90°C	Hot – Watery Cold – Molasses Dissolve – 2.5 hr	Hot – Watery Cold – Malleable Dissolve –2.5hr	Hot – Watery Cold – Flex solid Dissolve –2.5hr		
100°C	Hot – Water y Cold – Molasses Dissolve – 2hr	Hot – Water y Cold –Tacky solid Dissolve – 2hr	Hot – Molasses Cold – Flex solid Dissolve– 29 hr		
105°C	Hot - Watery Cold - Taffy Dissolve-2hr	Hot – Watery Cold – Silly Putty Dissolve – 2hr	Hot – Molasses Cold – Taffy Dissolve – 2hr	Hot – Flex solid Cold – Rigid solid Dissolve - 2 days	Hot – Rigid Solid Cold – Rigid Solid Dissolve - 14days
110°C		Hot – Gum Cold – hrdCandy Dissolve–2days	Hot – Rigid solid Cold – Rigid solid Dissolve-12days	Hot – Rigid solid Cold – Rigid solid Dissolve ~ 34days	Hot – Rigid solid Cold – Rigid solid Dissolve ~50days

It was observed that, with regards to dissolution times, there was a fairly abrupt step where the polymer went from dissolving in a few hours to taking multiple days to dissolve. It was hypothesized that the step marked the point where the polymer began to form cross-links. It

has proved difficult to test this since available measurement techniques require that the polymer be dissolved in solution; Glycerol/Citric Acid breaks down in water rather than dissolves; or they employ heat which would cause the structure of the polymer to be changed. Continued increases in bake temperature and time resulted in even longer dissolution times. However, due to time constraints, experiments did not extend far enough to test the upper limit where either the constituents burns or all possible bonds are made. The polymers weren't cooked long enough to get to a point where more water couldn't be lost.

Moles of H_2O Lost During Polymer Formation

After the baking process the polymer displayed a weight loss when compared with the combined mass the reactants. Since experimentation determined that glycerol did not evaporate under the vacuum conditions used; 17 in_{Hg}; it was assumed that the weight loss was a result of the water formed during the condensation reaction.

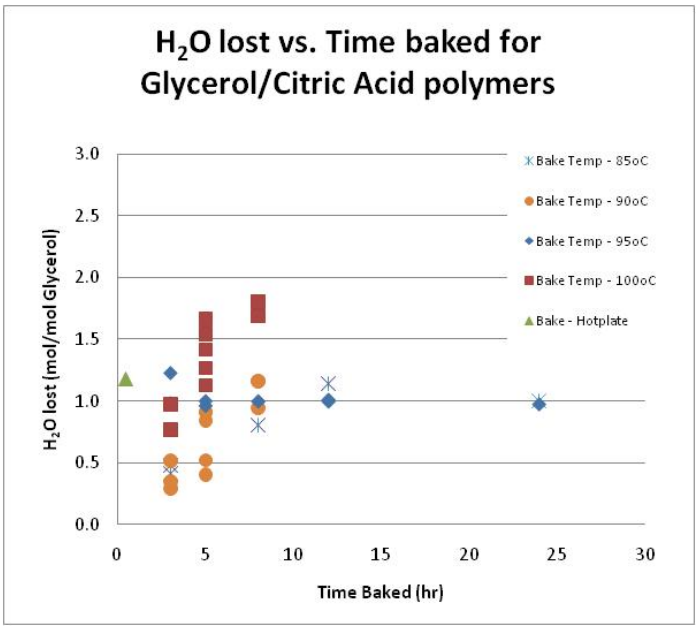

Figure 4) Moles of H_2O lost per Mol of Glycerol in comparison to the time the polymer was baked for the glycerol/citric acid polymer.

While the amount of water lost for a particular bake time did not have good repeatability (fig. 4) there was a general trend observed that longer bakes at the same temperature resulted in more water loss and that, generally, hotter bakes lost more water. The condensation reaction is:

$$C_3H_5(OH)_3 + C_6H_4O_3(OH)_4 \rightleftharpoons C_9H_9O_4(OH)_5 + H_2O$$

Thus more water lost, the more bonds formed. So longer, hotter bakes result in a more highly bonded polymer.

Rheology

To further test this hypothesis rheological measurements were run on the polymers. Experiments were also run on pure glycerol, glycerol/citric acid mixed in the absence of heat and 'Hot-Plate' glycerol/citric acid, glycerol/citric acid polymer which was made by heating on a hot-plate for half an hour while stirring to facilitate the escape of steam.

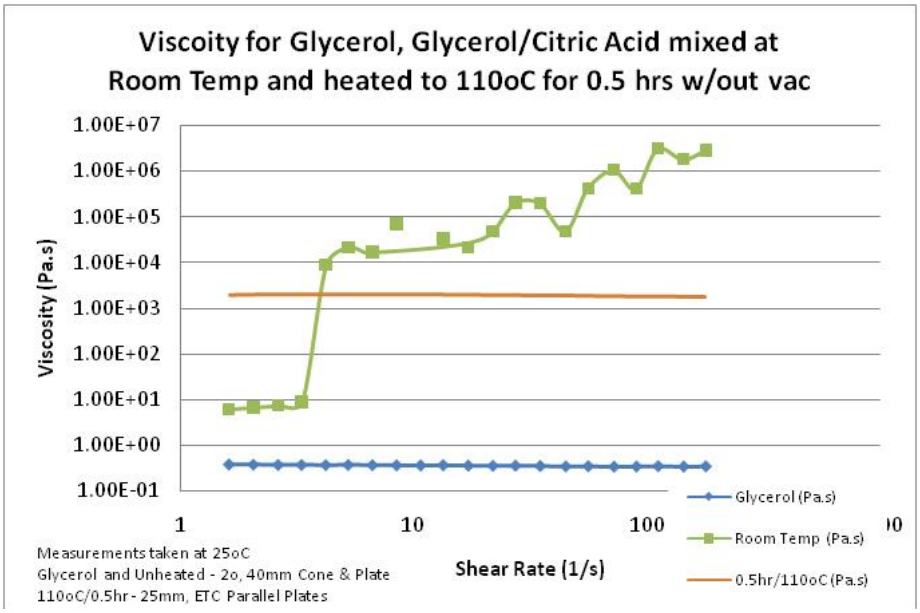

Figure 5) Steady shear data for glycerol, glycerol/citric acid mixed in the absence of heat and glycerol/citric acid made by the 'Hot-Plate' method

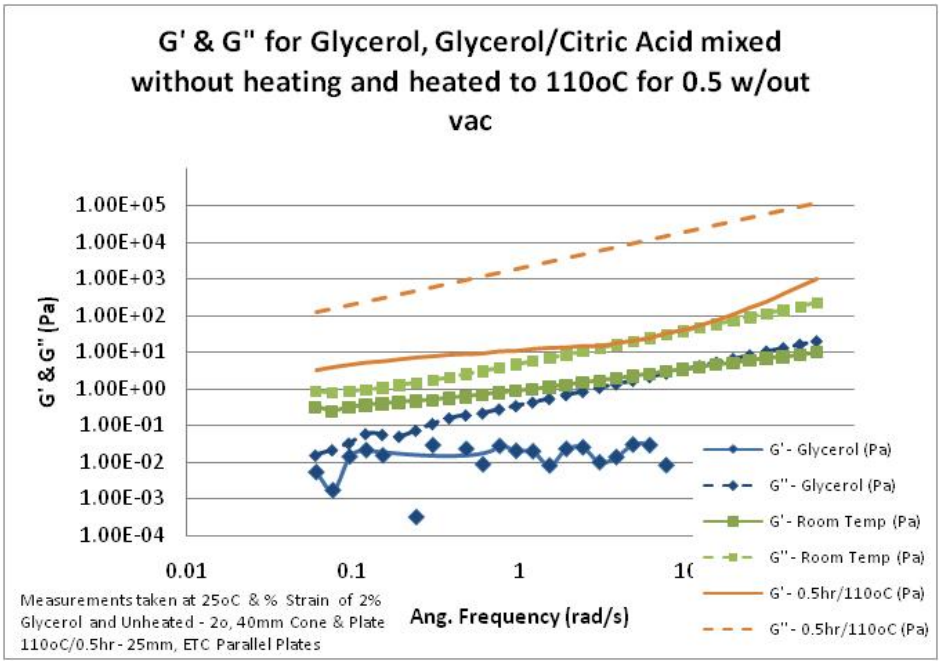

Figure 6) Dynamic oscillation data for glycerol, glycerol/citric acid mixed in the absence of heat and glycerol/citric acid made by the 'Hot-Plate' method

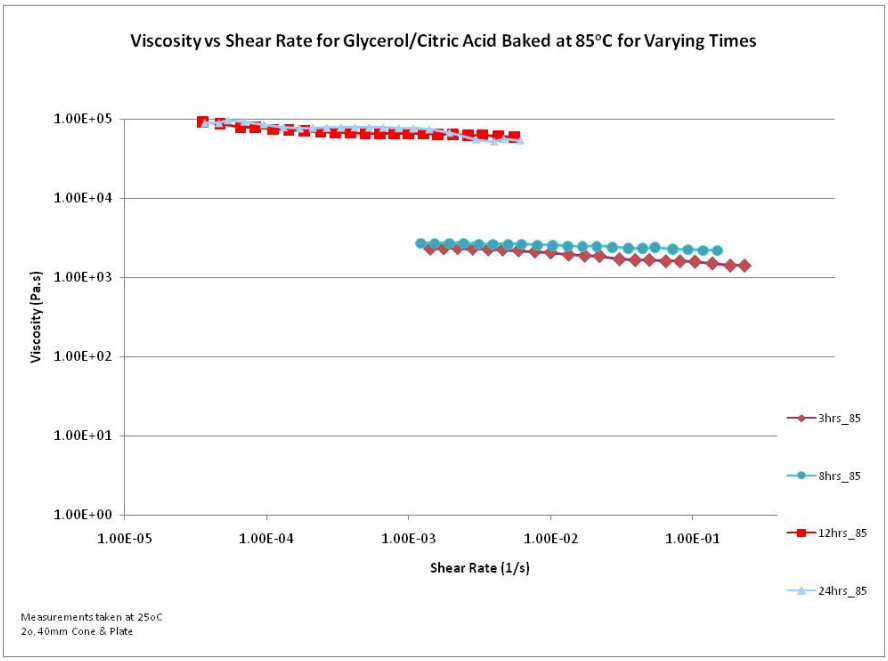

Figure 7) Steady shear data for glycerol/citric acid baked at 85°C for varying times under vacuum

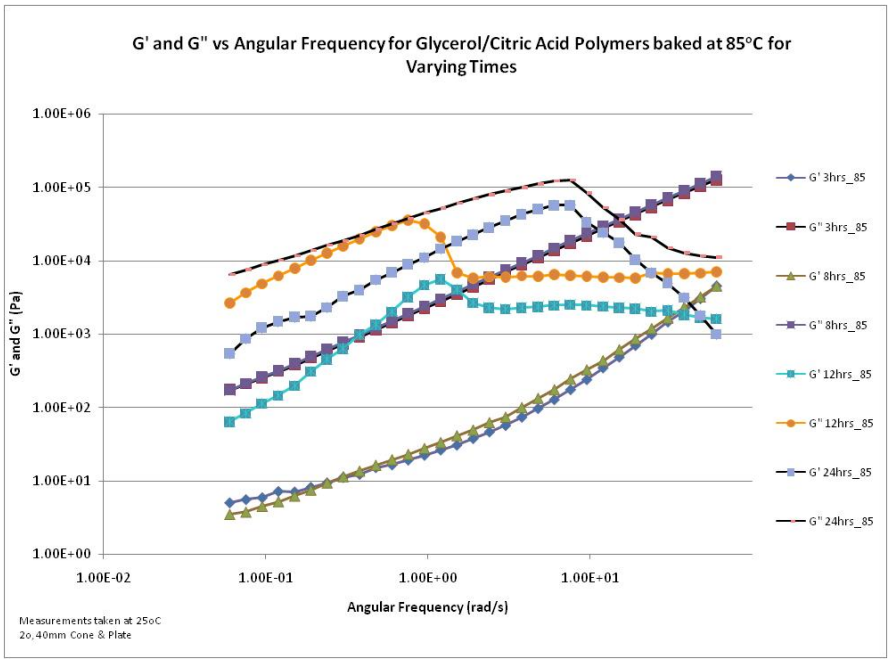

Figure 8) Dynamic oscillation data for glycerol/citric acid baked at 85°C for varying times under vacuum

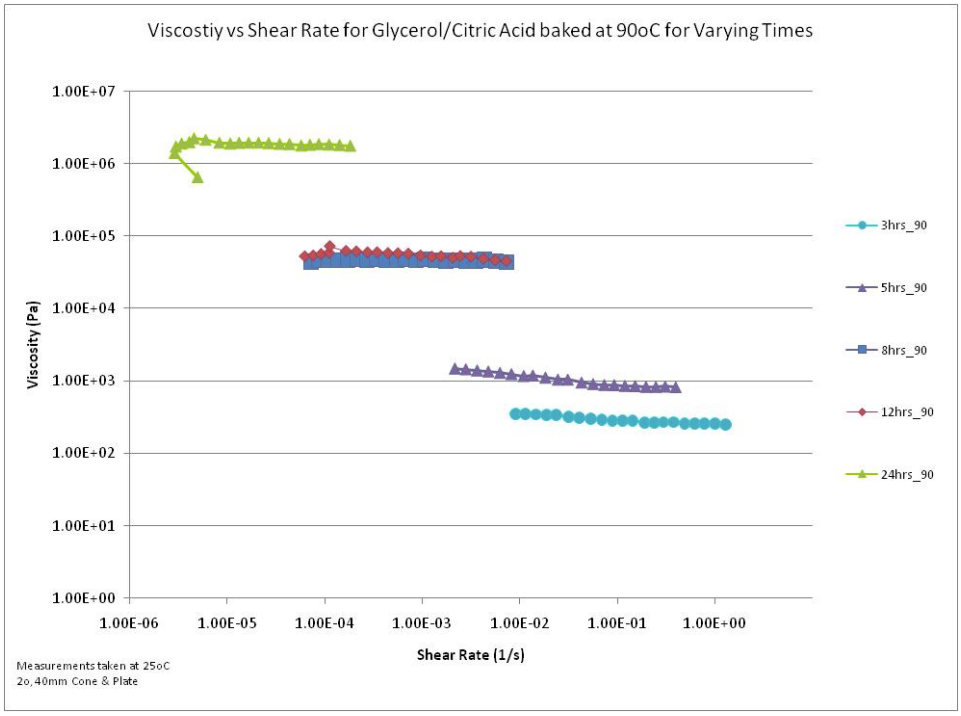

Figure 9) Steady shear data for glycerol/citric acid polymer baked at 90°C for varying times under vacuum

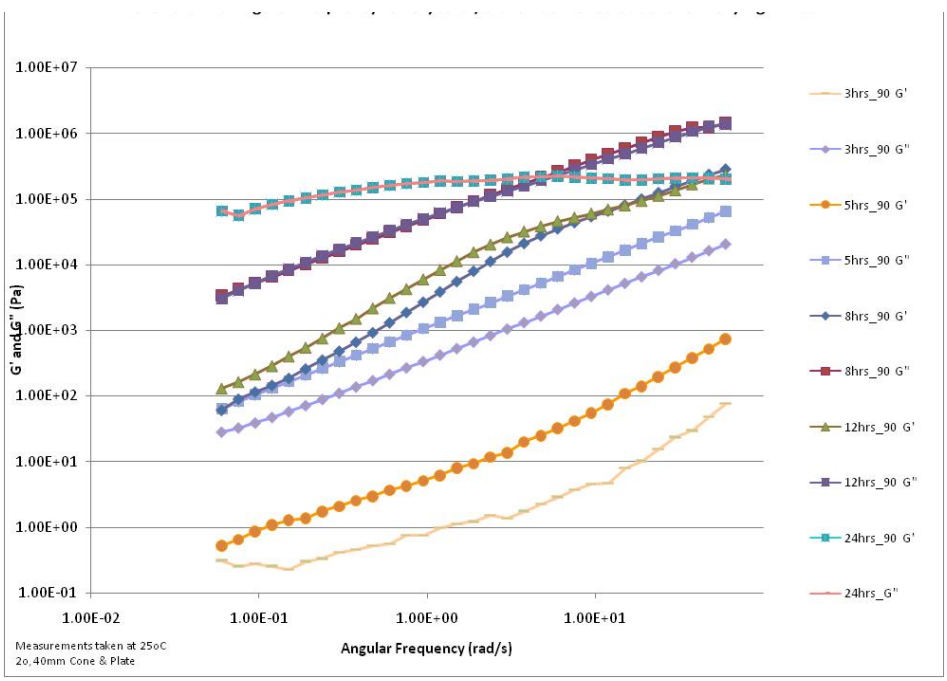

Figure 10) Dynamic oscillation data for glycerol/citric acid polymer baked at 90°C for varying times under vacuum

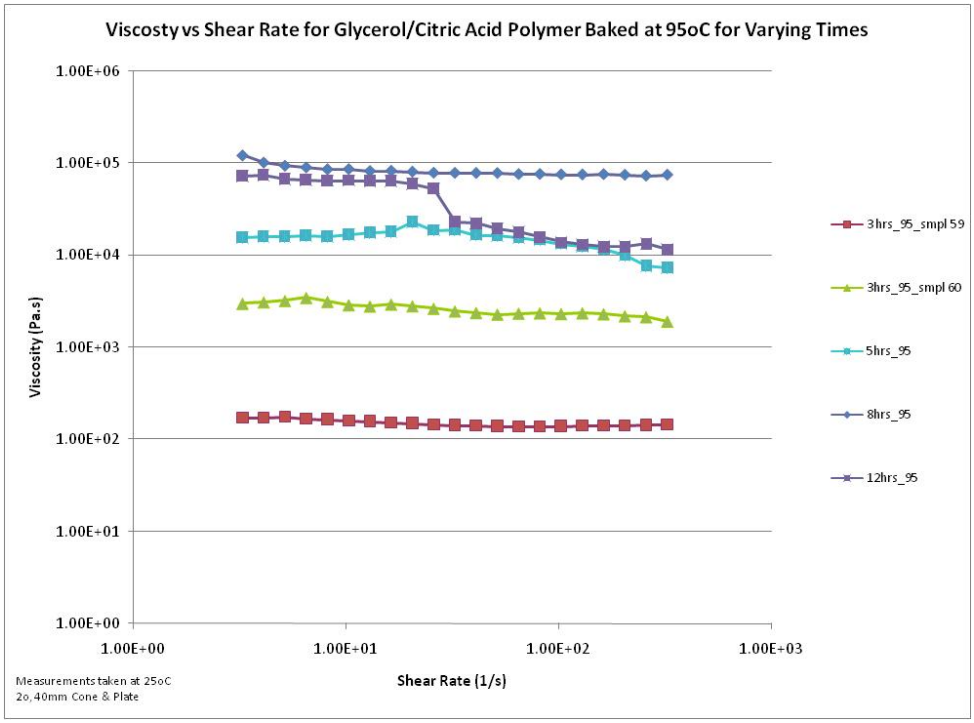

Figure 11) Steady shear data for glycerol/citric acid polymer baked at 95oC for varying times under vacuum

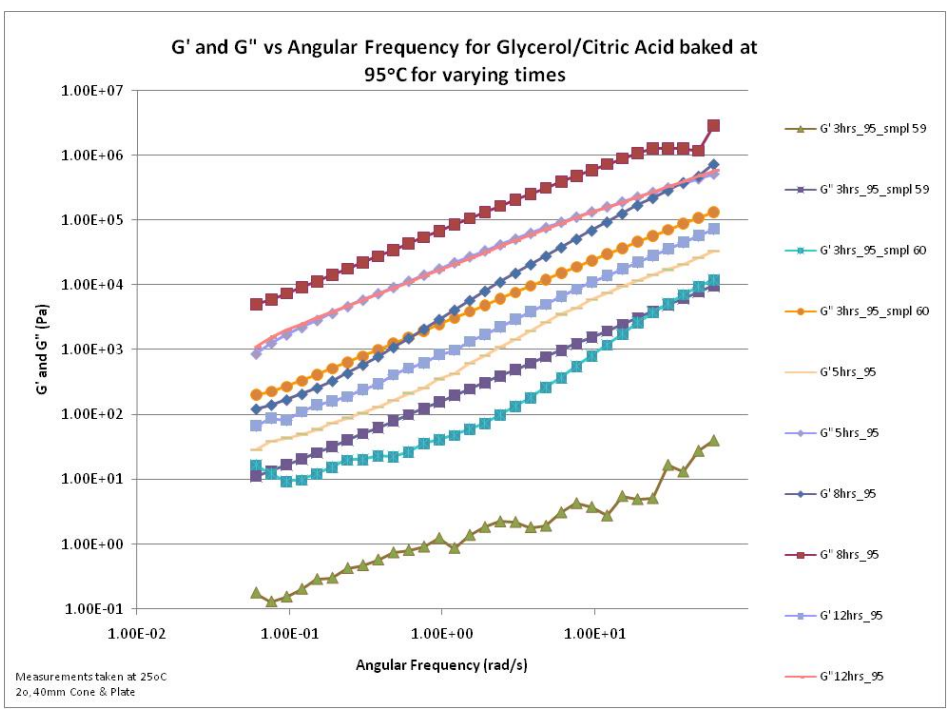

Figure 12) Dynamic oscillation data for glycerol/citric acid polymer baked at 95°C for varying times under vacuum

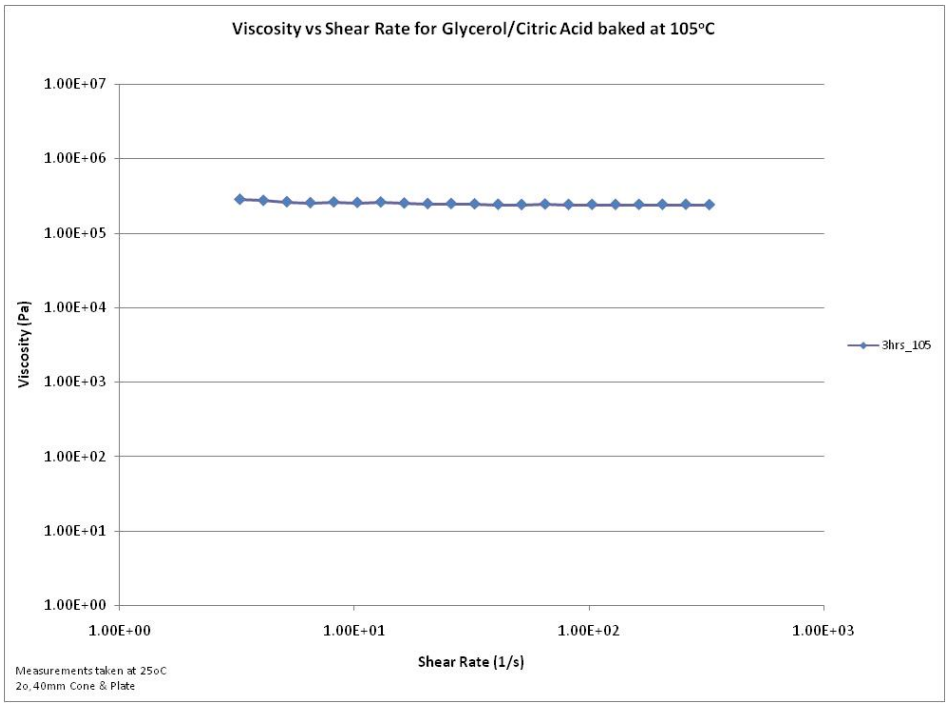

Figure 13) Steady shear data for glycerol/citric acid polymer baked at 105°C under vacuum

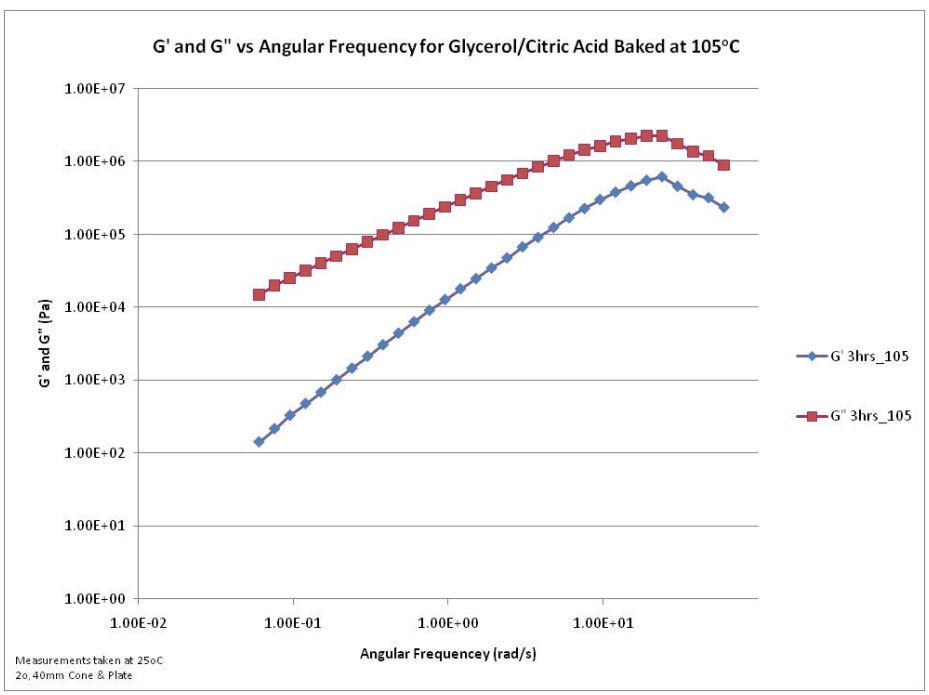

Figure 14) Dynamic oscillation data for glycerol/citric acid polymer baked at 105°C under vacuum

As anticipated the polymers trended toward greater viscosity with longer bake times, implying that the molecular chain length was increasing.

Synthesis with Impure Glycerol

Before purification the waste-glycerol that we have access to is diluted with fifteen percent water. Since the ultimate intent of the experiments was to make use of this waste-glycerol the following experiment was done to see what effect, if any, excess water would have on the formation of the polymer.

The glycerol was cut with 15, 50, 75 and 90 wt% DI water before being mixed with citric acid and baked. The mixture was baked at 175°C for 80 minutes at 17 in$_{Hg}$. After baking the resultant foams were weighed.

Table 2) Foam masses for polymers made from glycerol diluted with DI water

Sample	Glycerol (g)	Citirc Acid (g)	DI (g)	Mass Initial	Post-Bake (g)	H_2O Loss (g)	Reaction H_2O (g)
C70 a	6.26	13.05	3.41	22.71	12.24	10.47	7.06
C71 a	6.26	13.05	19.3	38.6	13.58	25.02	5.72
C72 a	6.26	13.04	57.9	77.19	12.09	65.10	7.20
C73 a	6.24	13.04	173.7	192.98	11.21	181.77	8.07

The masses of the foams were weighed, the water formed in the reaction was assumed to be the excess mass lost once the water used to dilute the glycerol was accounted for. While there was some variation seen in the mass of the foams and the mass of the water lost from the reactants the variations weren't related to the amount of water added to the system (tab 2). The foams synthesized with the varying dilutions of glycerol were visually indistinguishable from one another (fig 15).

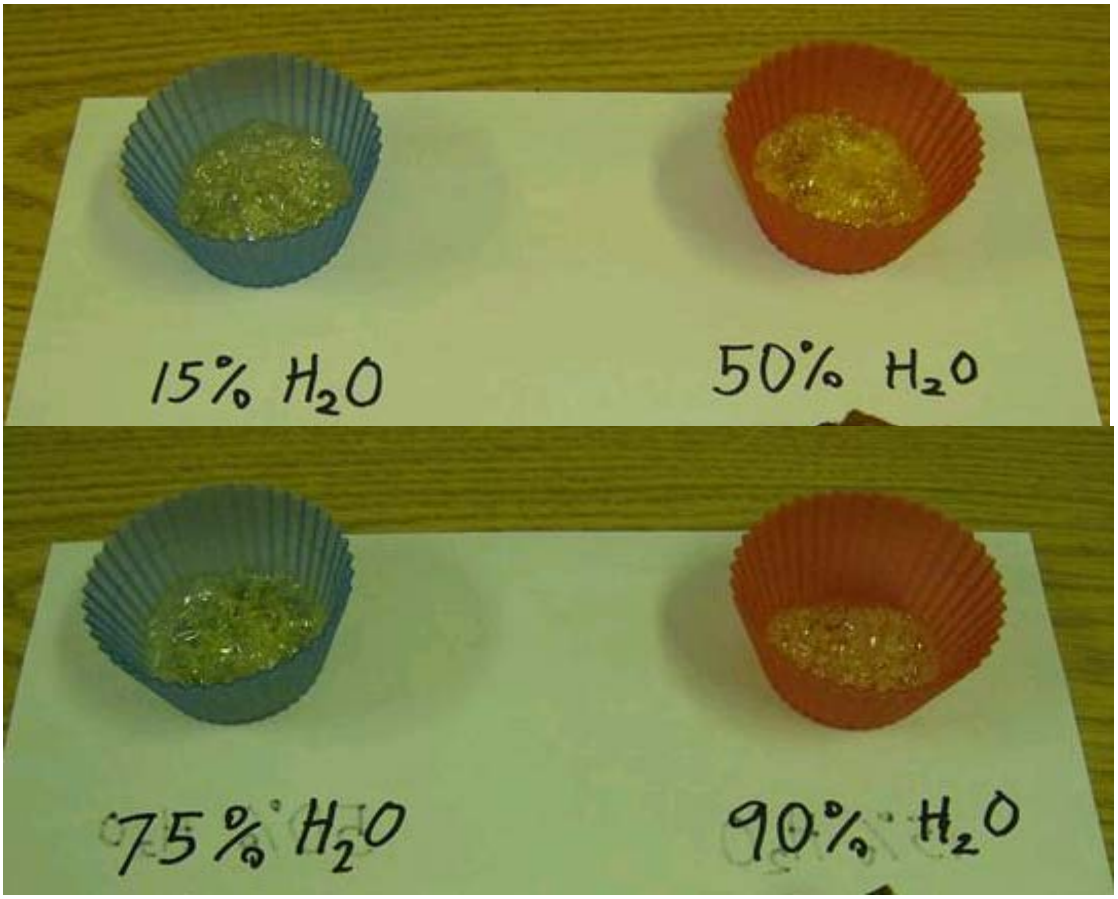

Figure 16) Foams produced from glycerol cut with 15, 50, 75 & 90 wt% DI water

Degradation: Glycerol/Citric Acid vs Glycerol/Tartaric Acid

The rate of degradation for the glycerol/citric acid and the glycerol/tartaric acid polymer foams were compared under several different conditions examining the mass lost over time and changes in the physical appearance of the foam. These tests all showed that glycerol/tartaric acid degrades more rapidly than glycerol/citric acid upon exposure to water or humidity.

Experiments were also run on the lower bake time and temperature versions of the polymers, to try to determine their rate of degradation in water using changes in the relative viscosity as an indicator of molecular chain length.

Degradation of Short Bake, Low Temperature Glycerol/Citric Acid

The purpose of this experiment was to verify that the polymer degrades by hydrolysis in water, as was found by D. Pramanick and T.T. Ray, "Synthesis and biodegradation of copolyesters from citric acid and glycerol" [1988] . In order to test for degradation of the polymer chain in water, viscometry was measured on samples of polymer which had been dissolved in water. The readings were taken over a period of weeks to observe changes in the viscosity. The hypothesis was that if the polymer was degrading the relative viscosity should decrease over time as the chain length of the molecule becomes shorter. A gradual decrease could indicate that the molecules were breaking off the end of the chain, while a larger drop could indicate hydrolysis of bonds in the middle of the chains.

For this experiment, the glycerol/citric acid polymer used was made by baking the sample for 5 hrs at 100°C in a 17 in$_{Hg}$ vacuum. The polymer was dissolved in 50mL water at 37°C under agitation for 2 hrs. The sample was then filtered to remove any undissolved particles. To get multiple samples at the same concentration, the solution was split into different repeats after the filtration step. All samples were run using the same Ubbelohde-type viscometer

with a solvent run done each time measurements were taken to allow temperature effects to be taken into account. Between runs the repeats were stored in sealed 20 mL vials to avoid evaporation losses. The relative viscosity (η_{sp}/c) was charted versus the time the glycerol/citric acid was in solution.

After 100 hrs in solution, the data seems to show a downward trend in the relative viscosity, which is consistent with what would be expected if the polymer chain were degrading (fig 16, tab 3). However, particles were seen forming in all four repeats between 414 hrs and 481 hrs. Particles had also been seen in an earlier attempt at performing this experiment. The earlier experiment did not produce useful results because temperatures effects hadn't been accounted for.

Once the particles had formed the data became unreliable. The measurements are affected more by particles getting caught in the capillary than by the viscosity of the solution.

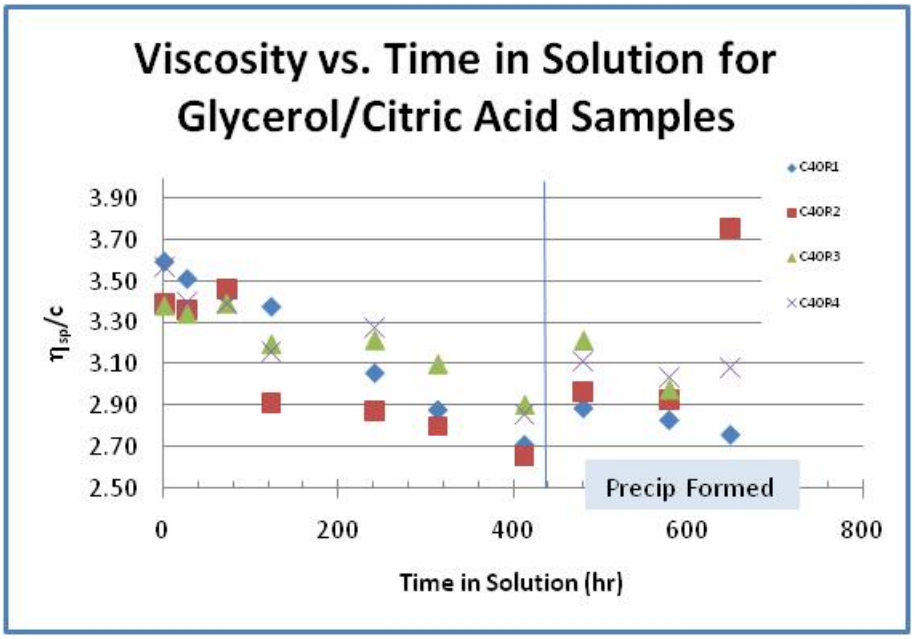

Figure 16) Degradation of low bake time/temp glycerol/citric acid polymer in water; relative viscosity vs. time

Table 3) Relative viscosity of glycerol/citric acid vs. time in solution with water

	Elapsed Time (hrs)	3	29	74	126	243	315	414	481	579	649
	T s (s)	109.49	92.42	99.26	95.66	104.21	96.74	89.94	104.09	106.69	107.49
η_{sp}/C	C40R1	3.59	3.51	3.49	3.38	3.06	2.88	2.71	2.69	2.69	2.76
	C40R2	3.39	3.35	3.46	2.91	2.88	2.80	2.66	2.97	2.98	3.76
	C40R3	3.39	3.35	3.40	3.20	3.22	3.10	2.90	3.22	2.98	9.46
	C40R4	3.57	3.40	3.39	3.16	3.27	5.41	2.86	3.11	3.09	3.08

The particles may have been caused by the solution reaching saturation and some of the polymer returning to a solid state, which would lower the concentration of glycerol/citric acid in the solution. Prior to the appearance of notable precipitates it is also possible that there were smaller particles present in the solution that escaped visual detection, which also might have affected the concentration of the solution.

The next step would be to determine the composition of the precipitates. This could be done by filtering out the precipitates, and then checking to see if they dissolve in hot water. If they do dissolve, HPLC can be run to determine the chemicals present. Due to time constraints this work has been left to future researchers.

<u>Degradation of Long Bake, High Temperature Glycerol/Tartaric Acid Polymer</u>

While not a controlled experiment, it was noted that two slabs of glycerol/tartaric acid, roughly 9in x 9in x 2in, which had been made to test the foam's potential use as an insulation material, were decomposing into a liquid after being left sitting on a shelf in the lab (fig 17).

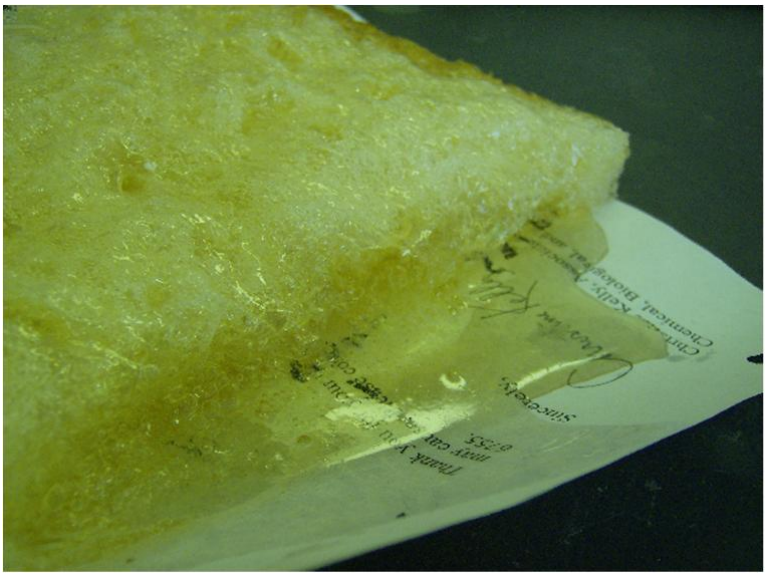

Figure 17) Glycerol/tartaric acid polymer slab degradation after two months at room temperature and humidity

The slab was made by baking the tartaric acid and glycerol at 120°C for 22hrs under a vacuum, making it one of the more highly cross-linked polymers created during this study. After roughly two months of room temperature and humidity the polymer had gone from a rigid foam to a soft spongy material that had partially degraded into a viscous, sticky liquid.

More controlled follow up studies were performed to determine how quickly glycerol/tartaric acid and glycerol/citric acid polymers would degrade.

Degradation of Polymer Cubes

The purpose of this experiment was to determine the relative rates of dissolution between glycerol/tartaric acid foam and glycerol/citric acid foam in water.

Initially, similar sized cubes of glycerol/tartaric acid and glycerol/citric acid were formed by taking the foams formed after the polymers had been baked for 15hrs at 100°C and crushing them into similar sized solid cubes then allowing the cubes to cool. Both foams were made from 0.034 moles of Glycerol and 0.034 moles of the respective acid. The cubes were measured and weighed then submerged in 20mL of DI water at 37°C and subjected to gentle agitation. After thirty hours neither polymer had remained in a cube. The solutions were filtered and the filter paper was dried in a vacuum oven for 24hrs at 100°C.

To get data on polymer swelling, the experiment was rerun with polymer foams that had been baked for 16hrs at 170°C. These foams were too stiff to crush even when they were hot. The samples were cut into similar sized cubes using a hacksaw. It was assumed that the void fraction and thus the surface area were comparable for the two polymers. The cubes were measured using a caliper and weighed then submerged in 200mL of DI water at 37°C while being agitated. Periodically the samples were removed from the water and measured to determine the percentage of surface area gained. Then the polymers were dried using a vacuum oven at 100°C and 17in$_{Hg}$. After being dried the polymers were weighed to determine the percentage of mass lost as the polymers dissolved.

In the initial experiment, after 30 hrs both cubes had dissolved. Visible fragments of the glycerol/citric acid cube remained in the solution. The glycerol/tartaric acid solution had an oily appearance but no visible solids. The percent mass lost was determined for both (tab 4).

Table 4) 15hr/100°C polymer dissolution after 30hrs in DI water

	Mass Initial (g)	Cube Area Initial (cm^2)	Mass Final (g)	% Mass Lost
Glycerol/Tartaric Acid	2.94	8.12	0.035	88.1
Glycerol/Citric Acid	3.67	11.18	1.07	70.7

The 16hr/170°C polymers dissolved more slowly allowing for greater data collection on the dissolution process (tab 5). As with the 15hr/100°C polymers the glycerol/tartaric acid dissolved more quickly. At the 70 hour check the glycerol/tartaric acid cube had broken up into fragments while the glycerol/citric acid cube continues to hold its shape at 760 hours and counting.

Table 5) 16hr/170°C polymer dissolution vs. time in DI water

		Tartaric						
Time soak (hr)	Time dry (hr)	H (cm)	L (cm)	W (cm)	Mass (g)	Cube Area (cm2)	% Area gain	% Mass Loss
0.00	0.00	2.40	3.00	2.80	2.09	44.64	0.00	NA
3.75	0.00	2.60	3.10	3.00	NA	50.32	12.72	NA
23.75	6.50	2.90	3.20	2.60	2.01	50.28	12.63	3.78
43.50	102.50	3.20	2.90	2.70	1.91	51.50	15.37	8.42
69.75	117.50	NA	NA	NA	1.61	Fragments	Fragments	23.13
142.50	138.00	NA	NA	NA	0.88	Fragments	Fragments	58.05
304.50	162.50	NA	NA	NA	0.09	Fragments	Fragments	95.51

		Citric						
Time soak (hr)	Time dry (hr)	H (cm)	L (cm)	W (cm)	Mass (g)	Cube Area (cm2)	% Area gain	% Mass Loss
0.00	0.00	2.50	3.00	2.70	1.83	44.70	0.00	NA
3.75	0.00	2.50	3.00	2.70	NA	44.70	0.00	NA
23.75	6.50	2.80	2.50	3.10	1.80	46.86	4.83	1.73
43.50	102.50	3.20	2.90	2.70	1.80	51.50	15.21	1.92
69.75	117.50	2.80	3.20	2.80	1.80	51.52	15.26	1.72
304.50	142.00	2.40	3.20	2.60	1.78	44.48	-0.49	2.64
142.50	138.00	2.80	3.10	2.90	1.81	51.58	15.39	1.01
505.50	184.50	2.80	2.40	2.50	1.75	39.44	-11.77	4.52
598.10	202.50	2.60	2.50	2.50	1.75	38.50	-13.87	4.52
760.70	370.50	2.50	2.70	2.40	1.72	38.46	-13.96	5.90

The glycerol/citric acid polymer swelled more slowly, but with both polymers the area of the cube increased just over 15% (fig 18). The glycerol/citric acid polymer remained at this size during almost a week of soaking while the glycerol/tartaric acid cube broke into fragments after 3 days of soaking. Since then the glycerol/citric acid has decreased in size as it dissolved, but it retained its form.

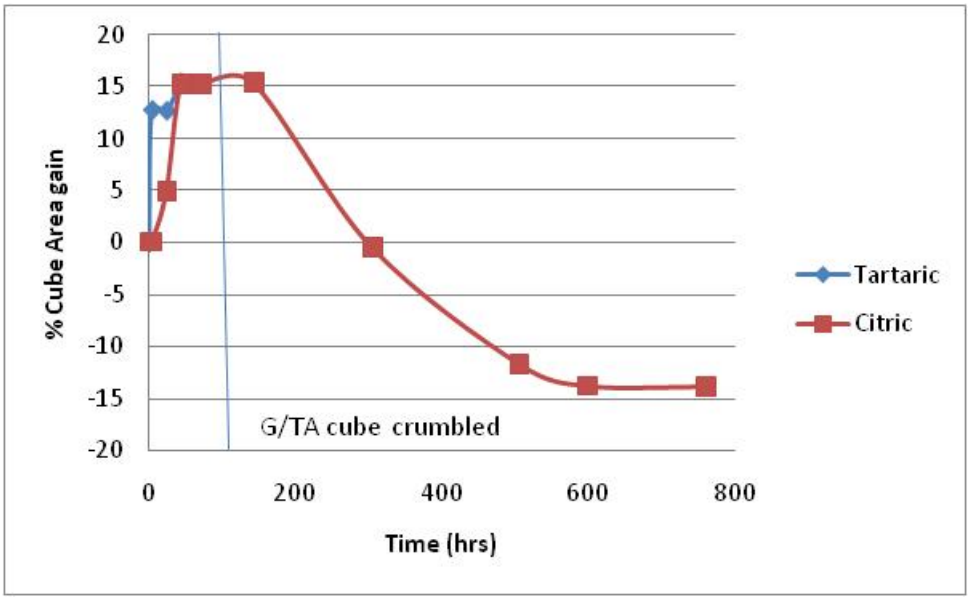

Figure 18) % surface area change of glycerol/tartaric acid and glycerol/citric acid cubes vs. time submerged in water.

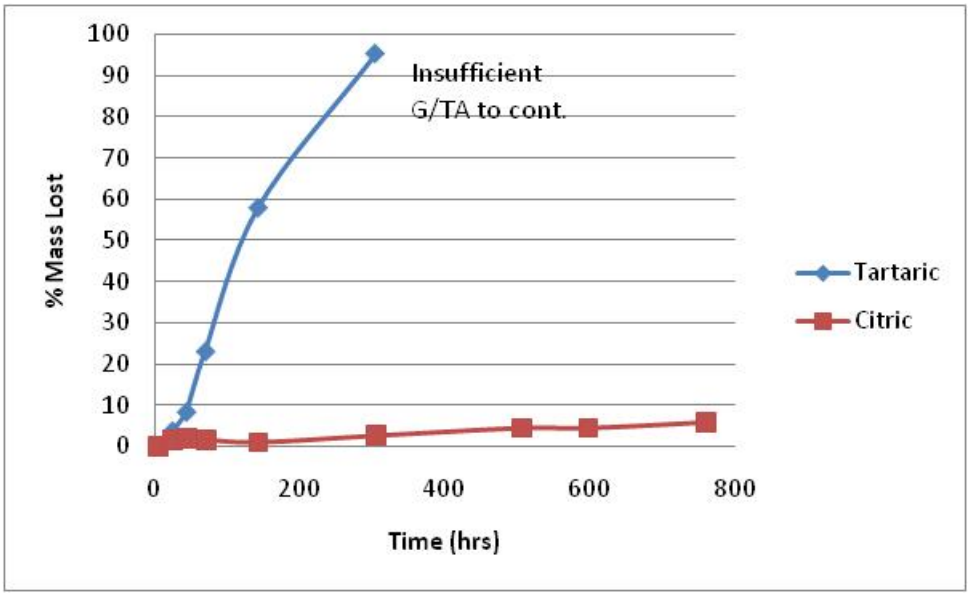

Figure 19) % mass change of glycerol/tartaric acid and glycerol/citric acid cubes vs time submerged in water

After repeated drying cycles the mass of the glycerol/citric acid sample has remained relatively constant (fig 19). It is proposed that the drying cycles are causing the polymer to form new links, preventing degradation. The condensation reaction which bonds the glycerol and citric acid is a reversible one. In the of absence of excess water the reaction equilibrium is shifted back toward forming bonds.

Upon running a DSC curve on a sample of glycerol/citric acid each subsequent run showed the T_m peak at a higher value than the one previous (fig 20-22). The melting temperature of a polymer is supposed to be a constant. DSC measurements of T_m and T_g is a common method of identifying polymers. The fact that these values changed each time the DSC was run indicates that the polymer is being altered by the measurement process, by heating the polymer.

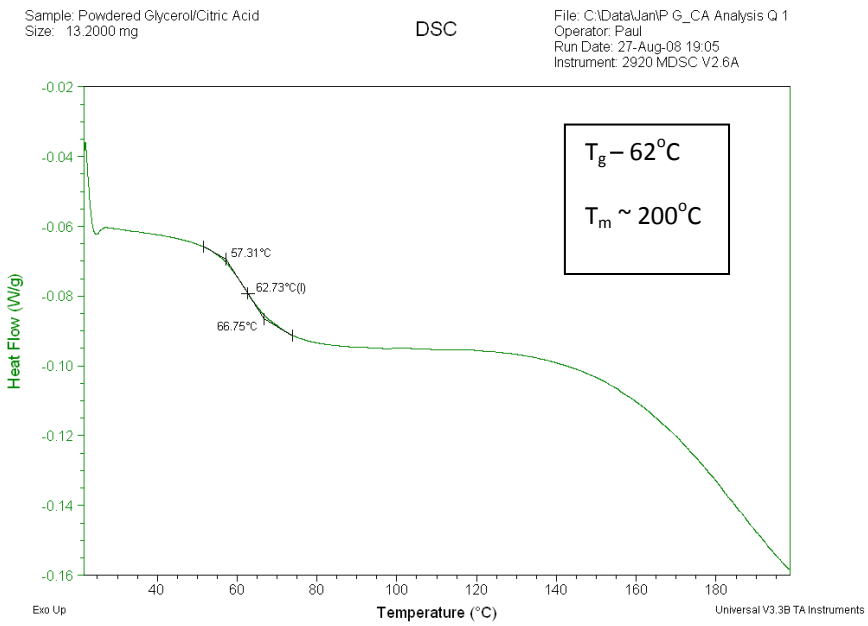

Figure 20) DSC first run

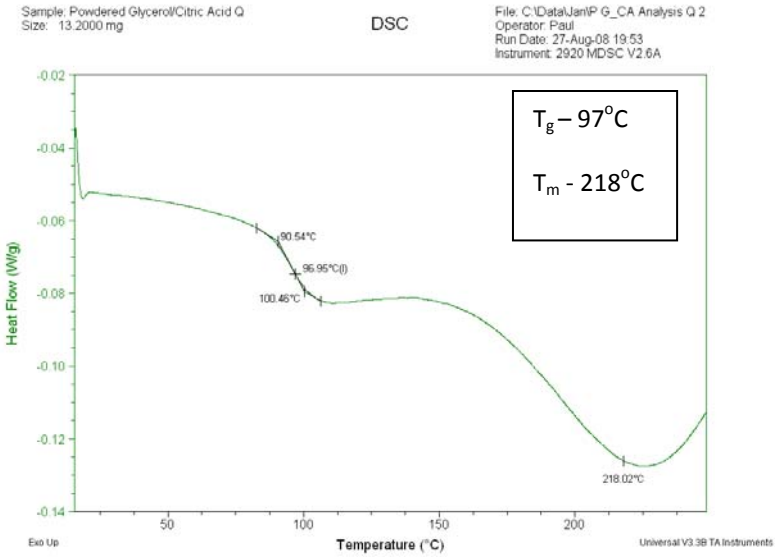

Figure 21) DSC second run

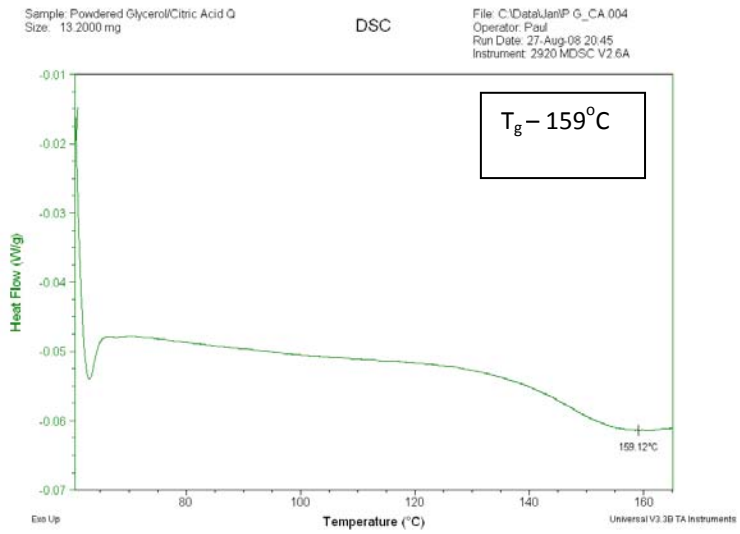

Figure 22) DSC third Run

Also it has been noted in other experiments, that when the polymer is left out in a humid atmosphere, over time the polymer will begin to soften; however, the softening can be reversed with additional baking.

Glycerol/tartaric acid is much more susceptible to degradation in water than glycerol/citric acid. In 300hrs, the glycerol/tartaric acid cube was almost entirely gone while the glycerol/citric acid cube had lost less than 3% of its initial mass. The rate of degradation for both materials is dependent on the initial baking conditions; longer bakes at hotter temperatures result in longer lasting polymers.

Baking the polymers in order to dry them for weighing likely extended the life of the polymers by reforming bonds that had been hydrolyzed. To get better results, this experiment should be rerun taking greater care not to over dry the polymer.

Degradation at Elevated Temperature and Humidity

This experiment was designed to replicate the block of polymer dissolving on the shelf under controlled conditions to determine the life of the polymer.

Samples of glycerol/citric acid and glycerol/tartaric acid that had been made by baking at 100°C for 18hrs were placed in a sealed container and held at 100% humidity and 37°C for several weeks, while the degradation of polymers was observed and photographed.

The experiment was started on 9/16/2008.

Figure 23) Left G/CA, Right G/TA, Time: 0 days

Both polymers began as rigid foam. The glycerol/tartaric acid foam had a slightly more yellow coloration than the glycerol/citric acid foam (fig 23).

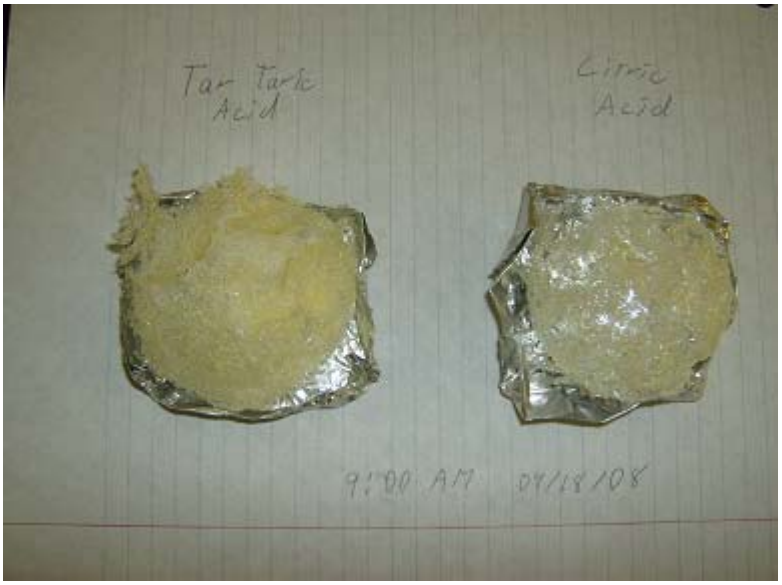

Figure 24) Left: G/TA, Right G/CA, Time: 2 days

Both foams had softened after two days at elevated temperatures and 100% humidity. The tartaric acid foam was beginning to lose integrity and peel apart (fig 24).

Figure 25) Left G/CA, Right G/TA, Time: 7 days

At seven days the glycerol/tartaric acid foam had completely decomposed, the glycerol/citric acid foam was soft and beginning to peel apart (fig 25).

Figure 26) Left G/CA, Right G/TA, Time: 14 days

At fourteen days the extent of peeling in the glycerol/citric acid foam had increased substantially (fig 26 & 27).

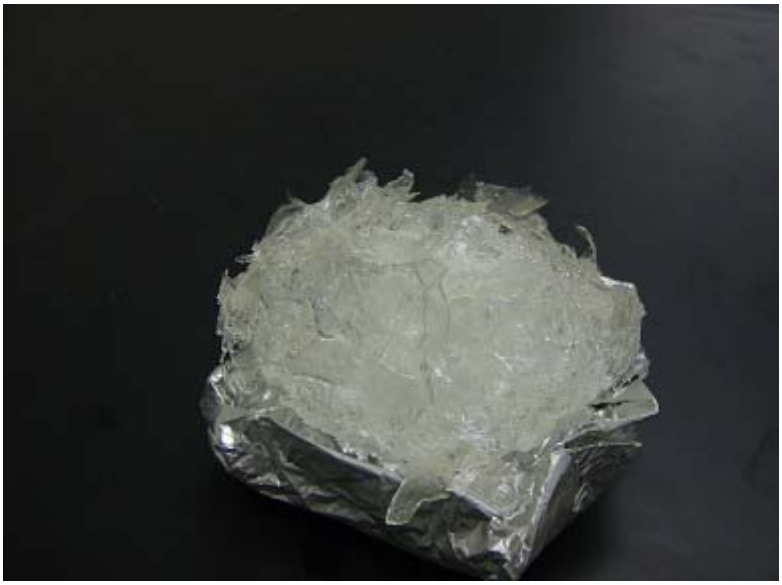

Figure 27) Close up of G/CA at 14 days

Figure 28) Left G/CA, Right G/TA, Time: 29 days

At twenty-nine days the glycerol/citric acid foam was soft and the peeling sections would fall apart with only minimal pressure (fig 28).

Figure 29) Left G/CA, Right G/TA, Time: 36 days

At thirty-six days the glycerol/citric acid could no longer be considered a foam. The structural integrity had been lost. The remaining material was a pile of soft, gel-like peelings (fig 29).

Figure 30) Left G/CA, Right G/TA, Time: 43 days

At forty-three days the glycerol/citric acid had dissolved and the experiment was ended(fig 30). During clean up a sticky gel like residue was found in the bowl beneath the samples.

Glycerol/tartaric acid degrades much more readily than glycerol/citric acid prepared under the same conditions.

Application: Potential for Glycerol/Citric Acid Polymer as a Replacement for Bitusize in Degradable Flower Pots

The glycerol/citric acid polymer was considered as a more environmentally friendly replacement for Bitusize (an asphalt emulsion) in the making of degradable Flower Pots. At the beginning of the trial it was believed that the Bitusize acted as a binder in the pots, gluing the fibers together, but during the course of experimentation it was discovered that the primary function of the Bitusize was to repel water and prevent the early degradation of the fibers holding the pot together.

Papier Mache` Pots

As a quick examination of the Glycerol/Citric Acid Polymer's ability to act as a binder, rough papier mache` pots were made by dipping strips of newspaper into solutions of the polymer and water.

For this experiment the glycerol was mixed with DI water to make solutions which were 15%, 50%, 75% and 90% water before the citric acid was added to determine how concentrated the polymer needed to be to have an effect. Strips of newspaper where dipped in the solution, then placed in a silicon muffin cup. The pots were baked, under vacuum ($17in_{Hg}$) at $175^{o}C$ for 1.5 hrs.

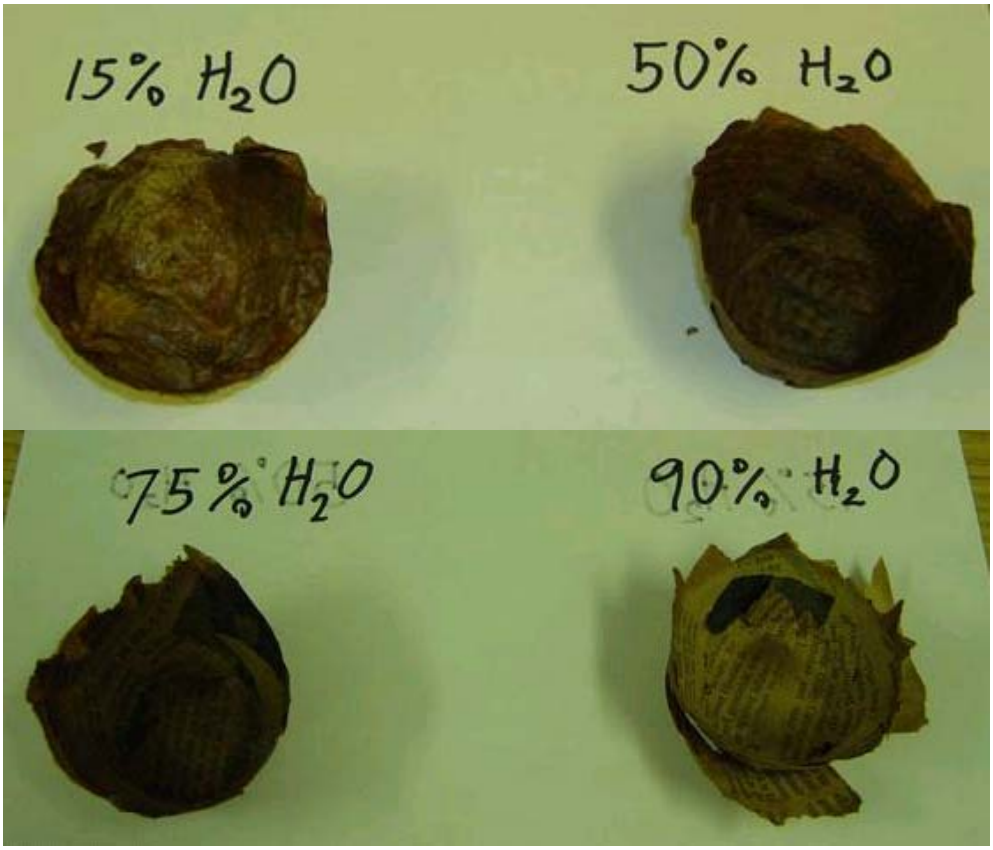

Figure 31) Papier Mache` pots

The 90% H_2O mixture failed to sufficiently glue the newspaper together. The 15% H_2O mixture distorted the pot when it foamed. Both the 50% and 75% H_2O mixtures produced good pots. The 50% 'pot' felt like it had a shellac of hardened polymer coating the newspaper, the 75% 'pot' didn't sound as plastic when tapped with a fingernail but it was rigid. Neither 'pot' was sticky (fig 31).

Given initial beliefs about the Bitusize's role in the pot, these results seemed promising.

<u>Coupons</u>

Before attempting to make a full pot using the glycerol/citric acid polymer as a substitute for Bitusize, test coupons were made. The coupons were examined for their mechanical strength when wet and dry and for water absorbance. Coupons made with three variations

of the glycerol/citric acid polymer were tested against Bitusize coupons and coupons made without any sort of chemical binder.

Coupon Making Procedure

Data was collected on coupons made with Bitusize and with just pulp (No Binder) to create a baseline as a standard of comparison for coupons made with the Citric Acid/Glycerol polymer.

Shredded Cardboard and newspaper was placed in a blender, and enough water was added to cover the mixture. This mixture was blended at low speed until the mixture had the consistency of oatmeal. Then the Bitz, 'Wet Strength', $AlSO_4$ which promotes adhesion between the Bitz and fiber, and Defoamer were added to the mixture. For the coupons made without Bitz, both the Bitz and the $AlSO_4$ was left out of the mixture. After the chemicals were added the mixture was blended again on a low speed until it was thoroughly mixed, then the remaining water was added. The mixture was blended on medium to high for roughly a minute.

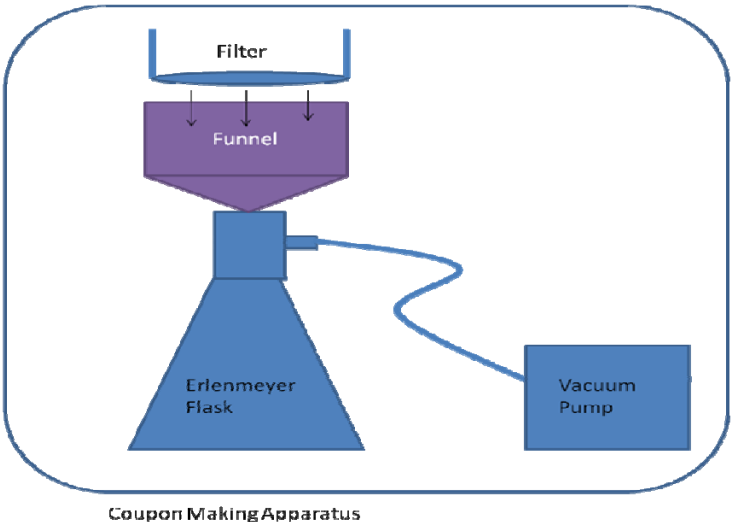

Figure 32) Coupon making apparatus

The mixture was placed in the coupon making apparatus (fig 32). The fiber/binder mixture was poured in on top of the filter. The vacuum drew the excess liquid out of the mix. The coupon was removed from the mold (the funnel) and baked. For the baseline coupons the bakes were 40min. at 350°F in a convection oven. After the bake a coupon was cut out of the sample using a cutting mold and a compressor (500 PSI).

Using the same method coupons were made substituting glycerol/citric acid polymer for Bitusize. Three variations in glycerol/citric acid polymer were used.

Glycerol/Citric Acid Polymer Preparations

The first, 'Liquid', was an uncross-linked version of the polymer made by heating a 1:1 molar ratio of glycerol and citric acid on a hot plate for half an hour while stirring to promote the release of steam. Heating the liquid reduces its viscosity, which was necessary when measuring the polymer for addition to the coupons.

The second, 'Ground', was a cross-linked version of the polymer made by baking the glycerol and citric acid mixture for 17hrs, at 170°C under a vacuum of 17 in_{Hg}, causing it to form into a hard, brittle foam. To prepare the foam for use in the coupons it was ground to a powder using a Spex Certiprep 8000 ball mill.

Initially the foam was broken into pieces small enough to fit in the ball mill by smashing it with a hammer after wrapping it in canvas. For the milling process stainless steel ball bearing were used within a titanium milling chamber. The heat of friction generated by the grinding process was sufficient to raise the polymer's temperature above the glass transition temperature. To prevent the polymer from softening, liquid nitrogen was added to the milling chamber along with the polymer. The polymer was milled in ten minute increments then the powder was collected and the larger particles were returned to the milling chamber along with fresh sample and liquid nitrogen. The milling process was repeated until sufficient amounts of powder had been produced.

When the initial powder was used in making coupons it was noticed that while the vacuum pressure in the Erlenmeyer flask normally stabilizes around 10 in_{Hg} during the coupon molding process, when using the powdered polymer the pressure stabilized around 5 in_{Hg}. It was believed that the size of the powder was causing more air pathways through the pulp, possibly reducing the packing density. A second batch of powder was made up. Using a

Tyler Standard Screen #32 all particles larger than 500μm were eliminated from the powder. Coupons made using the 'Fine' powder stabilized at 10 in_{Hg}, like those made using Bitusize, nothing or the 'Liquid' polymer.

Dry Burst Testing

Dry Burst Testing checks the mechanical strength of the coupon. The process involves first measuring the mass of the test coupon. Western Pulp used air pressure applied over a circular area one inch in diameter on the coupon, the PSI need to punch through the coupon is measured. Their standard for burst strength is PSI needed to break the coupon divided by the mass of the coupon (to average out the thickness of different samples).

$$DryBurstStrength = \frac{PSItoBurstDryCoupon}{DryMass}$$

Absorbance Testing

The coupons were soaked for 24hrs in a 0.1% solution of OmniPur Triton X-100 Surfactant and water. Then the dry weight is compared to the wet weight.

$$\%Abs = \left(\frac{(WetMass - DryMass)}{DryMass} \right) * 100$$

Wet Burst Testing

The Wet Burst test was run on the coupon after the 24hr soak for the absorbance test. As in the Dry Burst Test, the data collected is the PSI needed to break the coupon, as applied over a circular area 1 inch in diameter. The Burst Strength is normalized by dividing by the Burst Strength by the dry mass of the coupon.

$$WetBurstStrength = \frac{PSItoBurstWetCoupon}{DryMass}$$

Results: Baseline Coupons

Sixteen coupons were made using Bitz and another sixteen with just pulp. Of each batch, eight coupons were used for Dry Burst Tests and eight were used for Absorbance and Wet Burst Tests. Results were as follows (tab 6):

Table 6) Baseline coupon data

	Bitusize		No Binder		Analysis of Difference		
	Ave	StDev	Ave	StDev	F-test	T-test	T-Dist
Dry Burst Strength (PSI/g)	23.6	5.3	20.4	3.6	0.330	1.89E-01	6.27E-08
Wet Burst Strength (PSI/g)	15.4	2.8	9.7	2.4	0.686	7.21E-04	1.20E-06
% Absorbance	105.5	32.1	368.6	14.1	0.045	4.76E-12	1.81E-12
Dry Mass (g)	6.5	0.2	5.3	0.3	0.827	1.26E-07	3.26E-04

The F-tests showed no significant difference in the variance of the Bitusize and No Binder samples.

The Bitusize had surprisingly little impact on the Dry Burst and Wet Burst strength of the coupons. The difference between Bitusize and No Binder coupons was only significant with regard to the average dry mass of the coupons and in the % Absorbance (fig 33-35).

It seems that the Bitusize's primary function in the pots is its ability to repel water. The glycerol/citric acid polymers are not hydrophobic. Where the Bitusize emulsion, consisting of 45 wt% water, is distinctly a liquid, a mixture of glycerol/citric acid foam which has been ground into a powder and 45 wt% water is a paste. The glycerol/citric acid absorbs water.

Results: Glycerol/Citric Acid Coupons

Sixteen coupons were made with the 'Liquid' and 'Fine' glycerol/citric acid polymers and fourteen were made with the 'Ground' glycerol/citric acid. Results of Dry Burst, Wet Burst and % Absorbance are as follows (tab 7):

Table 7) Glycerol/citric acid coupon data

	Liquid G/CA	StDev	Ground G/CA	StDev	Fire G/CA	StDev
Dry Burst Strength	13.5	4.3	12.4	1.4	12.0	1.7
Wet Burst Strength	3.1	1.2	4.8	1.3	5.0	1.3
Absorbance	391.1	28.8	387.2	8.8	329.2	15.6
Dry Mass	5.7	0.6	7.2	0.4	7.5	0.2

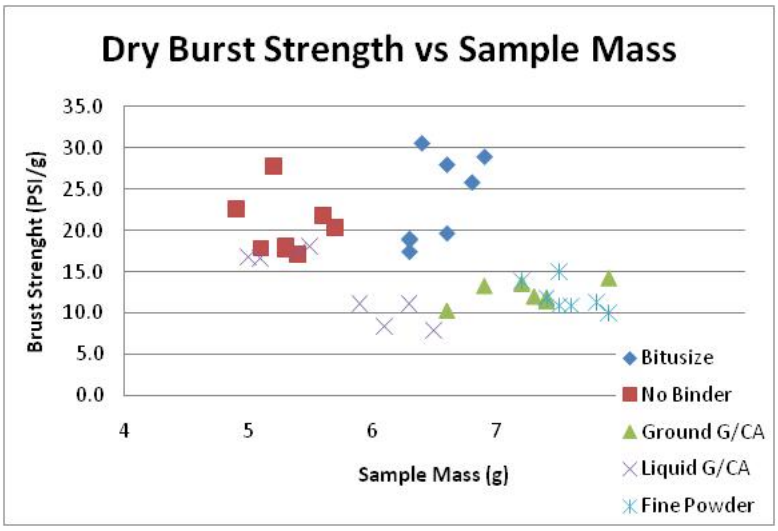

Figure 33) Dry burst strength vs. sample mass of coupons

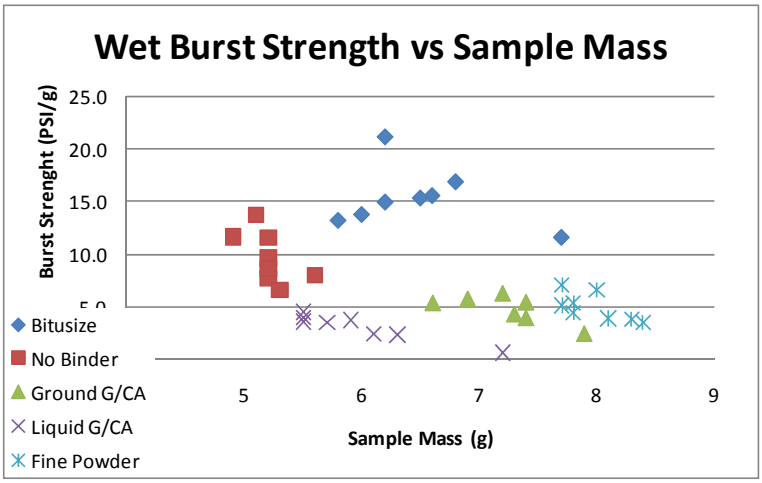

Figure 34) Wet burst strength vs. sample mass of coupons

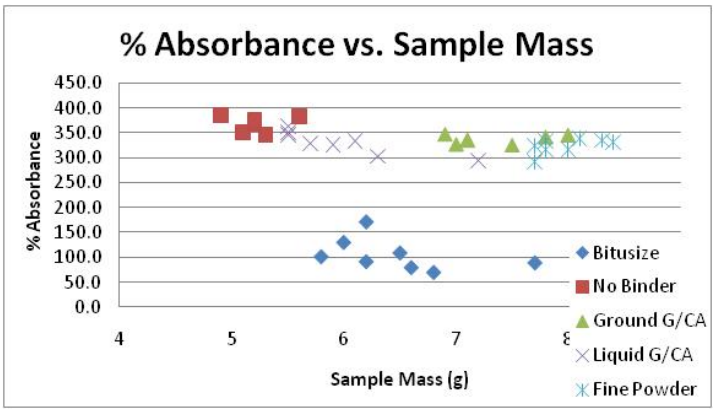

Figure 35) % absorbance vs sample mass of coupons

Regardless of how the glycerol/citric acid polymer is prepared, the behavior of coupons made with the polymer is the same with regards to Dry Burst Strength, Wet Burst Strength and % Absorbance. The Dry and Wet Burst Strength of the coupons made with polymer average at the bottom of the range of values for coupons made with 'No Binder' (fig 33 & 34). % Absorbance for the glycerol/citric acid polymers coupons were no better than those made with 'No Binder' (fig 35). For analysis of difference see tables 8-10.

Table 8) Analysis of difference for 'Liquid' glycerol/citric acid coupons

	Liquid G/CA to No Binder			Liquid G/CA to Bitusize		
	F-test	T-test	TDIST	F-test	T-test	TDIST
Dry Burst Strength	6.8E-01	3.6E-03	1.7E-07	5.8E-01	9.3E-04	6.3E-08
Wet Burst Strength	5.4E-05	7.8E-06	2.6E-05	2.9E-07	2.2E-08	1.2E-06
Absorbance	2.1E-01	1.6E-15	2.9E-16	4.2E-01	5.0E-14	1.8E-12
Dry Mass	6.0E-02	7.8E-02	1.1E-03	3.9E-02	2.2E-03	3.3E-04

Table 9) Analysis of difference for 'Ground' glycerol/citric acid coupons

	Ground G/CA to No Binder			Ground G/CA to Bitusize		
	F-test	T-test	TDIST	F-test	T-test	TDIST
Dry Burst Strength	3.1E-02	1.1E-04	1.7E-07	4.3E-03	1.3E-04	6.3E-08
Wet Burst Strength	3.8E-05	4.0E-04	2.6E-05	3.1E-06	6.1E-07	1.2E-06
Absorbance	2.0E-01	4.1E-20	2.9E-16	5.0E-03	2.7E-10	1.0E-12
Dry Mass	2.5E-01	5.7E-08	1.1E-03	1.8E-01	1.0E-03	3.3E-04

Table 10) Analysis of difference for 'Fine' glycerol/citric acid coupons

	Fine G/CA to No Binder			Fine G/CA to Bitusize		
	F-test	T-test	TDIST	F-test	T-test	TDIST
Dry Burst Strength	5.9E-02	9.5E-05	1.7E-07	7.0E-03	4.1E-05	6.3E-08
Wet Burst Strength	1.0E-05	9.1E-04	2.6E-05	5.4E-07	2.2E-07	1.2E-06
Absorbance	7.9E-01	9.3E-18	2.9E-16	7.6E-02	4.1E-16	1.8E-12
Dry Mass	7.9E-01	9.6E-11	1.1E-09	9.0E-01	4.9E-07	9.9E-04

White Water Analysis

While it was known that the polymer would break down in water, the glycerol and citric Acid would also reform the polymer if the water was baked out again. It was hoped that enough glycerol and citric acid would be retained in the pulp to react with one another during the baking process. However some basic analysis of the water pulled out of the pulp during the coupon making process showed that most of the glycerol/citric acid was staying in the water.

Viscometry

Viscometry was done to compare a glycerol/citric acid polymer sample and a glycerol/tartaric acid sample made using the 'hot-plate' method of synthesizing the polymer to a glycerol/water mixture of the same concentration. The relative viscosity of a 10% solution of glycerol in water was found to be higher than the relative viscosities of either of the polymers, indicating that the polymer had already degraded back into the constituent glycerol and diacid (tab 11). The solutions were mixed for 10 minutes using a magnetic stirrer. This mixing process is much gentler than what the polymer would see in the blender during the coupon making process.

Table 11) Viscosities of glycerol and 'Hot-Plate' glycerol/citric acid or glycerol/tartaric acid in a DI water solution

	Glycerol	Glycerol/Citric Acid	Glycerol / Tartaric Acid
Ts (s)	105.01	105.01	96.37
Conc (g/mL)	0.11	0.11	0.12
η_{sp}/C	7.13	5.56	1.47

From this it is concluded that the 'hot-plate' glycerol/ acid polymer will have largely broken back down into glycerol and citric acid after a relatively short exposure to water.

Evaporation Test

Whitewater samples were taken from coupons made with glycerol/citric acid, Bitusize and ones made with 'No Binder'. Roughly ten grams of whitewater from each sample was placed in a vacuum oven at 100°C for 24hrs. Then the solids which remained after the water evaporated were weighed to determine how much of the binder was staying in the pulp (tab 12).

Table 12) White water analysis

Binder Type	% Binder Int.	% Binder Waste
Glyc/Citric - Liquid	0.78	0.55
Glyc/Citric/$AlSO_4$ - Liquid	0.77	0.59
Glyc/Citric/$AlSO_4$ - Ground	0.74	0.29
Bitz	0.71	0.07
None	0.00	-0.13

Because there was no measurable mass of solids found in the whitewater from the coupons made without binder, it is assumed that all solids found in the whitewater from coupons made with a binder comes from that binder.

With the Bitusize $AlSO_4$ is added to the coupons to help bind the Bitusize to the fiber. Polymer coupons were made both with and without the $AlSO_4$. In the initial mixture of water and chemicals the binder started off at roughly 0.74 wt% of the coupon mixture. After the coupon had been formed, analysis of the whitewater showed that very little of the Bitusize (0.07 wt%) was found in the waste water; therefore most of the Bitusize was trapped in the fibers. . This finding is probably due to the physical size of the Bitusize particles. Examination of the Bitusize under magnification shows that the asphalt particles are ball milled to be 3 – 10um in size (fig 36).

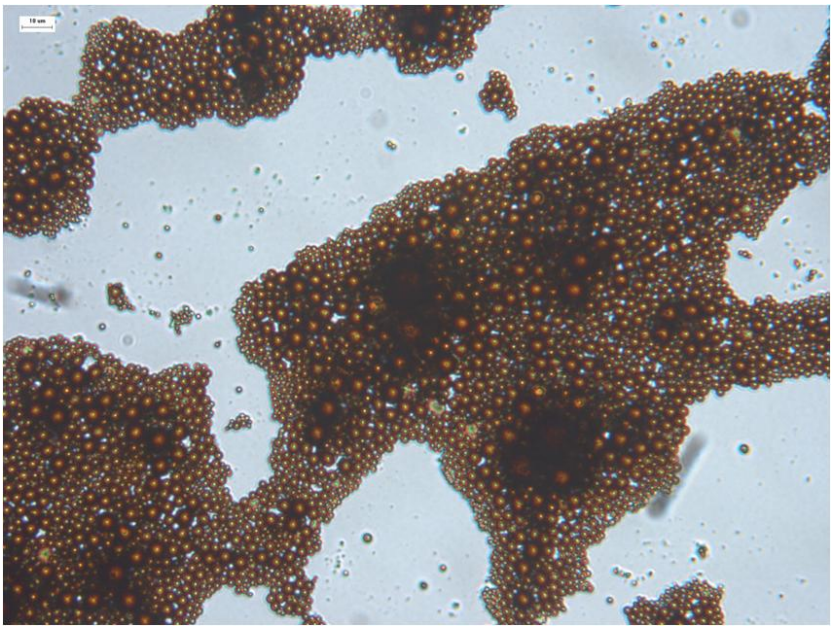

Figure 36) Magnification of Bitusize particles

For the 'Liquid' glycerol/citric acid polymer, with or without $AlSO_4$, only about 25% of the initial 0.74 wt% binder remained in the fiber matting. With the 'Ground' glycerol/citric acid 60% of the initial 0.74 wt% binder remained in the matting. Initial attempts to make papier mache` pots using glycerol/citric acid as a binder were not effective when using a water/polymer solution that was 10% polymer and using a process that evaporated the water, leaving all the polymer behind rather than a vacuum system that removed a significant portion of the polymer before the baking process began.

Amount of Blinder

Further testing was done by making coupons with a range of Bitusize: 2 g/coupon – low, 4.5 g/coupon – medium, and 7 g/coupon – high and a range of Polymer: 2g/coupon – Low, 6g/coupon high. Four of each type of coupon and four coupons made without Bitusize were tested for Wet Burst Strength and % Absorbance (tab 13).

Table 13) Results for range of binder data

	Wet Burst Strength (PSI/g)	% Absorb
No Binder	5.6	385.3
Low Bitz	6.4	230.4
Med Bitz	13.8	151.9
High Bitz	12.4	148.0
Low Polymer	5.9	364.4
High Polymer	6.0	365.1

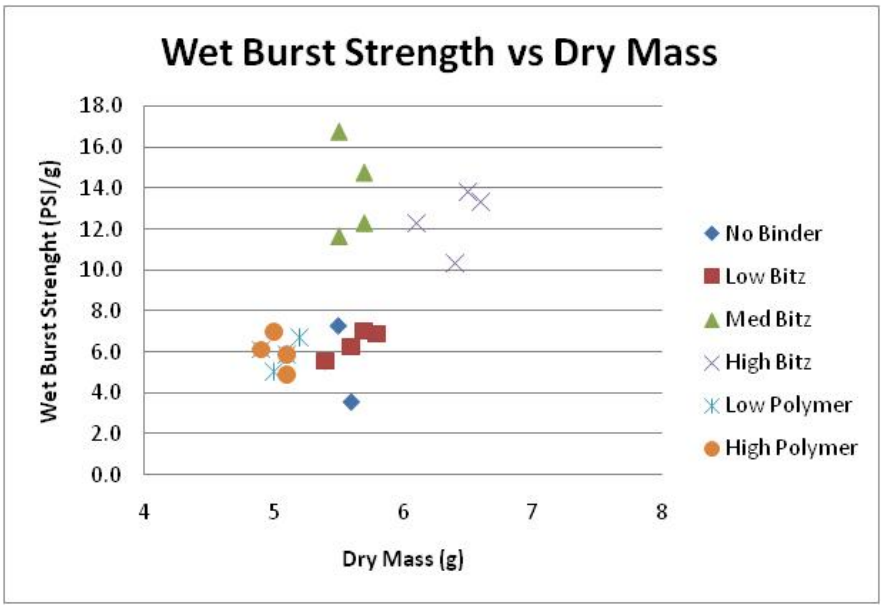

Figure 37) Wet burst strength vs. dry mass for coupons made with a range of binder

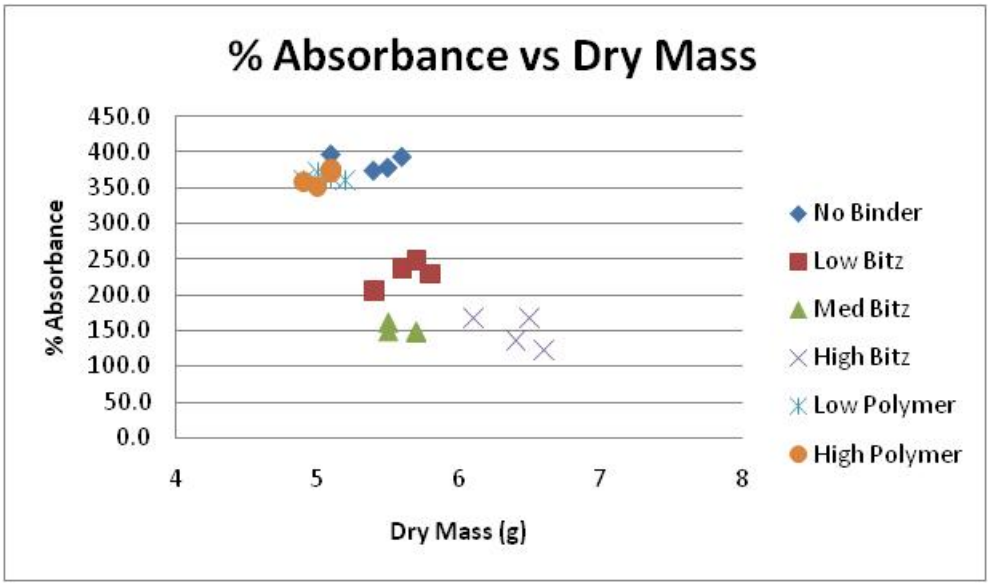

Figure 38) %absorbance vs dry mass for coupons made with a range of binder

The low Bitusize coupons didn't prevent water absorption quite as well as the high or medium Bitusize coupons, but it was better than no binder or the glycerol/citric acid polymer coupons (fig 38). However, the Wet Burst strength of the low Bitusize coupons was no better than that of the no binder coupons, or the Polymer coupons (fig 37). For analysis of difference between the different binder and no binder see table 14.

Table 14) Analysis of difference for range of binder

		Low Bitz vs No Bitz		Med Bitz vs No Bitz		High Bitz vs No Bitz	
	T-Dist	F-test	T-Test	F-test	T-Test	F-test	T-Test
Wet Burst Strength (PSI/g)	0.01	0.21	0.34	0.50	0.00	0.97	0.00
% Absorb	0.00	0.40	0.00	0.46	0.00	0.34	0.00

		Low G/CA vs No Bitz		High G/CA vs No Bitz	
	T-Dist	F-test	T-Test	F-test	T-Test
Wet Burst Strength (PSI/g)	0.01	0.25	0.60	0.37	0.06
% Absorb	0.00	0.30	0.01	0.99	0.04

These coupons were also examined under a microscope to see how the breaks occurred:

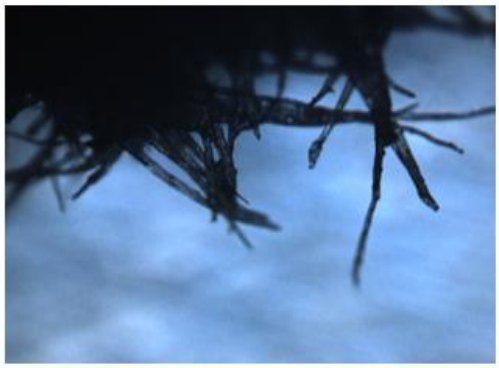

Figure 39) No Binder, 50x Mag

Figure 40) Low Bitz, 50x Mag

Figure 41) Med Bitz, 50x Mag

Figure 42) High Bitz, 50x Mag

Figure 43) Low Polymer, 50x Mag

Figure 44) High Polymer, 50x Mag

Regardless of the amount of Bitusize or Polymer used, all the breaks appear to be the result of the fibers pulling apart. With the High Polymer Coupons bits of polymer are seen clinging

to the polymer, indicating that the polymer was acting as a glue in the polymer, but it wasn't strong enough to impact the burst strength at the concentrations used.

Due to variations in the convection oven used for baking the coupons, testing different bake times and temperatures has not been productive. 40 mins at 350°F generally bakes the moisture out of the coupons without scorching them. This time and temperature seems to be at the middle of the operating range, but some batches still turn out burned or damp.

From the baseline data gathered for these experiments, it was discovered that the main function of Bitusize in the product is to prevent or reduce the absorbance of water. Bitusize coupons had a marginally higher Dry Burst Strength than coupons made without binder, but the difference wasn't statistically significant. The difference between the Wet Burst strength was more notable, but it is most likely an artifact of the Bitusize repelling water and thus protecting the fibers from degradation rather than because the Bitusize strengthened the bonds between the fibers. % Absorbance for coupons made with Bitusize was 105.5%, for coupons made with No Binder it was 386.6%. It seems that the Bitusize does not act as an adhesive in the pots. It acts as a water repellant. This is supported by the fact that the photographs of the ruptures sites on the samples do not show any fractured fibers.

The polymer slightly decreases the burst strength of the coupons, but only to the lower end of the range of values for the No Binder coupons. The polymer does nothing for the % Absorbance. To get the sort of effects seen when making the papier mache` pots, the amount of chemical used per pot would need to be increased from less than 1 wt% of the solution to greater than 10 wt%. Such a massive increase in chemical usage would make the process more expensive and the current operating system, which recycles the waste water may not be usable as the polymer concentration in the waste water would build up over time.

Using quantities of binder comparable to the amount of Bitusize currently used, pots made with No Binder would be as good as, or better, than pots made with the polymer.

Conclusions

The glycerol/citric acid polymer naturally foams when baked due to the evaporation of the water released by the condensation reaction that forms the polymer, unless the bake is for a short time at a low temperature. However the low temp/short time polymers degrade rapidly in the presence of water. The longer and hotter the bake the more water lost, meaning the more bonds formed. The polymer breaks down through the process of the bonds undergoing hydrolysis, the reverse of the reaction that formed the polymer initially, so the fewer bonds created the faster it degrades. The process used to make Western Pulp's degradable flower pots completely broke down the low temp/short bake glycerol/citric acid, allowing the glycerol and citric acid to be washed through the fiber along with the waste water, rather than having it stay in the matrix where it might have effected the pot.

There is a sharp jump in the time it takes for the polymer to dissolve in water. At temperatures above 110°C, or 105°C in conjunction with a bake 12 hours or longer the polymer goes from dissolving in 2 hrs to taking days to dissolve. It is hypothesized that this might be the point where the polymer begins to form cross-links. A small amount of polymer swelling (a 15% increase), which is characteristic of cross-linked polymers, was seen when testing the degradation of cubes of 16hr/170°C glycerol/citric acid and glycerol/tartaric acid. These long time/high temp polymers are solids even when hot.

The glycerol/citric acid polymer will not work to replace Bitusize in Western Pulp's flower pots. Bitusize does not act as an adhesive in the pots as was originally believed. It repels water and thus protects the fibers, which make up the pots, from early degradation.

Glycerol/tartaric acid degrades more readily than glycerol/citric acid made under the same conditions.

The presence of excess water in the glycerol does not interfere with the formation of the polymer.

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