

THE CRITICAL EFFECT OF MIXING AND BATCH TEMPERATURE IN
THERMOSET CERAMIC INJECTION MOLDING

BY

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A THESIS
SUBMITTED TO THE FACULTY OF

ALFRED UNIVERSITY

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF

MASTER OF SCIENCE

IN

MATERIALS SCIENCE AND ENGINEERING

ALFRED, NEW YORK

SEPTEMBER 2016

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ACKNOWLEDGEMENTS

First and foremost I would like to thank my advisor, Dr. Bill Carty, for the countless hours of guidance and advice throughout this project. Working with Dr. Carty and having the chance to absorb as much of his knowledge as possible over the past three years (B.S. and M.S. theses) has been an absolutely invaluable opportunity.

Secondly, I would like to thank GE Aviation and GE Global Research who funded this project thus allowing me to strive towards my goal of obtaining a Master's degree in engineering without the added financial stress.

Also, thanks to Gerry Wynick and Hyojin Lee for their technical support and help throughout this project. Your efforts are most greatly appreciated.

Special thanks goes to the entire office research group (Ben, Alex, Ryan, Matt, and Dan) and Ladonis whose physical help, comic relief, and camaraderie in and out of the lab kept me going. Thanks also to Krishna who has always gone above and beyond not only as a secretary, but especially as a friend.

Finally, the biggest of thanks goes to my family: Mom, Dad, Brandi, Davis, Morgan, and Marissa, all whom have provided me with so much more support than I ever could have asked for. Each of you has shown me an incredible amount of unconditional support throughout this entire project and I can never thank you enough. I absolutely could not have done this without each and every one of you.

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ABSTRACT

Injection molding is a common industrial process used to create near-net shaped ceramic parts. In today's industry, it is most common for injection molding batches to use thermoplastic binder systems; however the advantages seen with the use of thermosetting binders still makes them an attractive alternative. It was proposed that ideal rheology of injection molding systems could be better predicted with the development of a rheological process control diagram (RPCD). A series of suspensions were prepared and then analyzed using a rheometer with the intention of mapping out their behavior as a function of rheological parameters to allow for prediction of material performance. Lack of repeatability in the data has led to the new hypothesis that mixing and batch temperature are more vital parameters than was previously suspected. It is now proposed that rheological behavior is more highly controlled by a combination of mixing and temperature, rather than the batch composition itself.

INTRODUCTION

Thermosetting binders exhibit irreversible behavior and provide greater strength and dimensional stability than the more popular thermoplastic polymer systems for injection molding.

The ability to predict injection molding performance is a subject that is not currently well understood. Coupling rheological measurements with injection molding performance is a task which can be better achieved with an understanding of the importance of mixing and batch temperature in the injection molding process.

The significance and level of comprehension on the subject of mixing in injection molding is best illustrated with a statement made by Mutsuddy:

“The mixing process is a complex phenomenon and its importance in developing ceramic injection molding has not been fully appreciated”.¹

Prior to this work, it was assumed that rheology was the primary factor controlling injection molding however, this study now suggests that there is an unexpectedly significant importance of mixing in this process.

Additionally, understanding of the importance of specimen temperature during rheological analysis is vital if greater comprehension of the material's flow behavior is desired. An investigation into the effect of rheological analysis temperature on sample viscosity and repeatability was performed.

The pre-determined requirements for an injection molding batch to be considered a viable system for this research are as follows: thermosetting, flowability, strength (needs to be handleable), and repeatability.

Four different binder systems were each tested as a potential ceramic injection molding system. These systems include:

1. TEOS (tetraethylorthosilicate)
2. PMMA (polymethyl methacrylate, two part resin)
3. PC-7 (two part epoxy paste)
4. Polyester resin (two part low viscosity resin)

An outline of the systems and the requirements which each met and failed to meet can be seen in Table I.

Table I. Four Tested Systems Showing which Requirements were Met by each. The "X" Indicates the Requirement(s) which was/were Not Met for each System

	Binder System	Thermo-setting	Flowability	Strength	Repeat-ability
Slurry mixture	TEOS	✓	✓	X	n/a
	PMMA	✓	✓	X	n/a
Plastic mixture	PC-7	✓	✓	✓	X
	Polyester resin	✓	✓	✓	X

TEOS and PMMA both demonstrated thermosetting and flowable properties as a binder system, however the lack of sufficient handling strength for both systems was cause for discontinuation of research with these systems. Additionally, no attempt was made at rheological analysis of these systems due to high fluidity.

Thermosetting behavior, flowability, and sufficient handling strength were achieved by two separate binder systems: PC-7 and polyester resin. However, a series of rheological measurements illustrated that both systems lacked repeatability. The inability to reproduce rheological data for both the PC-7 and polyester resin batches indicated that perhaps differences in injection molding performance do not stem

from variations in batch and/or rheology, but rather differing rheological behavior is caused by poor mixing and/or temperature control of the batch.

In order to evaluate sample behavior under numerous different mixing+temperature combinations, a series of rheological analyses were performed. Four different batches were produced via mechanical mixing for 8, 16, 32, or 64 minutes. Rheological behavior of each batch was then analyzed at five temperatures: 27, 31, 35, 39, and 43°C. Four iterations of every combination were executed to demonstrate repeatability, or lack thereof.

This study revealed a complex relationship between mixing time and sample temperature with both viscosity and repeatability.

It was determined that at higher temperatures, viscosity was not only lower, but also more consistent (i.e. repeatable), independent of mixing time. This behavior, however, was not seen at lower temperatures.

At lower temperatures the dependence of viscosity on mixing time is more notable, and the viscosity behavior tends to deviate from the typically expected behavior. Viscosity showed a peak in the middle of the tested mixing time range. Speculation can be made as to the cause of this behavior, but further work is necessary to confirm the exact cause of this peak in viscosity. In addition to the irregular viscosity behavior, an optimum window of mixing time to produce the best repeatability of low temperature analysis was seen between 16 and 32 minutes of mixing. Outside of this range sample repeatability was unattainable at low temperatures.

Overall, if used for injection molding, an optimum window for repeatability can be found between 16 and 32 minutes of mixing time (additional work necessary to determine exact range) greater than 36°C but no higher than 39°C in order to avoid the potential for curing due to the fact that the binder is a thermosetting polymer.

LITERATURE REVIEW

A. THERMOPLASTIC VS. THERMOSETTING POLYMERS

1. History

One of the first ever synthetically produced polymers was called Bakelite. Bakelite is a thermosetting phenol formaldehyde resin developed in 1907 by chemist Leo Baekeland.² Some of its properties included ease of moldability, an excellent ability to retain shape, and high heat resistance. However, since the development of thermoplastic binders the use of thermosets has become far less common due to the ease of use in thermoplastics. The following section aims to discuss the chemistry of thermoplastic and thermosetting polymers, how each may be used in injection molding, and the advantages and disadvantages of each. A more in depth discussion of the injection molding process will come later (Section B).

2. Chemistry

The physical difference between thermoplastic and thermoset polymers is how they are linked together and each one's response to an increase in temperature. Thermoplastic polymers are linear and branch-like in nature and undergo a reversible change upon the application of heat.³ Thermosetting polymers have a cross-linked structure and undergo an irreversible change when heated. A schematic illustrating the nature of each polymer is shown in Figure 1.

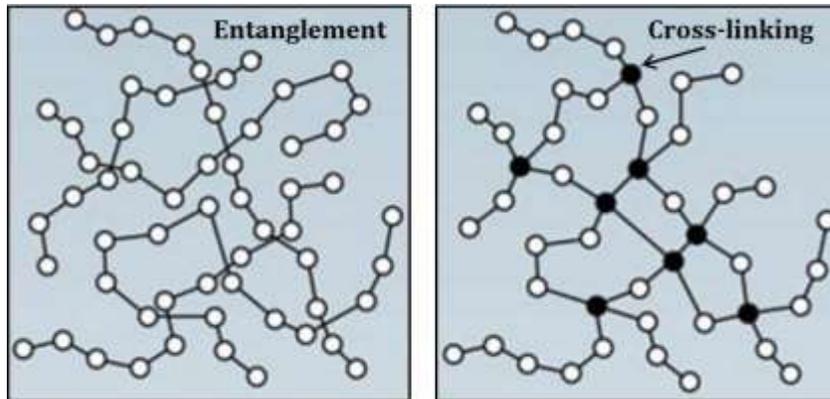


Figure 1. Schematic of the entangled nature of thermoplastic polymers (left) and the cross-linked nature of thermosetting polymers (right).⁴

Whether a polymer exhibits thermoplastic or thermosetting behavior is determined by the nature of the material's bonds. In linear and branch linked polymers (generally thermoplastic) the chains are held together by secondary bonds.⁵ Increasing temperature results in a decrease in strength of these bonds, allowing the chains to easily glide past one another. Once the temperature is decreased the polymer will experience less flowability and eventually solidify again. This heat-cool/melt-solidify cycle can be repeated over and over, making it a reversible process.¹

In cross-linked polymers (generally thermosetting) the chains are held together by very strong primary covalent bonds.⁵ Upon heating, the degree of cross-linking will further increase to result in a strongly bonded three-dimensional network of polymer chains.⁶ Once cured, a decrease in temperature will have no effect on the bonding network, making it an irreversible reaction (aka. curing). While an increase in temperature will not result in re-melting of the polymer as with thermoplastics, it may result in degradation.

3. Thermoplastic Polymers in Injection Molding

As discussed in the previous section, thermoplastic polymers undergo a reversible solidification event to produce a final part. Typical injection molded bodies are comprised of a binder system which is thermoplastic in nature. Simply applying heat to a hardened thermoplastic polymer will soften the polymer, and cooling the softened polymer will cause it to reharden. The schematic adapted from German in

Figure 2 aims to show the injection molding process used for a batch composed of a thermoplastic binder.⁷

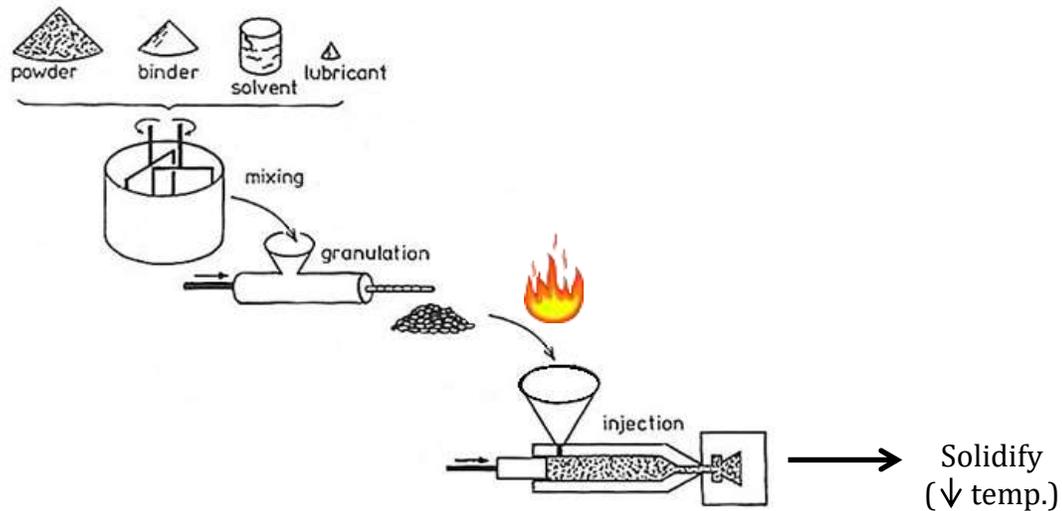


Figure 2. Schematic of thermoplastic injection molding.

Thermoplastics are often used in injection molding because of their fast solidification time as well as their ease of use in batch preparation. A big advantage of thermoplastics is their ability to be heated, thus improving flow characteristics, without causing a solidification event to occur. Additionally, thermoplastics are appealing for their ability to be recycled or reused in this process.

Some disadvantages of thermoplastics for use in injection molding include a lack of dimensional stability, poor integrity at elevated temperatures, low strength, and high cost. The potential for deformation at high temperature eliminates thermoplastics as a feasible option for high temperature-use injection molded products. For products with high temperature applications a better option would be one made with a thermosetting binder.

4. Thermosetting Polymers in Injection Molding

Unlike thermoplastic polymers, thermoset polymers are irreversible. This irreversible nature is due to cross-linking taking place within the polymer as a result of a heat induced chemical reaction.⁸ At higher temperatures the thermoset material

will begin to degrade. Figure 3 shows the injection molding process using a thermosetting binder.

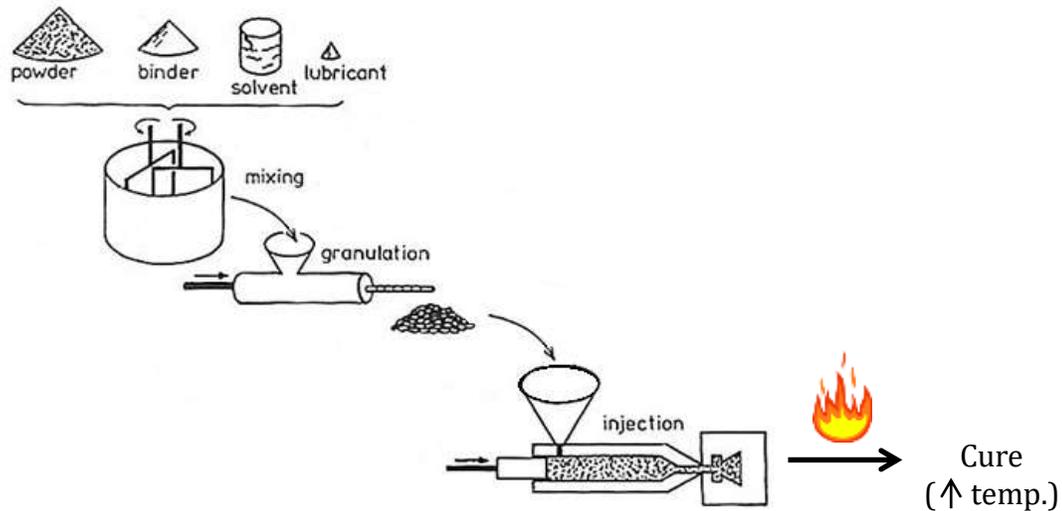


Figure 3. Schematic of thermosetting injection molding.

This indicates that, unlike with thermoplastic binders, heat is applied to the sample after injection rather than before.

Thermoset materials have the advantage over thermoplastics when it comes to strength and dimensional distortion. Injection molded pieces made of thermosets will have a higher level of strength and a decreased level of dimensional distortion, as well as better integrity at high temperatures than those made of thermoplastic materials.

On the other hand, thermoset materials are less commonly used as binders than thermoplastic materials because their slow cure time makes them less time efficient than their faster setting counterparts. Another disadvantage of using thermoset polymers in injection molding is the difficulty of achieving a homogeneous mixture. If, however, a homogeneous powder-binder mixture is obtained then it is possible to see better properties from the thermosetting system than a similar thermoplastic system.

B. BASICS OF INJECTION MOLDING

1. History

The first ever injection molding process patented by L. E. Shaw in 1959 was known as “transfer molding”.⁹ The method of transfer molding is described by the inventor as a processing method “for molding thermosetting materials whereby the material is subjected to heat and pressure and then forced into a closed mold cavity by this same pressure and held there under additional heat and pressure until cure is complete”.

At the time of this development, thermoplastic polymers were not well known or understood. One typical method for molding thermoplastics was compression molding. Later, with the introduction of fully automatic machines, thermoplastics were able to be molded via Shaw’s process which then became known as “injection molding”. It was not until much further down the road that this automated version of Shaw’s transfer mold was adapted to handle thermosetting materials.

2. Advantages of Injection Molding

Five major advantages of injection molding ceramics as discussed by Randolph are listed below:¹⁰

- Reduction of cost per part due to molding in multi-cavity molds
- Production of more complexly shaped parts in large quantity because of the method of mold filling
- Easier reproducibility of dimensions from part to part than that of machining
- Smoother surfaces of molded pieces than extruded or machines parts
- Closer tolerances are feasible as compared to traditional dry pressing methods due to the use of materials which are less sensitive to processing variables such as moisture and humidity

Money savings, improved product quality, and increased ease of production all make injection molding an attractive alternative to more traditional forming processes.

3. Disadvantages of Injection Molding

While there are many advantages of injection molding, it is also important to discuss its disadvantages. One major disadvantage of injection molding is the initial start-up costs. This includes machinery as well as molds. Another disadvantage of injection molding is the high level of binder needed for the batch which can cause complications in the binder burnout stage which could potentially result in poor quality parts.

4. The Process

Before an injection molding mixture can be formulated, powder preparation is necessary.¹¹ Appropriate processing must be performed to obtain the desired particle size, distribution, and morphology. Only after the finished powder is uniformly mixed together with the binder can the powder-binder system be placed into the injection molding machine. The injection molding machine will heat the system to a temperature above the melting point of the binder in order to form a fluid powder-binder system. This fluid system is then injected into a cold die cavity where it will begin to cool and solidify. A more thorough discussion of the molding cycle is covered

in Section 5 discussed on page 11. Before complete solidification the binder must be removed via a slow heat treatment process. This part of the injection molding process is crucial because if the binder removal occurs too rapidly it may result in a cracking and/or failure of the part.¹

Generally, binder systems are comprised of multiple components each having different melt temperatures and viscosities. Achieving a temperature that will vaporize the minor binder components and soften the major binder components will aid in the prevention of cracking. A slow heat treatment process allows for the gradual creation of capillary passages. It is important that the heating rate is slow enough to ensure that the binder is not vaporizing faster than it can escape through the pores, otherwise cracking and/or blistering may occur. The binder removal process can take between 70 and 100 hours. The final step of injection molding is to fire the debinderized part in order to achieve the final product. A schematic summarizing the injection molding process is seen in Figure 4.

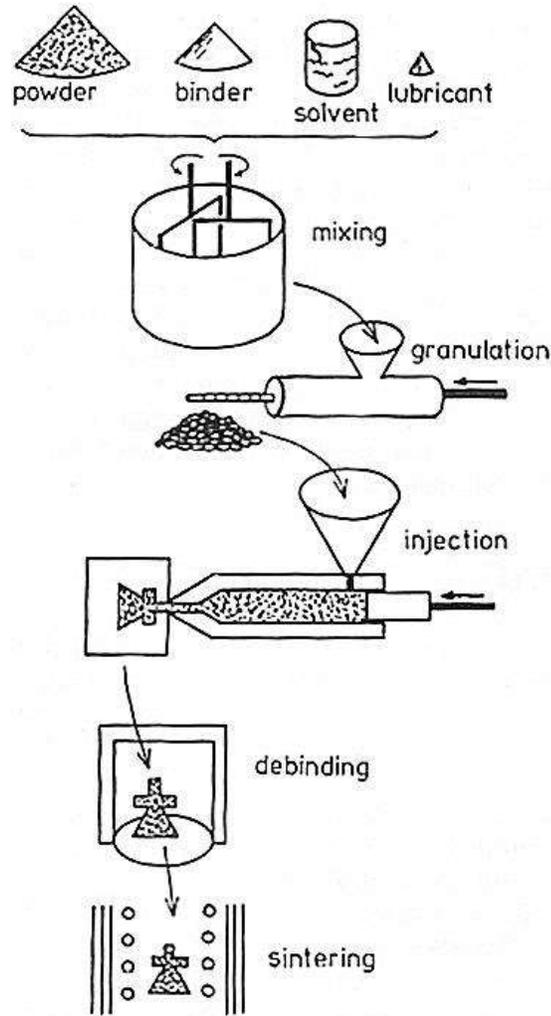


Figure 4. Schematic of the injection molding process.⁷

5. Molding Cycle

The process of injection molding consists of a six stage molding cycle. The phases are listed and outlined below as described by Mutsuddy.¹ A corresponding schematic of the described phases is shown in Figure 5.

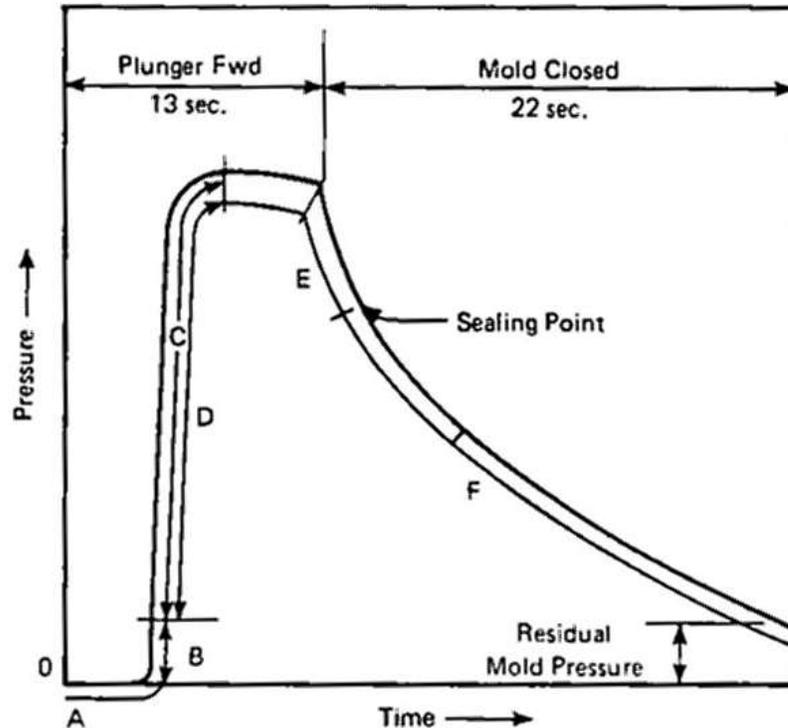


Figure 5. Molding cycle: A, dead time; B, mold-filling time; C, pressure buildup time; D, packing time; E, discharge; F, cooling with gate frozen.¹

Stage A – Dead period: the time after the plunger begins movement but before the material begins to flow into the sprue bushing.

Stage B – Mold filling period: the time during which the material flows into the mold and fills the cavity.

Stage C – Pressure build-up period: the time after the cavity is filled and the material begins to cool during which pressure in the cavity builds up to the injection pressure.

Stage D – Packing period: the time (including Stage C) during which the material flows into the cavity at a relatively low rate. The injection cycle ends with this period, and the plunger/screw retracts.

Stage E – Discharge period: the time during which the material in the gate is still fluid (and with zero pressure on the runner side and slightly less than hold pressure in the cavity) the material flow reverses.

Stage F – Cooling period: the time during which the material in the cavity cools. During this time there is no flow through the gate in either direction.

6. Molding Parameters

Pressure and temperature are both largely important parameters in the injection molding process.¹ There are three different types of pressure in injection molding which are important: injection pressure, holding pressure, and cavity pressure. A more thorough discussion of each can be found in Mutsuddy's book on page 191.¹ The second important parameter of molding is temperature. The role of temperature is important in dealing with both the batch and the mold. A change in batch temperature will alter the batch's flowability upon injection, while a change in temperature of the mold may allow the user to better tailor the set time.

EXPERIMENTAL APPROACH

Four different systems were tested as viable options for injection molding. After experimentation and evaluation, three of the systems were eliminated. In order for a system to be considered a success it must meet four specific criteria deemed essential for injection molding. These criteria include: thermosetting behavior, flowability, sufficient post-cure strength for handling, and repeatability. Table I indicates which of the requirements each system met and failed to meet. The samples in rows 1 & 2 were slurry mixtures while the in rows 3 & 4 were plastic mixtures. The difference was dictated by the binder system being used; the use of a highly-flowable binder resulted in slurries while the paste-like binders produced plastic mixtures.

TEOS and PMMA were eliminated due to their lack of strength post-cure. PC-7 was evaluated and proved to have sufficient post-cure strength, but fell short in the repeatability category. The remaining system uses a polyester resin (Polyester Fiberglass Resin, Cargroom, U.S. Chemicals & Plastics) as a binding agent.

For the purpose of clarity, four sub-sections will follow; each discussing the procedure and results of one of the four binder systems evaluated.

Tetraethylorthosilicate

A. BACKGROUND

Tetraethylorthosilicate (TEOS) was the first potential thermosetting binder to be tested. TEOS was selected as a potential binder for its ability to be slowly catalyzed, similar to thermoset injection molding, as well as its potential for high post-cure strength. Sol-gels can be produced from TEOS either by acid-catalysis or base-catalysis. Acid-catalysis of TEOS is a time consuming polymerization reaction which results in silica fibers. Base-catalysis is a nearly instantaneous reaction which results in the formation of Stober silica, or colloidal silica. The acid-catalyzed TEOS is more representative of a thermoset because of the longer time necessary to cure. For this reason, acid-catalyzed TEOS was explored as a viable option as a thermosetting binder system. A phase diagram of acid-catalyzed TEOS in a methanol medium can be seen in Figure 6.

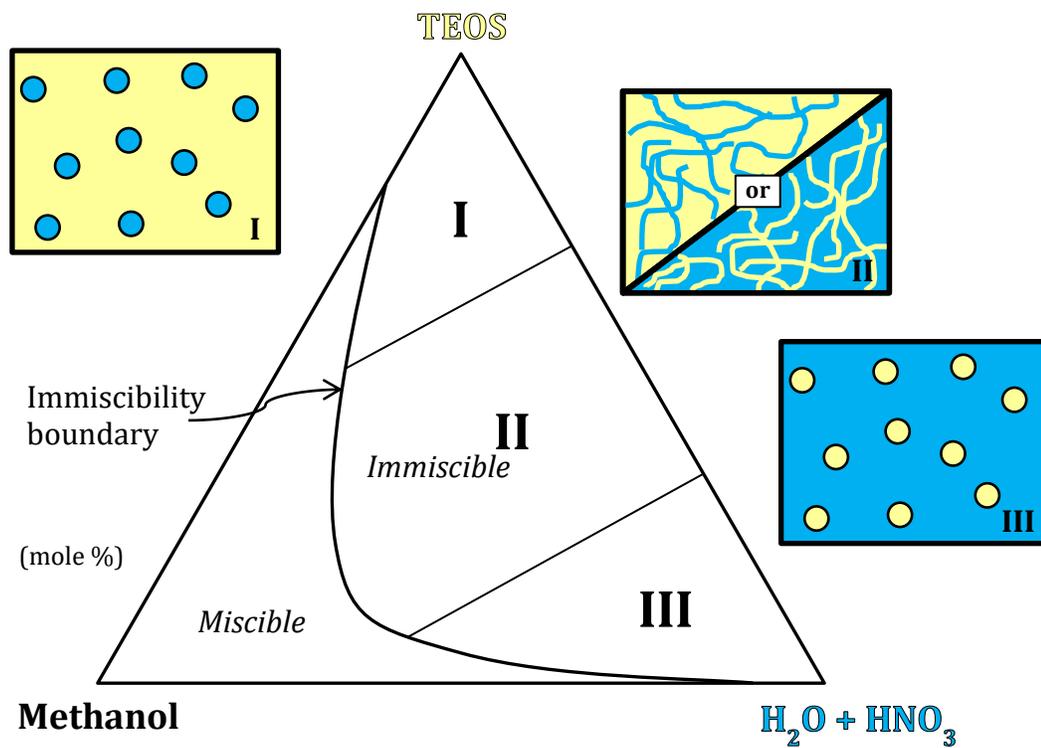


Figure 6. Phase diagram of acid-catalyzed TEOS showing the immiscibility boundary¹² and the three sub-regions within the immiscible region.

B. EXPERIMENTAL PROCEDURE

1. Regions of Immiscibility

When combined together in certain proportions, the aforementioned ingredients will experience immiscibility, or phase separation. A proposed immiscibility boundary based on past work is indicated in Figure 6.¹² Within this region of immiscibility, there are thought to be three sub-regions in which different forms of immiscibility will be seen. Region I is thought to be droplets of water + nitric acid in a matrix of TEOS, Region II will have a matrix of TEOS with large domains/regions of water + nitric acid or vice versa, and Region III will be a water + nitric acid matrix containing droplets of TEOS. The exact composition points experimentally produced in each region are shown in Figure 7.

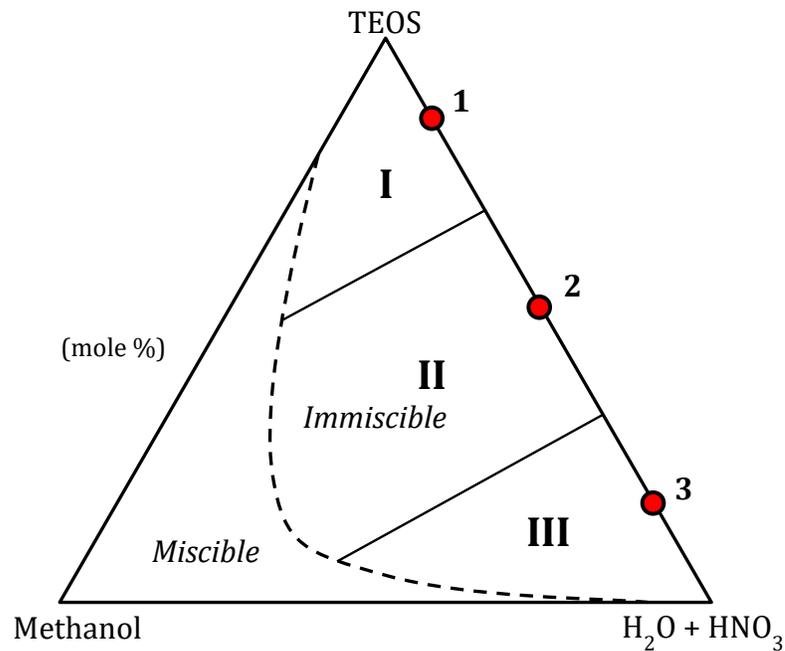


Figure 7. Dots indicate different compositions created in order to better see the effect that the acid has on the strength of the synthesized gel.

Two different concentrations of HNO_3 (0.6M and 6.0M) were used to make samples at each point in an effort to view the effect of acid strength on the final strength of the gels.

First, $\text{H}_2\text{O}+\text{HNO}_3$ solutions (bottom right corner of phase diagram in Figure 7) were made by combining water and nitric acid at a molar ratio of 1:0.0007. Two different solutions were made, one using 0.6N nitric acid and the second using 6.0N nitric acid. The first sample, Composition 1, was created as a 35g batch by combining together TEOS and water+nitric acid (using solution made with 0.6N nitric acid) in a 50mL beaker according to the molar ratio seen in Figure 7. The same procedure was repeated using the solution made with 6.0N nitric acid. This entire process was repeated to create Composition 2 and Composition 3 samples. All samples were mixed on a stir plate until homogeneous, and then covered with a glass petri dish and placed in the drying oven at 40°C for six days.

2. Gelation Trials

Once a region of ideal binder formation was determined, a sample matrix was produced (Figure 8) in order to further evaluate TEOS as a potential binder system.

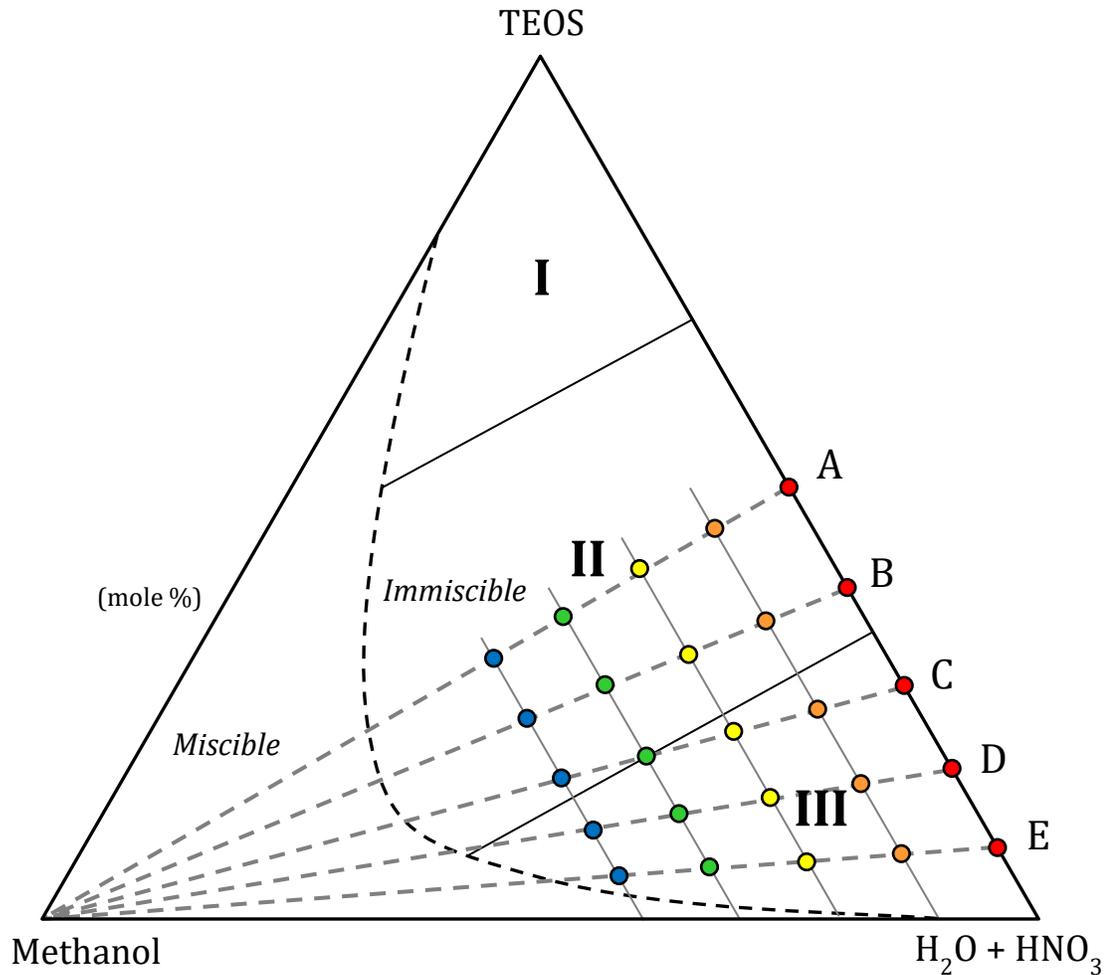


Figure 8. Phase diagram with the sample matrix overlaid.

100g batches were produced for each point on the matrix. The order of ingredient addition was TEOS, $\text{H}_2\text{O}+\text{HNO}_3$, then methanol. Mixing was achieved by placing the covered beaker on a stir plate for 1 hour, or until homogeneous. Each of the mixed 100g batches was then divided equally into six 50mL beakers and labeled for the different drying times: 3, 6, 12, 24, 48, and 96 hours. Beakers in sets of three were then covered with a petri dish and placed into a drying oven at approximately 50°C .

Samples were then removed from the drying oven at their respective drying times, photographed, and observations were recorded.

3. Incorporation of Particles

The next step in the analysis was to create compacts with glass frit (Frit 3124) and the gelling binder system to determine feasibility and select candidates for injection molding. 75mL batches of frit and gel were produced at 38v/o frit. The gels were prepared in the same manner as described previously, and then the glass frit was slowly incorporated into the gel and mixed until homogeneous. Once homogeneity was achieved, the suspension was poured into a small cylindrical mold (approximately 1.5" in diameter) and placed in the drying oven at 50°C.

4. Evaporation Trials

A suspicion that the high volatility of methanol was resulting in unanticipated and unpredictable changes in batch solids concentration lead to consideration of a new, less volatile alcohol: isopropanol.

The gel solutions were produced using the same process as before (adding TEOS, alcohol, and H_2O+HNO_3 and mixing while covered until homogeneous) and then the appropriate amount of glass frit was added slowly with mixing. This was completed at 20, 30, and 35v/o frit levels.

5. Increased Binder Level

In an effort to improve the overall integrity of the samples, another TEOS to H_2O+HNO_3 ratio, one with a higher level of binder (TEOS), was tested.

Composition F (shown in Figure 9), having a significantly higher level of TEOS, aimed to improve the sample integrity by increasing the binder yield.

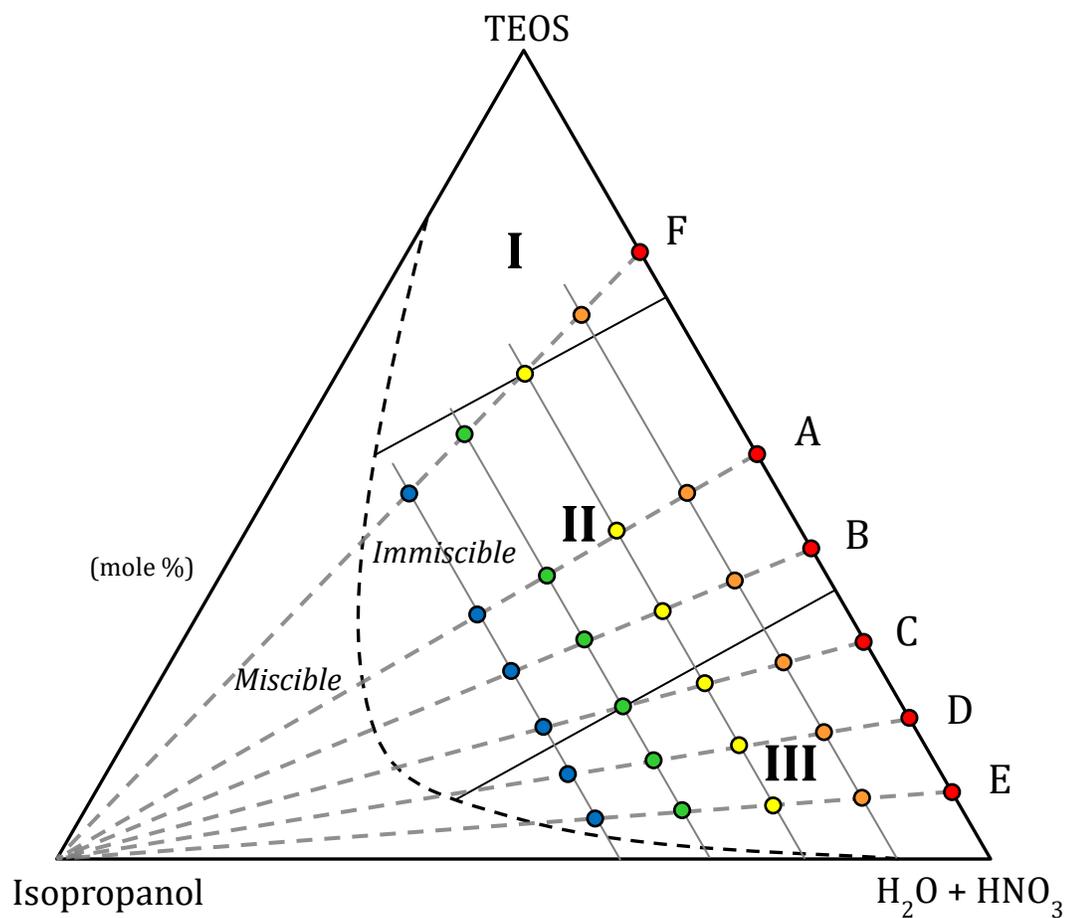


Figure 9. Sample matrix with the new TEOS-heavy samples (Composition F) indicated.

Samples were produced according to the same procedure as previously discussed, but with the use of isopropanol instead of methanol.

C. RESULTS AND DISCUSSION

1. Regions of Immiscibility

Images and observations of the samples produced according to Figure 7 can be found in Figure 10.

Composition	0.6N HNO ₃	6.0N HNO ₃	Observations
1			Mostly liquid with a few precipitated chunks
2			Partially liquid system with large rigid precipitates
3			Rigid, brittle precipitates

Figure 10. Pictures and observations of acid-catalyzed TEOS after curing for six days at 40°C.

The goal of this experiment was to evaluate the difference in sol-gel quality between the three different proposed immiscible regions and to assess the effect of acid concentration on the final quality of the gel to better determine the ideal region to produce a strong, thermosetting binder. From this trial it was concluded that Regions II and III show the most promise in terms of producing a strong binder system. Additionally, the acid concentration only appeared to have a notable effect on

the samples in Region I where having a higher concentration of acid resulted in a greater final quantity of precipitates.

2. Gelation Trials

The gel time necessary to achieve the highest strength of each sample is indicated in Figure 11. Additionally, many of the samples experienced degradation of strength with time; this is indicated on the plot in Figure 11 using a color code.

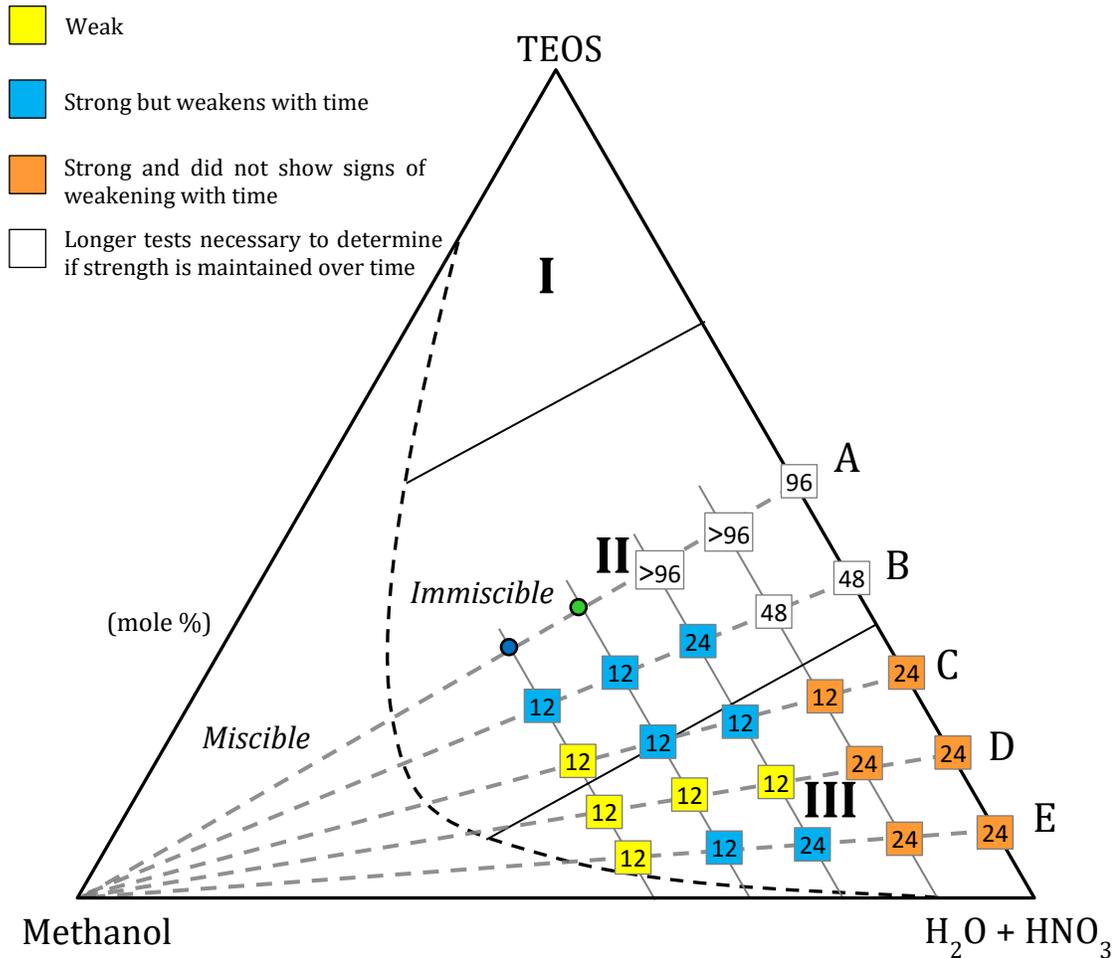


Figure 11. Gel time (in hours) until the highest strength was achieved. Hours are seen in the boxes located at each composition point. The color code helps illustrate which samples experienced strength degradation.

Contact angle measurements of the TEOS binder solution compositions were performed to ensure that the binder will in fact wet the particles as is necessary to produce a strong part. This testing confirmed that all of the TEOS binder solution compositions will exhibit wetting behavior of the particles in a loaded suspension.

3. Incorporation of Particles

Figure 12 shows the results/observations of introducing frit into the gels.

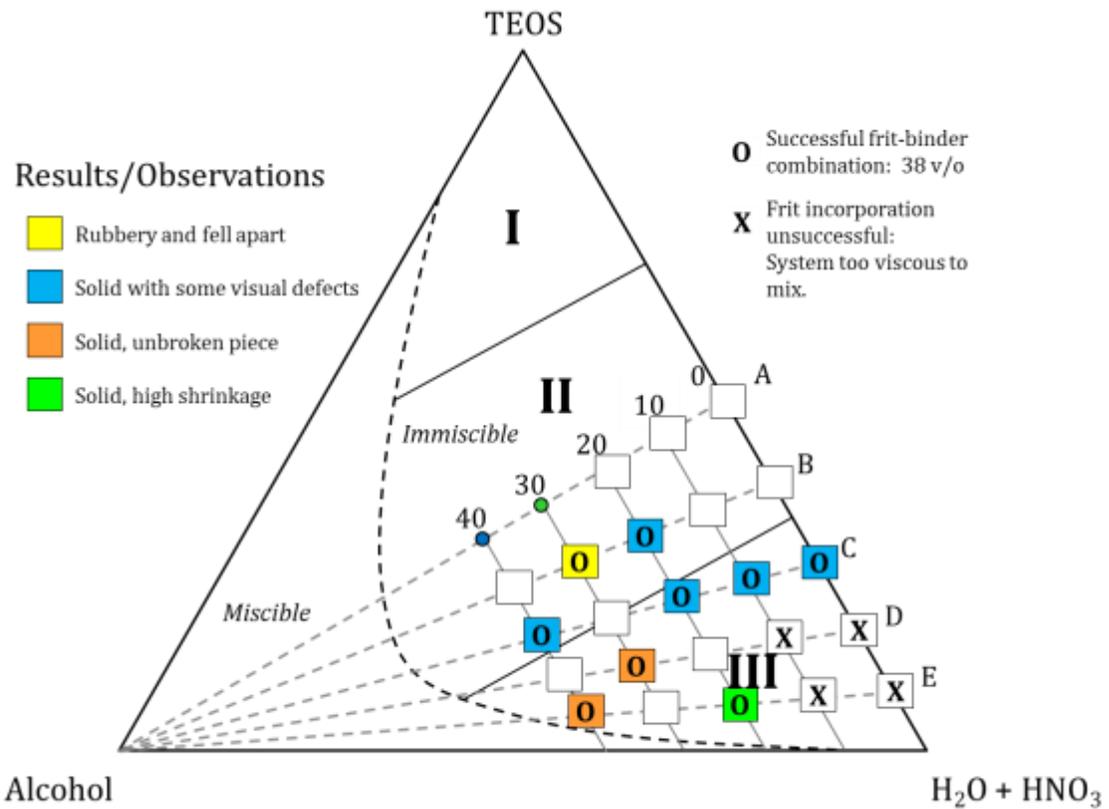


Figure 12. Results of combining gels with powder (Frit 3124).

Some of the compositions were unable to achieve homogeneity without substantial agglomeration resulting in a batch too viscous to mix; these instances are indicated with an “X” on the phase diagram shown in Figure 12. Other samples tested that successfully combined together the frit and gel are represented on the same diagram with an “O”. The post-cure observations and varying physical integrity of the different compacts is illustrated using the color code.

Digital and SEM images of samples 30B and 30D were captured to examine the microscopic structure of a poor sample and a good sample. These images are seen in Figure 13.

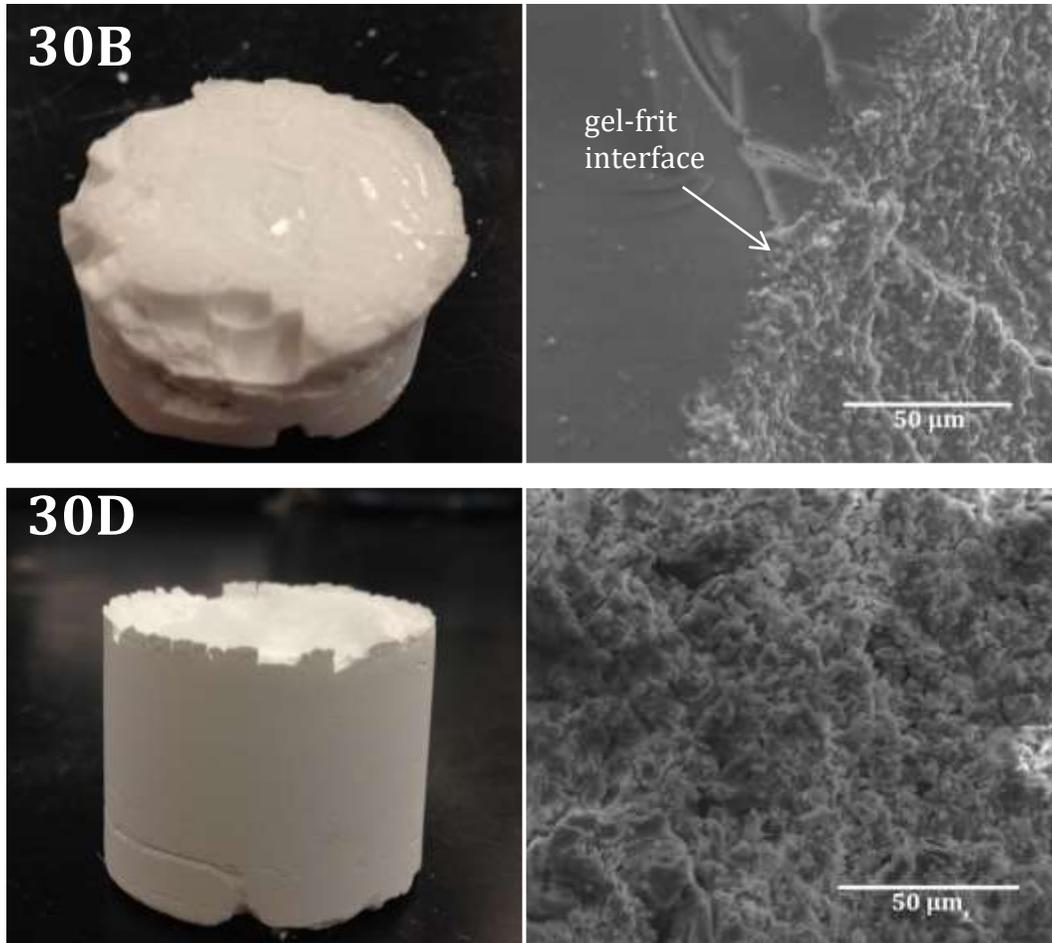


Figure 13. Digital images (left) and SEM images (right) of samples 30B and 30D.

Post-cure, sample 30B had a rubbery appearance and feel, and lacked physical integrity as it crumbled and fell apart upon handling. This is likely due to the segregation of the binding gel from the particles. A distinguishable gel-frit interface is seen in the SEM image of this sample to support this hypothesis. Sample 30D was a solid, unbroken piece which was much more uniform in microstructure. The improved integrity of this sample can likely be attributed to the uniform distribution of the binding gel system throughout the powder matrix. In order to assign a quantitative value of strength to each compact, B-bars were created for samples 30D, 30E, 40D, and 40E. Due to the affinity of the suspensions to the aluminum mold, the bars were not allowed to shrink freely and thus did not result in any testable B-bars. The trial however, did allow for qualitative shrinkage information to be determined

based on the cracking of each sample. The performance of the samples from lowest to highest level of shrinkage was 40E, 30E, 40D, and 30D. So, the level of shrinkage appeared to increase as a function of the level of TEOS present in the samples. However, the primary issue is that the samples all lacked the integrity desired of an injection molded part.

4. Evaporation Trials

Investigation into an alternative alcohol for use in this binder system lead to the conclusion that isopropanol is an acceptable substitute. Table II shows the evaporation rates of both methanol and isopropanol under covered and uncovered conditions.

Table II. Evaporation Rate Measurements of Uncovered and Covered Methanol and Isopropanol

	Evaporation rate @ 21°C [mg/min]	
	Uncovered	Covered
Methanol	74.5	5.26
Isopropanol	34.8	1.67

It is observed that the lowest rate of evaporation is achieved using a covered isopropanol sample.

5. Increased Binder Level

Samples produced having a greater yield of TEOS binder did not result in improved post-cure integrity of samples.

D. CONCLUSIONS

Despite the increase in the level of TEOS as well as the switch to an alcohol with a lower evaporation rate, a favorable batch was still not achieved. In the past, the frit plus methanol-containing gel resulted in a cake batter-like consistency. Isopropanol did not produce acceptable results due to the fact that the frit agglomerated and settled out quickly, leaving the gel on top and unmixed. It was concluded that

methanol produced better results with limited segregation (suggesting that methanol is functioning as a dispersant). Since a binder system having sufficient integrity was not produced using either methanol or isopropanol, the TEOS trials were terminated.

Polymethyl Methacrylate

A. BACKGROUND

The second potential binder evaluated for use as a thermoset injection molding binder system was polymethyl methacrylate (PMMA) which is a self-setting two part epoxy resin known as Quickmount manufactured by Fulton Metallurgical Products Corporation. This two part epoxy resin consists of a powder resin and a liquid catalyst. PMMA was selected as a potential candidate binder system because being a two part system allows the potential to tailor solidification rate and/or strength by altering the ratio of the two parts.

B. EXPERIMENTAL PROCEDURE

1. Tailoring Set Time

One important condition for rheological testing is that the samples do not begin setting during testing. This is vital for two reasons: setting while collecting measurements can 1) result in variable data since the material is changing during measurements, and 2) cause breakage of the equipment if the system becomes too rigid. All rheological tests are planned to run no longer than ~40 minutes, so an ideal system would have a set time ≥ 45 minutes. Phase separation and poor strength are also two other properties which would eliminate a potential system from consideration. The epoxy ratios tested are shown in Figure 14.

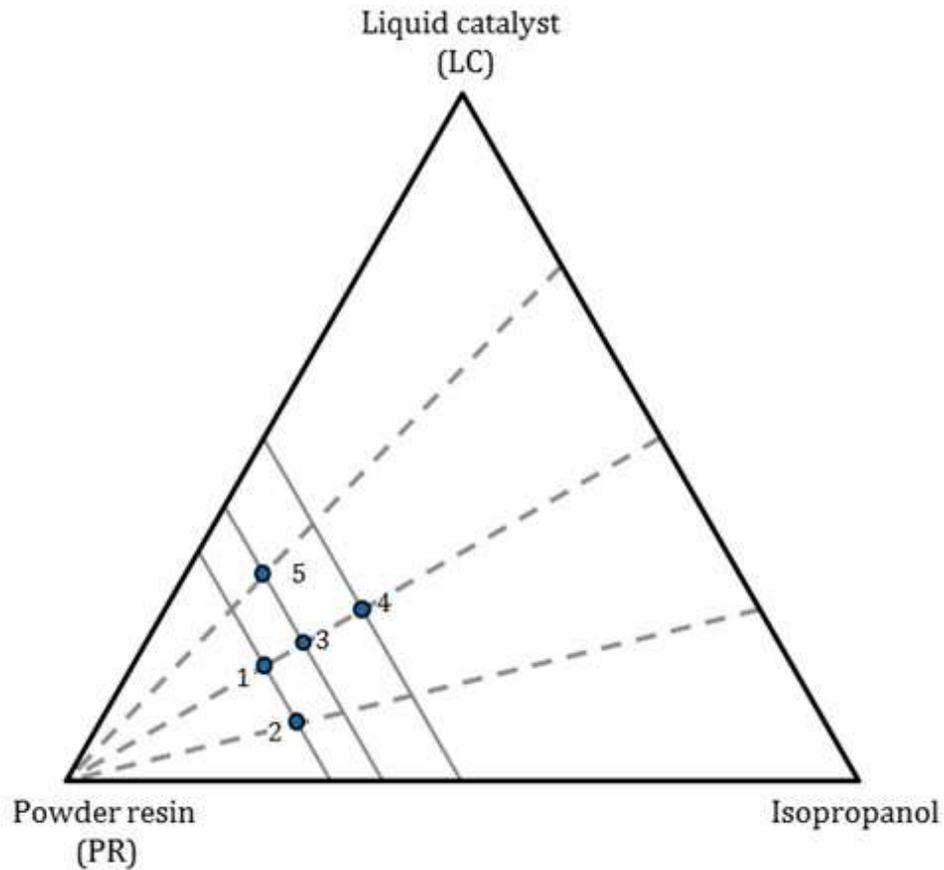


Figure 14. Ternary diagram outlining the different ratios of liquid catalyst, powder resin, and isopropanol tested to produce the ideal binder system.

2. Selecting Binder Level

After determining the binder composition, the next step was to determine the quantity of binder necessary to give the system sufficient strength while maintaining flow. When using binders it is important to determine the lowest level necessary to result in the desired strength. Excess binder can result in greater shrinkage or open porosity after the burnout cycle. To better determine the ideal binder level necessary for this system, batches having different binder levels were produced. All batches were 38v/o A-15 SG. Dry ingredients (A-15 and powder resin) and wet ingredients (isopropanol and liquid catalyst) were measured and mixed separately before combining and mixing by hand to homogeneity in a plastic weigh boat.

3. Injection Molding

Having developed a binder system that fulfills all of the criteria previously mentioned (flowability, slow set time, high cure strength), the next step was to produce an injection molded piece. Important criteria for the injection molding process include flowability, set time, and post-cure handleability of the piece. A 30v/o A-15 SG batch with 5w/o binder was created according to the same procedure outlined in section 2. Once homogeneity was achieved, the sample was injected into the mold and allowed to cure at room temperature for 24 hours.

C. RESULTS AND DISCUSSION

1. Tailoring Set Time

Qualitative results of the set time trials can be found in Table III. Sample numbers in **Table III** can be cross-referenced with the ternary diagram in Figure 14. The composition which resulted in the best combination of final properties was Sample 5. A slow cure and no phase separation upon mixing will allow for proper rheological testing of the system.

Table III can be cross-referenced with the ternary diagram in Figure 14.

The composition which resulted in the best combination of final properties was Sample 5. A slow cure and no phase separation upon mixing will allow for proper rheological testing of the system.

Table III. Ratios of PMMA Ingredients Tested and Corresponding Results. The Best System Produced is Outlined in Bold. (LC=liquid catalyst, PR=powder resin)

Sample #	LC : isopropanol	PR : LC+isopropanol	Results
1	1:1	2:1	Solid in 7-10 minutes
2	1:3	2:1	Not flowable
3	1:1	3:2	Slow cure. Isopropanol separated out
4	1:1	1:1	Slow cure. Isopropanol separated out, but not as much as sample 3
5	2:1	3:2	Slow cure. No separation

2. Selecting Binder Level

The binder levels tested in sequential order with qualitative results are shown in Table IV.

Table IV. Determining the Ideal Binder Level of Rheology Testing Using PMMA. The Selected Binder Level is Outlined in Bold

Binder level (w/o)	Results
9.5	Semi-flowable ~4 minutes until non-flowable 20+ minutes until solidified
1.25	Highly flowable No strength once cured
5	Semi-flowable Moderate to high cure strength
4	Semi-flowable (better than 5w/o) Brittle and weak once cured

The reason(s) for rejection of each eliminated sample is highlighted in bold. For example, 9.5w/o binder was eliminated from consideration because it would not have been flowable long enough to complete rheological measurements. On the other hand, qualitatively, 1.25w/o had the best flow of all of the samples, but exhibited no strength after cured. The sample which had the best combination of flow and strength was the 5w/o sample.

3. Injection Molding

The result of injection molding was a solid, green part (Figure 15, left image) having a large amount of open porosity, poor to fair green strength, and good handleability until it dried. Upon drying, the part became too fragile to handle (Figure 15, right image).



Figure 15. Green injection molded part with a PMMA binder system. On the left is the part before drying. The right image is the part after drying.

D. CONCLUSIONS

Despite the success in producing an injection molded piece, the strength was not sufficient to be considered a good quality injection molded part when using 5w/o binder. An effort to improve the overall strength was made by performing additional binder level analysis at finer increments. 38v/o A-15 SG samples were made with binder levels from 4.0 to 6.0w/o at 0.25 intervals, the balance being isopropanol. However, this set of tests confirmed that the binder level previously being tested, 5.0w/o, resulted in the best possible combination of flow and strength for this binder system. Due to this, PMMA testing was discontinued.

Two Part Epoxy – PC-7

A. EXPERIMENTAL PROCEDURE

1. Batching

A switch to tabular alumina (T-64, 325mesh, Almatix, Leesburg, PA) was made in an effort to achieve more predictable powder behavior due to uncertainty of the current A-15 SG alumina powder lot. 38v/o alumina batches were produced with a 5w/o binder (20v/o) and the balance being isopropanol. The procedure for batching was as follows: Mix together Part A and Part B of the epoxy at a 1:1.78 volume ratio in a plastic weigh boat. Once uniform, isopropanol was poured in and stirred until the epoxy began to soften up and dissolve into the isopropanol. Alumina was then added and mixed by hand with a small metal spatula until homogeneous. Homogeneity was an ongoing challenge with this system due to the paste-like nature of the epoxy.

2. Determining Rheological Procedure

Rheological procedure is a set of different parameters that when combined together will allow for the measurement of reliable sample rheology data. These parameters include shear rate, points collected per decade, equilibrium time, and averaging time.

It is important to perform shear rate sweeps from high to low shear rates (as opposed to low to high shear rates) so that the sample has the same shear history at each collection point. “Points collected per decade” is the number of points collected per shear rate decade. This parameter can be adjusted to improve the resolution of the data (such as eliminating scatter or smoothing the curve). The trade-off for improved data resolution is a longer sample analysis time. “Equilibrium time” is the time during which the sample is undergoing shear before any data for that particular shear rate begins generating. The amount of time that data is collected before being averaged to result in one data point is known as the “averaging time”.

A series of steady state trials was performed in order to determine an ideal set of parameters for all future rheological testing. Table V outlines the different combinations of parameters tested in chronological order.

Table V. Various Procedures Tested to Determine an Appropriate Procedure to Use for Future Testing

Procedure Name	Shear rate [s⁻¹]	Points collected per decade	Equilibration time [s]	Averaging time [s]
SS_01	100-0.01	5	20	10
SS_02	100-0.1	5	20	10
SS_03	100-0.01	5	10	5
SS_04	100-0.01	3	20	10
SS_05	100-0.01	3	10	5

The batch used for these procedural analysis tests was a 38v/o alumina batch with 5w/o epoxy using an isopropanol medium.

3. Sample Preparation and Selection

Upon completion of parameter testing, the best of the five was selected: Procedure SS_04 as noted in Table V. All tests were run using an angular frequency of 10rad/s. To perform rheological testing of a sample the sample must be loaded onto the bottom parallel plate so that a barrier can then be produced around it to prevent any evaporation of isopropanol during analysis. A schematic showing the barrier can be seen in Figure 16.

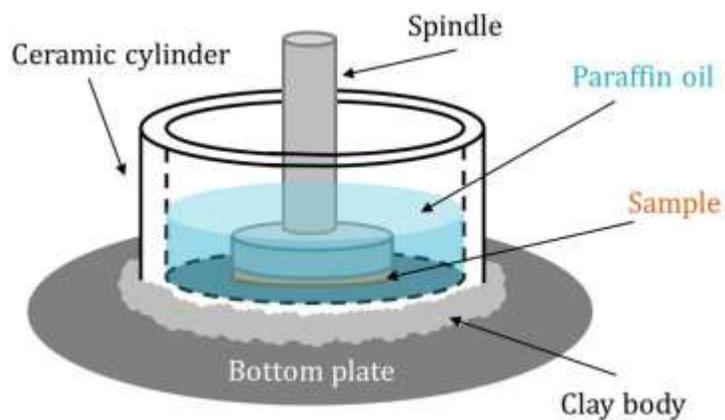


Figure 16. Schematic of the sample within a paraffin-filled reservoir.

The barrier consists of a ceramic cylinder around the sample and a clay body along the cylinder-plate interface to act as a seal. Once sealed, the spindle is lowered to the “geometry gap” to create contact with the sample. Paraffin oil is then poured into the cylinder until it reaches a level to sufficiently cover the sample on all sides. After completing the barrier, testing can begin.

The tested compositions are shown in the ternary phase diagram shown in Figure 17. These samples were batched according to the procedure outlined in Section 1 on page 34.

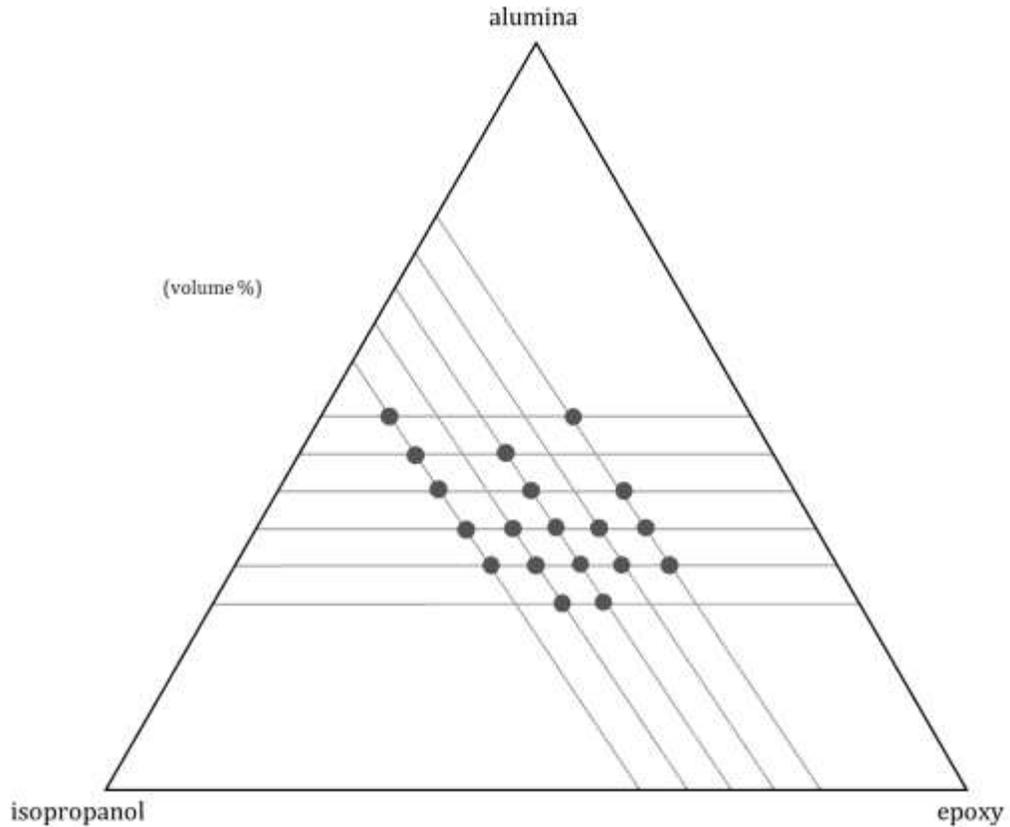


Figure 17. Compositions tested for rheological behavior.

B. RESULTS AND DISCUSSION

1. Flowability and Integrity

Previous systems resulted in batches having a viscosity too low for rheological analysis due to their slurry-like nature. This system's paste-like nature had flowability allowing for easy rheological analysis. Due to this sufficient level of flow, rheological analysis was able to be executed to further establish the viability of this system as an injection molding candidate.

The post-cure strength of this system allowed for great handleability and no fear of disintegration upon drying. Difficulties in producing mechanical strength test bars arose due to the fact that PC-7 is often used for metal adhesion thus eliminating the possibility of producing test bars with a metal mold, however the qualitative strength of these specimen exceeded that of the previous systems, thus allowing for further investigation.

2. Rheological Procedure

Preliminary oscillatory rheological testing was performed using a stress-controlled rheometer (DHR-2, TA Instruments, New Castle, DE) at an angular frequency of 10 radians per second, strain sweep from 100 to 0.01%, 3 data points collected per decade, and an equilibration and sampling time of 30 and 15 seconds respectively. The data collected from these runs contained a large amount of scatter so the gap distance between the parallel plates was increased (from 1mm to 1.5mm) in an effort to increase the amount of sample being tested, and the sampling time per point was lengthened to allow for a greater data collection period; these changes resulted in an improvement, but not complete elimination, of data scatter.

A series of steady state trials, as outlined in Table V, lead to the final selection of Procedure SS_04 (shear rate: 100-0.01s⁻¹, points per decade: 3, equilibration time: 20 seconds, and averaging time: 10 seconds). This was procedure was used for all future rheological measurements. All measurements were collected at an angular frequency of 10rad/s.

3. Rheological Analysis

The results of the rheological analysis are shown in a ternary diagram in Figure 18. An “X” over a composition point indicates an unmixable sample or one that exhibited little to no flow and thus was ineligible for rheological characterization. The remaining compositions were characterized using the rheometer in an effort to produce a contour map of viscosity – seen in the magnified portion of Figure 18.

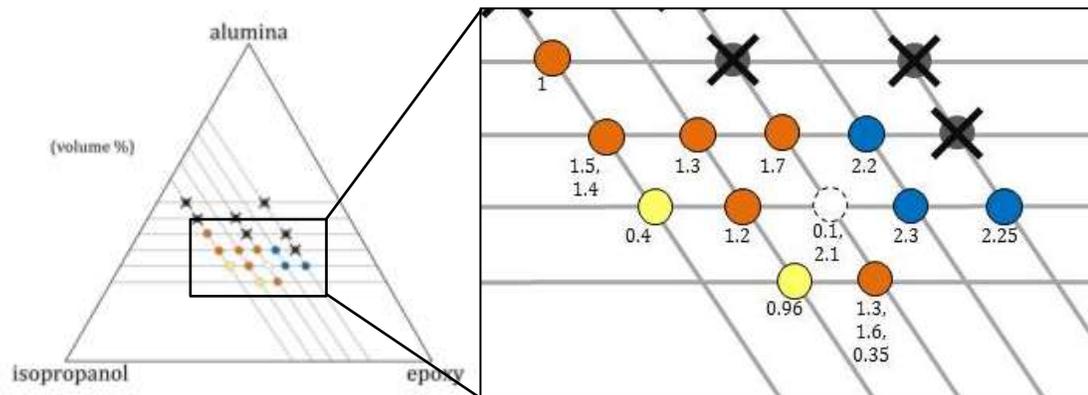


Figure 18. Log viscosity at 1.0s^{-1} is shown below each tested composition point. For ease of comprehension, each order of magnitude is indicated by a different color (in order of increasing magnitude: yellow, orange, blue). The white point indicates a composition that was unable to achieve repeatable data.

Despite many attempts, repeatable data for the composition point indicated with the white circle was not achieved. Due to this irreproducibility the validity of all other points, which were only tested once, was called into question. This observation led to additional measurements at other points, which ultimately revealed a lack of repeatability among not one, but numerous composition points. This poor repeatability would explain the seemingly random data observed in Figure 19.

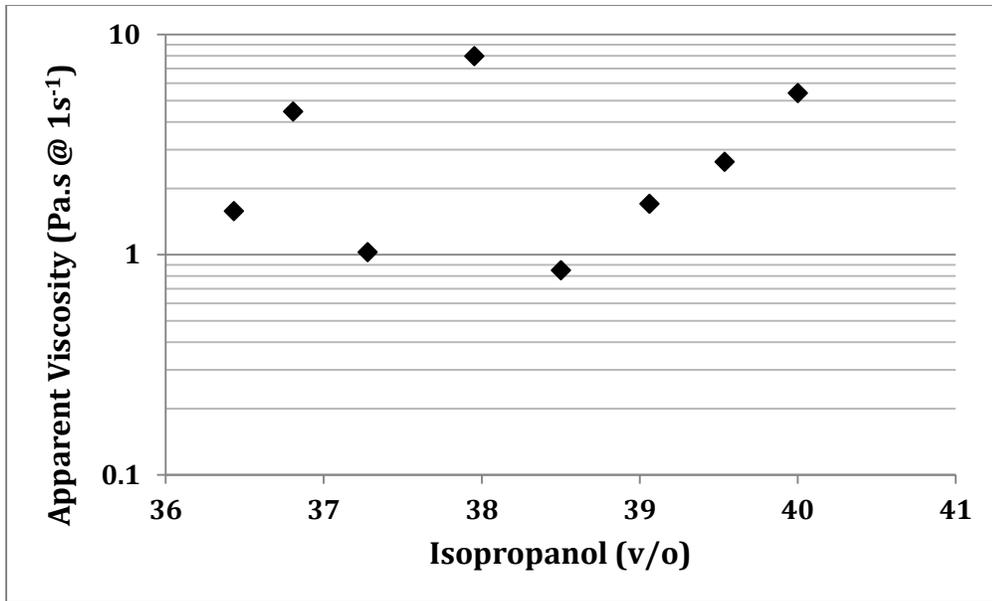


Figure 19. Plot of viscosity as a function of isopropanol level showing a lack of trend at low liquid levels (v/o isopropanol) and a trend at higher liquid levels indicating that viscosity increases with liquid level.

The data shown in Figure 19 was collected by producing a batch having the following composition: 30v/o alumina, 40v/o isopropanol, 30v/o epoxy. Rheological analysis was then performed on a 2mL sample of the batch at 31°C and according to the previously discussed rheological analysis parameters. During testing the batch was left exposed to the atmosphere to allow for evaporation of isopropanol, thus changing the solids concentration of the batch but maintaining a one-to-one volume ratio of alumina to epoxy. The new solids concentration was then calculated and analysis was repeated on a small sample of the new batch. This was repeated until a total of eight different compositions were tested. As the solids concentration increases (i.e. isopropanol level decreases) it would be expected that the viscosity should increase, however this data demonstrates a lack of trend between solids concentrations and viscosity.

C. CONCLUSIONS

A sound rheological procedure was successfully developed for use during rheological analysis of specimens. Additionally, a paraffin barrier system was produced to decrease the amount of environmental contact the specimen has during analysis.

Despite the fact that the PC-7 system demonstrated sufficient flow, strength, and thermosetting properties for injection molding, the inability to produce a reliable set of data was reason enough for the termination of these trials.

Polyester Resin

A. EXPERIMENTAL PROCEDURE

1. Sample Preparation

Two different sample preparation avenues were explored, each dealing with a different mixing technique. The first was hand-mixing and the second incorporated the use of a mechanical screw mixer known as a sigma mixer (Prep-mixer, C.W. Brabender Instruments Inc., So. Hackensack, NJ). Samples composed of various ratios of alumina, isopropanol, and polyester resin were produced. The different compositions created are shown in Figure 20.

2. Hand Mixing

To produce the hand-mixed samples, isopropanol and polyester resin were combined together in a plastic weigh boat and mixed by hand with a metal spatula until the appearance of homogeneity was achieved. Once mixed, alumina was added in slowly and mixed to uniformity. Each of the composition points shown in Figure 20 were produced using this hand mixing method. The quantitative compositions of the corresponding points are listed in volume percent and weight percent in Table VI.

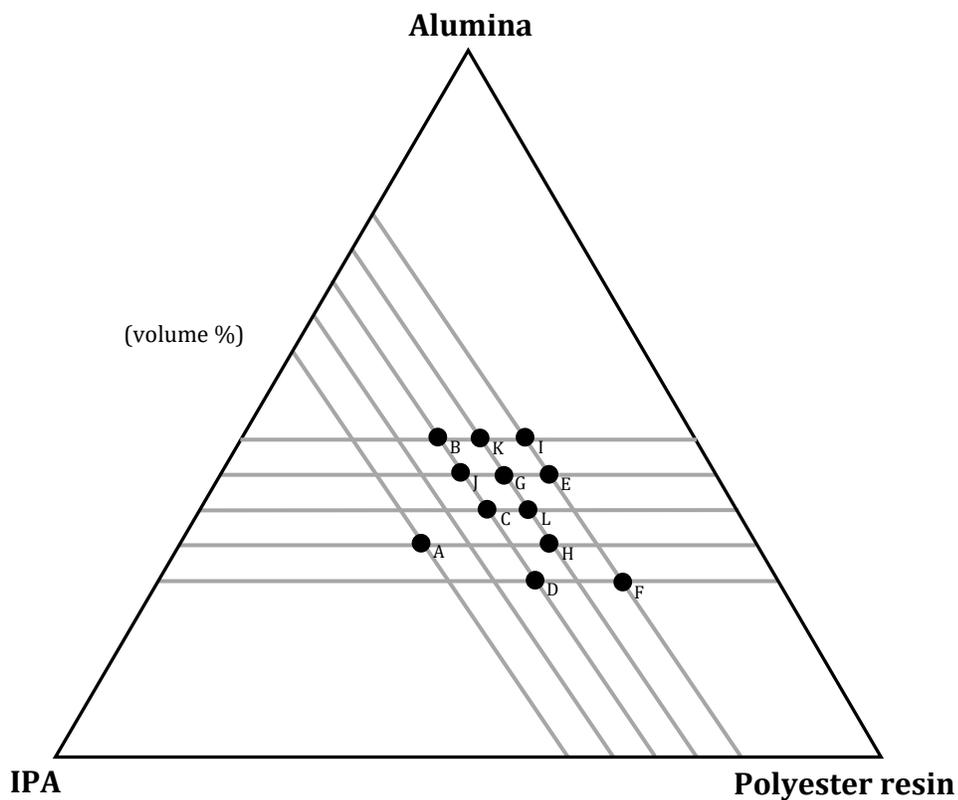


Figure 20. Sample matrix illustrating the compositions that were produced using a polyester resin binder system.

Table VI. Compositions of Tested Samples in Volume Percent and Weight Percent

Volume percent (v/o)			Sample ID	Weight percent (w/o)		
Alumina	IPA	Polyester resin		Alumina	IPA	Polyester resin
25	20	55	F	56	9	36
25	30	45	D	57	13	30
30	25	45	H	63	10	27
30	40	30	A	65	17	19
35	25	40	L	68	9	22
35	30	35	C	69	11	20
40	20	40	E	72	7	21
40	25	35	G	73	9	18
40	30	30	J	73	11	16
45	20	35	I	76	7	17
45	25	30	K	77	8	15
45	30	25	B	78	10	12

3. Mechanical Mixing

Mechanically mixed samples were produced to better determine the effect of mixing on sample repeatability. For this test, Composition I (indicated in Figure 20) was produced repeatedly with varying levels of mixing. All samples were mixed in a sigma mixer. Images of the sigma mixer used for mechanical mixing are shown in Figure 21. 250mL batches were produced. Alumina and polyester resin were each weighed out in individual weigh boats while a glass beaker was used to hold the isopropanol. No catalyst was added to the system so as to avoid the sample curing within the mixer. Once ingredients were measured, the sigma mixer was turned on and half of each ingredient was poured into the chamber in the following order and allowed to mix: alumina, polyester resin, isopropanol. The remainder of each ingredient was then added using the same order as before. To determine the effect of mixing, a number of batches were produced with mixing times of 8, 16, 32, and 64 minutes. Upon completion of mixing, approximately 100mL of sample was removed from the sigma mixer and divided between two 60mL syringes to reduce evaporation of isopropanol since the characterizations do not occur simultaneously, but rather consecutively.



Figure 21. Sigma mixer as it would appear during use (left) and opened up to show the screws which rotate within the mixing chamber (right).

4. Sample Characterization

a) Rheology

Rheological characterization of samples was performed using a stress-controlled rheometer (DHR-2, TA Instruments, New Castle, DE) with a 40mm parallel plate and

a high temperature spindle (#998738). The parameters used to collect rheological data are listed in Table VII and were determined based on a series of trials outlined in the section titled PC-7.

Table VII . Testing Parameters for Rheological Analysis

Parameter	Specification
Temperature	test dependent
Soak time	30 seconds
Shear rate	100-0.01s ⁻¹ (tested from high to low)
Points collected per decade	3
Equilibration time	20 seconds
Averaging time	10 seconds
Geometry gap distance	1500μm

With a clean platen and spindle, the specimen (calculated to be approximately 2mL) can be loaded onto the bottom platen. The spindle is then lowered to the “trim gap” (geometry gap distance + 200μm). At this point the spindle and specimen come in contact causing excess material to be pushed out from between the spindle and bottom platen. This excess material is trimmed, or wiped, away. The spindle is then instructed to go to the “geometry gap” which is the gap distance at which the measurement will take place. Once at the geometry gap a cover is placed over the spindle and specimen to decrease the amount of specimen-to-environment interaction and the test is begun.

Measurements were performed under the aforementioned conditions for each of the four different mixing times at 27°C, 31°C, 35°C, 39°C, and 43°C.

b) Microstructure

Microstructural imaging was performed via SEM on cured then fractured samples (FEI Quanta 200f Environmental Scanning Electron Microscope (ESEM), FEI, Delmont, PA). Specimens were fractured and mounted to metal stubs using carbon tape and sputter coated with Au-Pd prior to imaging.

B. RESULTS AND DISCUSSION

1. Hand Mixing

Three specimens having the composition of Sample I shown in Figure 20 were created using the hand-mixing procedure previously discussed. Rheological analysis shows a lack of repeatability from specimen to specimen. This is seen in the plot of viscosity as a function of shear rate shown in Figure 22. At high shear rates the same sample compositions were resulting in notably different viscosity measurements.

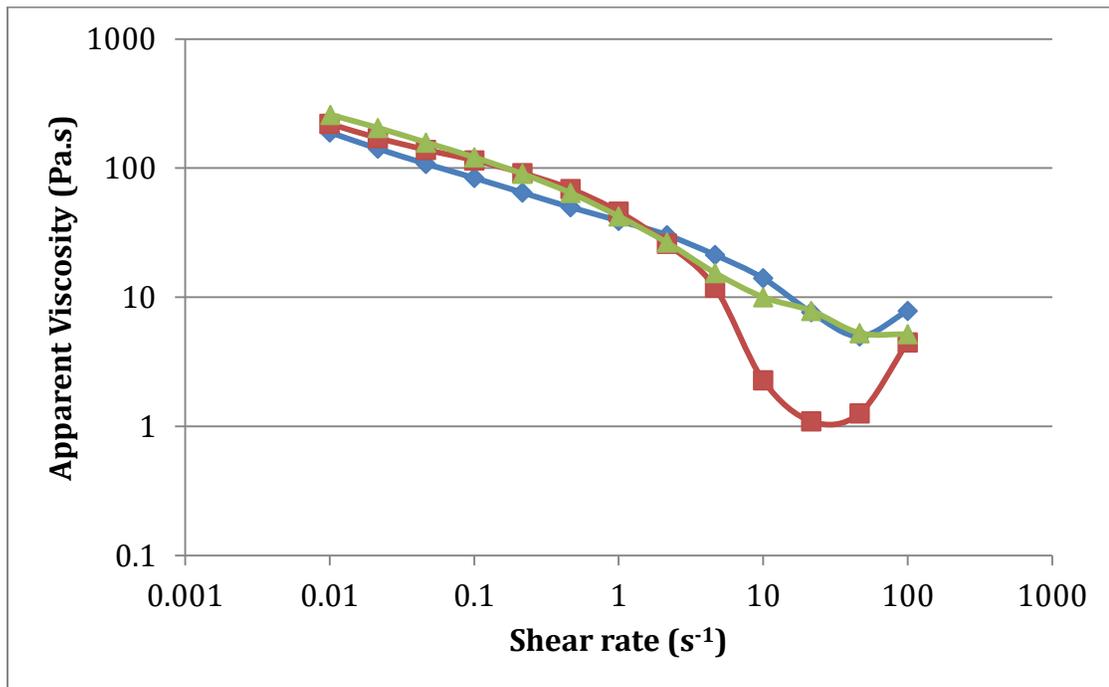


Figure 22. Plot of viscosity as a function of shear rate for three iterations of Sample I. Plot shows lack of repeatability in high shear rate regions.

SEM images were collected to get a microscopic visual of the hypothesized poor mixing of the samples. An example is shown in Figure 23.

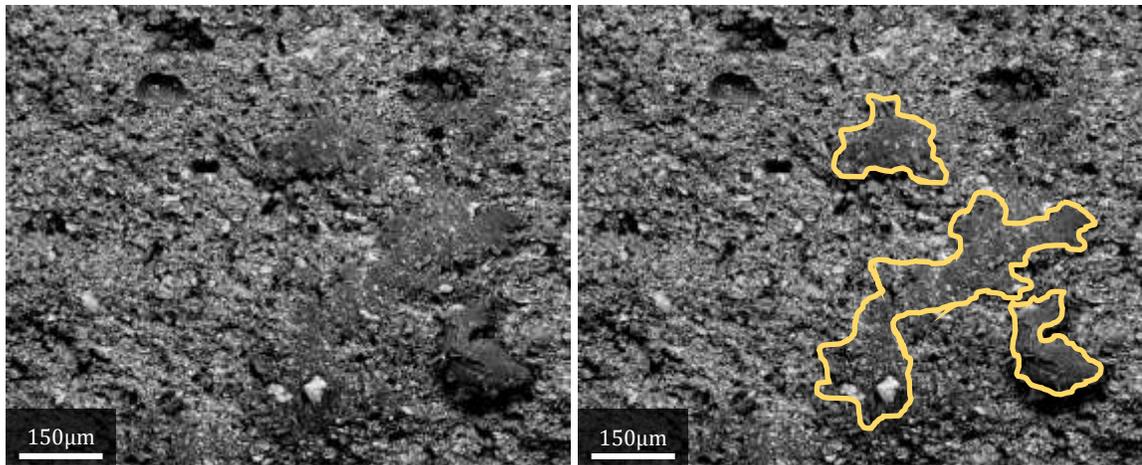


Figure 23. BSE SEM image of a cured sample that was hand-mixed. The same image is shown side by side, but regions of non-uniformity are outlined in yellow in the right image demonstrating the poor level of mixing at a microscopic level.

This backscattered SEM image shows the presence of alumina (light regions) and binder (dark regions outlined in yellow) domains rather than the desired uniform distribution of ingredients throughout the specimen. Another specimen having the same composition showed a vastly different microstructure. SEM images of this specimen are seen in Figure 24.

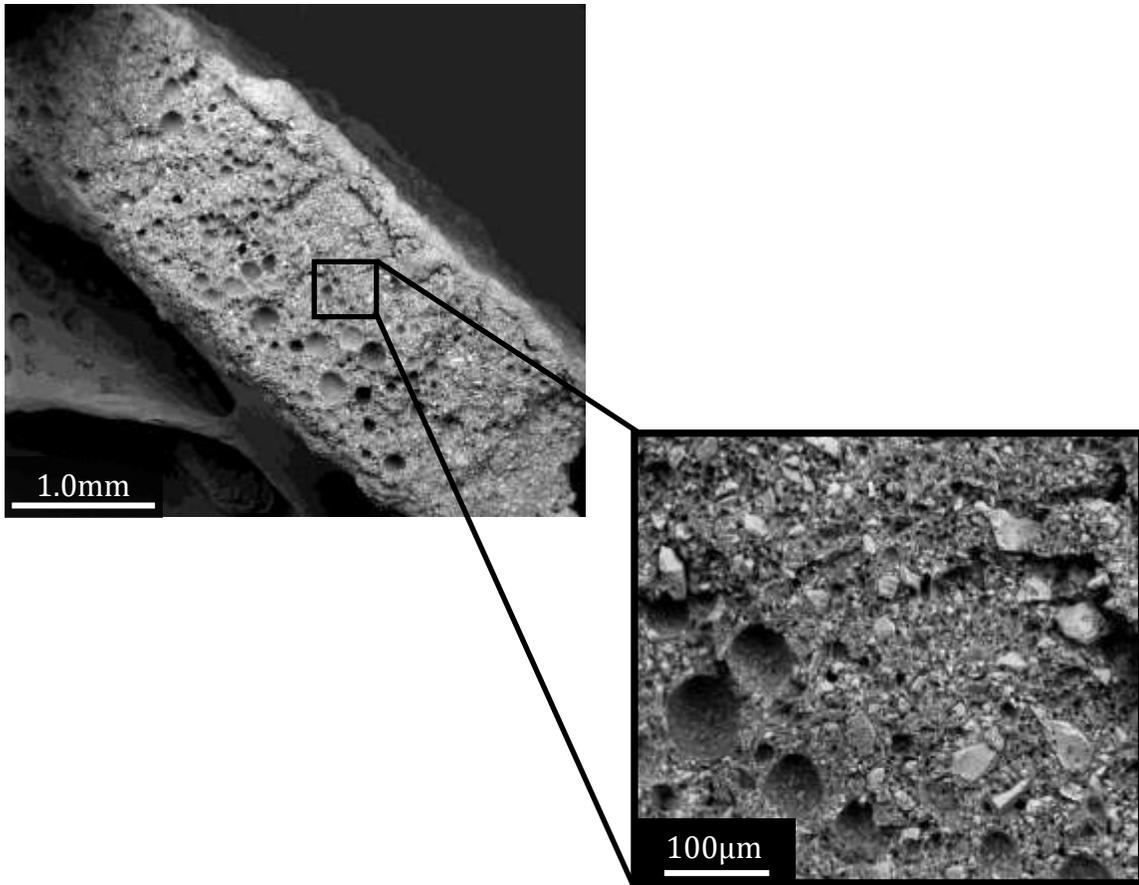


Figure 24. BSE SEM images of a cured specimen that was hand-mixed. These images illustrate the macroscopic effect of poor mixing.

Large, macroscopic bubbles can be seen in each of the images. Not only are the bubbles non-uniformly distributed, but their presence will lead to a decreased density and strength of a final piece.

The bubbles were thought to be caused by poor mixing, however a chemical reaction resulting in binder off-gassing could also cause bubbles to form. The best and simplest way to determine if the bubbles were a result of a resin-catalyst chemical interaction causing off-gassing or due to mixing was to simply combine the two parts of the binder system together, once without mixing and once with mixing. Images of the before (“pre-cure”) and after (“post-cure”) of each test are shown below in Figure 25.

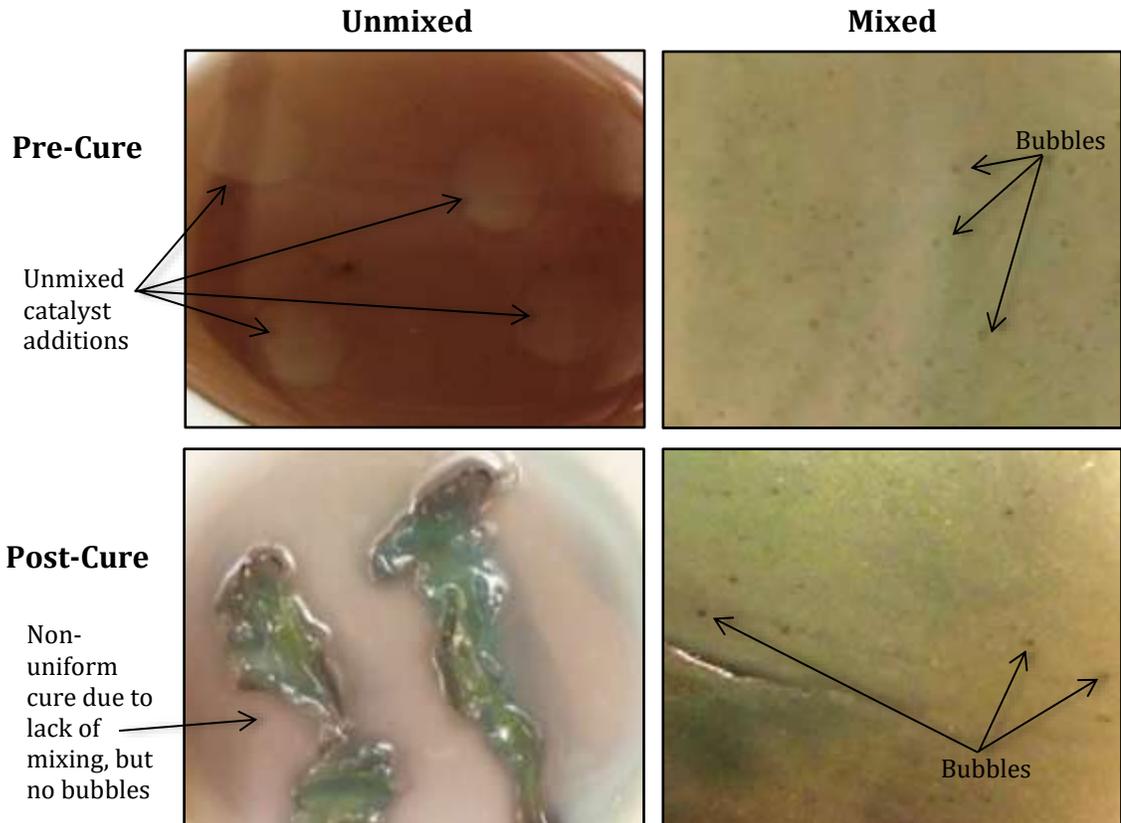


Figure 25. Resin and catalyst combined together (unmixed and mixed) to determine whether bubbles are a result of a chemical off-gassing reaction or mixing.

The left-hand side of Figure 25 shows the trial where the catalyst was simply dripped onto the resin and allowed to cure without mixing. On the right-hand side are images of the resin and catalyst combined together via mixing. It can be clearly seen that even before a reaction occurs there are bubbles present in the specimen that underwent mixing; the same cannot be said for the unmixed specimen. Additionally, after the curing reaction occurred, no bubbles are present in the unmixed specimen, suggesting that an off-gassing reaction did not take place.

2. Mechanical Mixing

Specimens produced via mechanical mixing showed a variable level of improved repeatability when compared to hand-mixed specimens. Four iterations of the same composition were tested at each different mixing time at a constant temperature of 31°C. The data seen in Figure 26 shows that the specimen mixed for 8 minutes has a

large amount of scatter in the higher shear rate region. This scatter was significantly decreased by increasing mix time to 16 minutes. Specimens mixed for longer than 16 minutes began to decrease in repeatability.

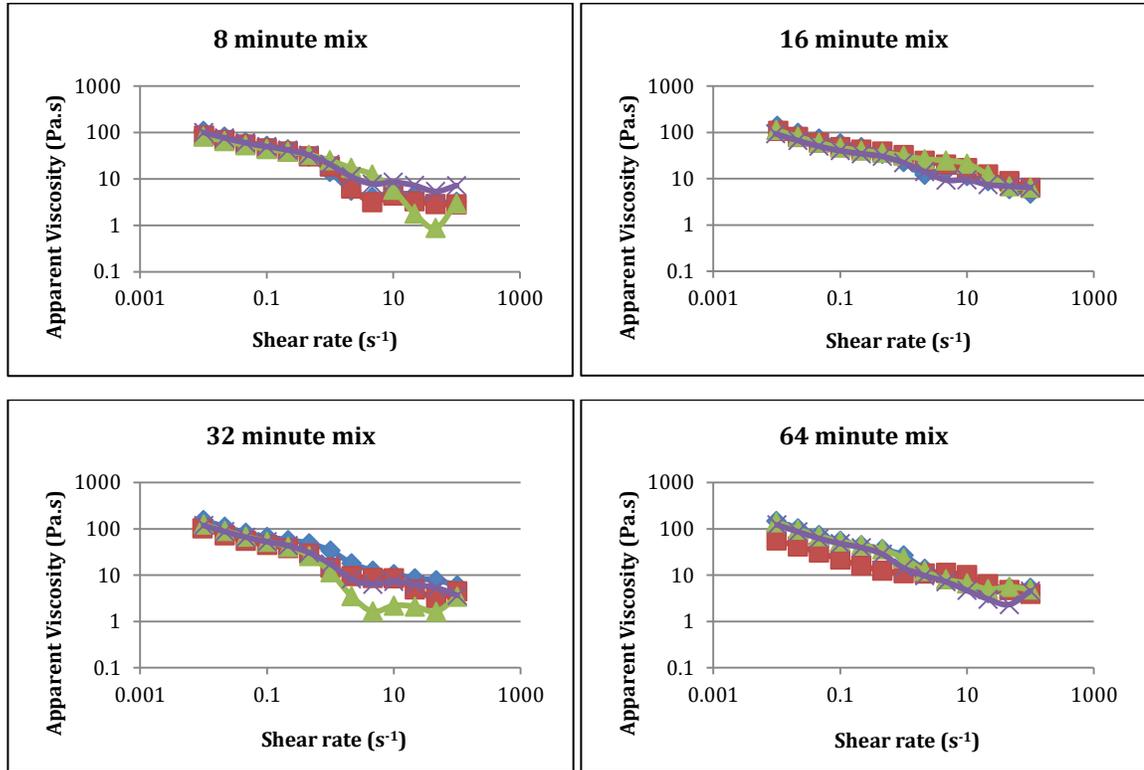


Figure 26. Different mixing times tested to determine the effect of mixing on repeatability.

3. Application of Temperature During Rheological Analysis

By considering both mixing time and rheological analysis temperature, a contour plot of viscosity at a shear rate of 1.0s⁻¹ was produced to illustrate expected viscosity at any tested combination of the two parameters. Mix times of 8, 16, 32, and 64 minutes were analyzed at temperatures of 27, 31, 35, 39, and 43°C. A map showing the various combinations of mixing time and temperature analyzed on the rheometer is shown in Figure 27. Four iterations were completed at each test point.

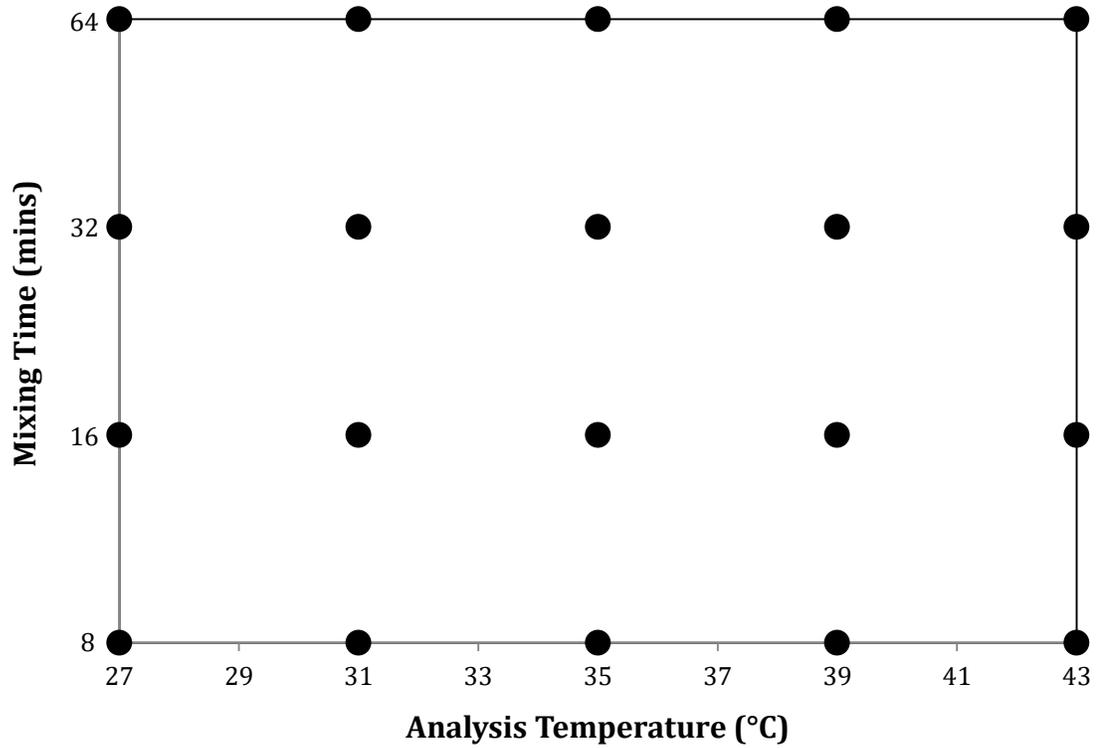


Figure 27. Points represent the different mix time-temperature combinations which underwent rheological analysis.

It was necessary, during testing, to order a second lot of resin to complete the trials. Rheological analysis was performed to ensure consistent viscosity from lot to lot. The results of this measurement can be seen in Figure 28. Due to the offset in viscosity between lot 1 and lot 2, a ratio of the two was determined in order to be used as a correction factor when determining viscosity of specimens which utilized the second lot of resin.

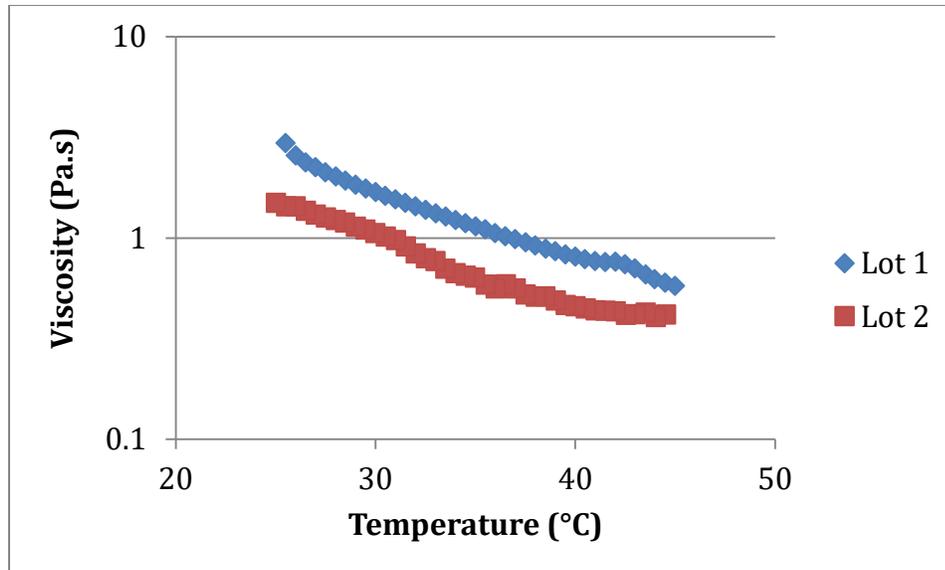


Figure 28. Apparent viscosity as a function of temperature between two different lots of resin.

a) Viscosity Behavior

Data from the points indicated in Figure 27 is used to cast a net over the entire plot area of mixing time (8-64 minutes) and rheological analysis temperature (27-43°C).

The geometric mean of viscosity is determined using a spreadsheet (Microsoft Excel 2010, Microsoft Office Professional Plus 2010, Version: 14.0.7166.5000) which uses the following equation:

$$Geometric\ Mean_{\bar{y}} = \sqrt[n]{y_1 y_2 y_3 \dots y_n} \quad (1)$$

The use of the geometric mean as opposed to the arithmetic mean is important because it provides a more representative mean value for logarithmic data than an arithmetic mean.

A plotting program (SigmaPlot 12.5, Systat Software Inc.) is then able to approximate the viscosity behavior at the remaining intermediate points producing an equivalent value contour map of viscosity (Figure 29).

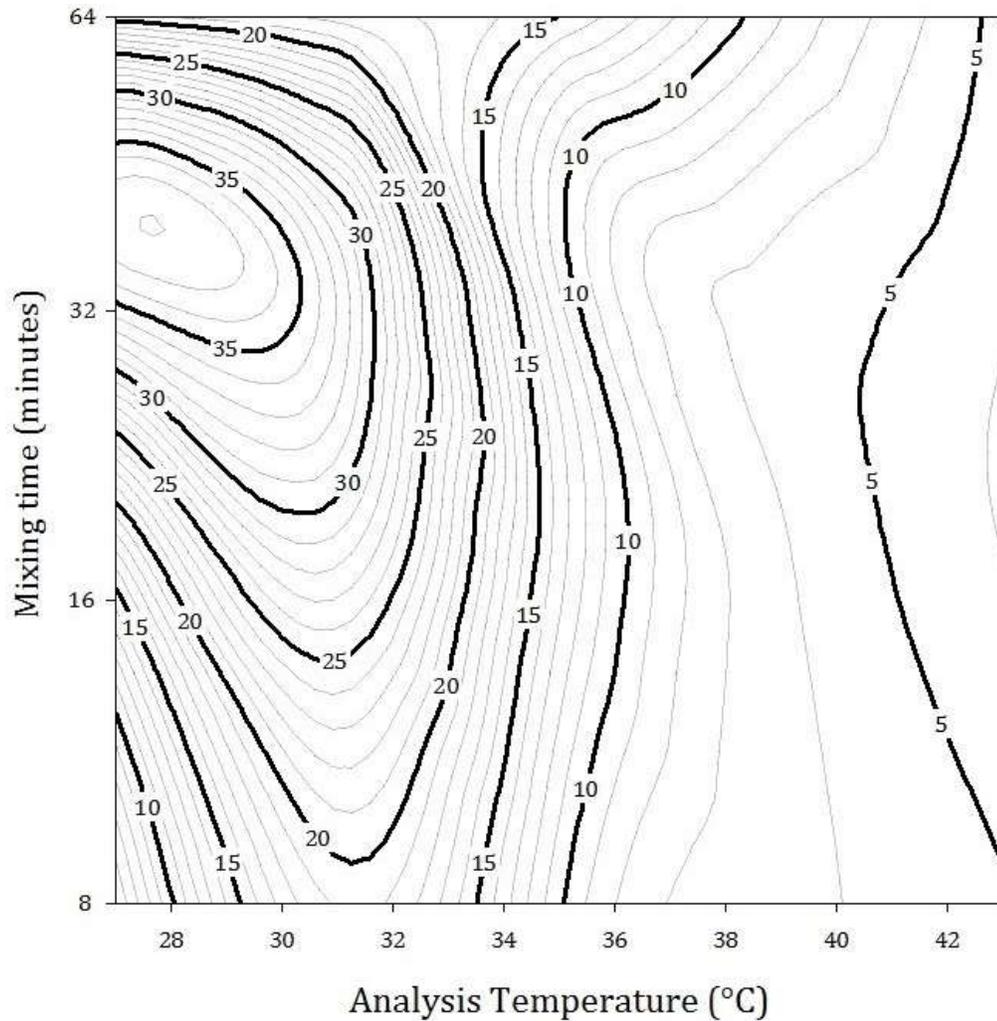


Figure 29. Plot of viscosity (geometric mean) at a shear rate of $1.0s^{-1}$ as a function of mixing time and analysis temperature. Produced using SigmaPlot plotting software.

From this contour map it is seen that in higher temperature regions the viscosity is lower and more consistent (less rapidly changing with minor change in temperature) than in the lower temperature regions, independent of mixing time. In the lower temperature region, $\sim 27-32^{\circ}C$, the dependence of viscosity on mixing time is more notable and deviates from the typically expected behavior. As mixing time increases, an increase in viscosity is seen until it peaks between 32 and 64 minutes and begins to decrease in viscosity. A few probable causes for this were thought to be incorporation of air, difference in domain size, and change in particle structure.

Incorporation of Air

Mixing, by nature, always poses the risk of incorporating air into a batch. This risk is magnified when working with highly viscous batches as the high viscosity prevents bubbles introduced into the batch from easily escaping. However, it is believed that air is not the culprit for the deviant viscosity behavior.

In a ceramic suspension, an air bubble will act as a deformable particle. This means that an increase in the number of air bubbles in a suspension is comparable to increasing the solids concentration, thus increasing viscosity. As shear rate increases, deformable air bubbles will then begin to elongate, lessening the significance of their drag on the suspension viscosity, resulting in a decrease in the shear thinning exponent.

Under the same mixing conditions, air introduced into a batch should continue to increase with increased mix time, thus continuing to increase viscosity. The decrease in viscosity between 32 and 64 minutes would therefore suggest that the bubbles are then being eliminated by further mixing. As mixing time increases, the friction in the batch could theoretically lead to an increase in batch temperature which would decrease viscosity allowing for easier escape of the bubbles. In-situ mixing temperatures were taken using an IR thermometer (Figure 30) which confirmed that the change in temperature as a result of prolonged mixing time was minimal ($\sim 2.7^{\circ}\text{C}$).

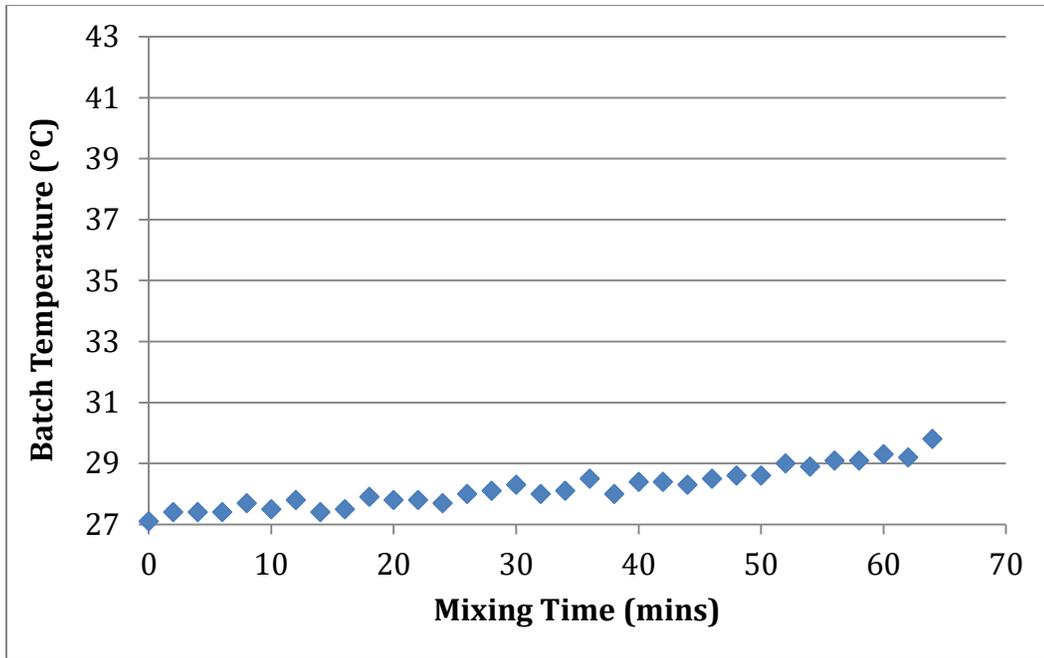


Figure 30. In-situ batch temperature during mixing; measured using IR thermometer. A broad y-axis is shown because experimental rheological measurements of all batches ranged between 27 and 43°C.

As a result, this theory was rejected due to the unlikeliness that air in the batch would be eliminated via excess mixing.

Domain Size

Domain size can be thought of as “particle size” in the sense that a domain is a cluster of particles which acts as its own particle within a larger system; this is illustrated in Figure 31.

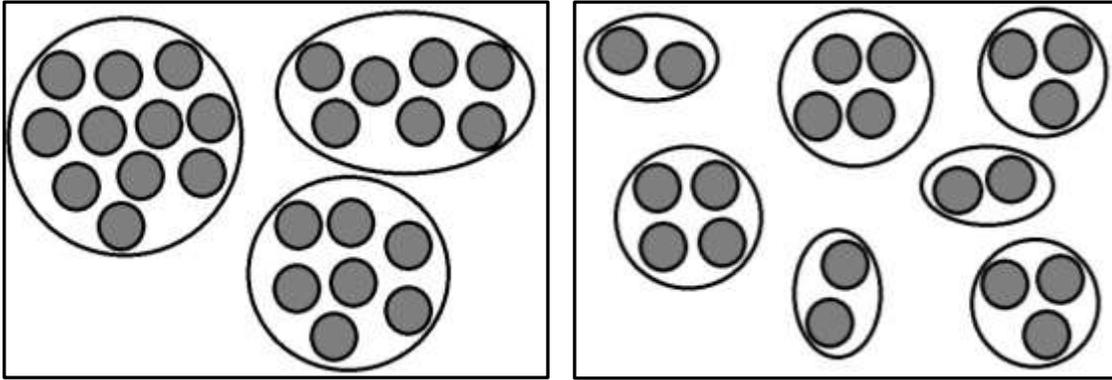


Figure 31. Large domains (left) act as a few large particles within a system. Conversely, small domains (right) act as many small particles.

Based on the underlying assumption that mixing reduces the size of domains, an increase in mixing time will result in an increase in domain quantity but a decrease in domain size throughout the system. As domain size decreases, the viscosity of the system becomes closer to that of the suspension medium and less dictated by the particles. This means that with smaller domains comes a decrease in viscosity since the resin’s viscosity will be lower than that of a loaded system.

Another potential theory regarding domains could suggest that at low mixing times the domains are growing in size, thus increasing viscosity, due to poor mixing and shear induced segregation, and will only decrease in size after reaching a critical mixing time at which point the domains begin to break up resulting in a decreased viscosity. Further work is necessary to investigate this hypothesis.

Particle Structure

Discontinuous or abruptly changing viscosity behavior can be intimately tied to a change in particle structure as a result of changing shear rate. A model used by Hoffman¹³, schematically illustrated in Figure 32, can be used to best explain this phenomenon. According to Hoffman “at low shear rates, where shear thinning occurs, layers of particles packed in a two-dimensional hexagonal packing slide over one

another in the direction of flow (image A in Figure 32). These layers are parallel to planes of constant velocity. Increasing the rate of shear ultimately leads to an instability where particles tend to break out of their layers and jam into one another (image B in Figure 32). Particle jamming between layers is the cause of the rise in viscosity". Further increasing the shear rate leads to a total loss of long-range order among the particles (image C in Figure 32) and an even greater increase in viscosity. This change in particle structure as a result of shear rate could begin to explain the increasing viscosity at higher mixing times as seen in Figure 29. Additional work may be able to provide more evidence of a correlation between mixing time and batch viscosity, specifically at low temperatures.

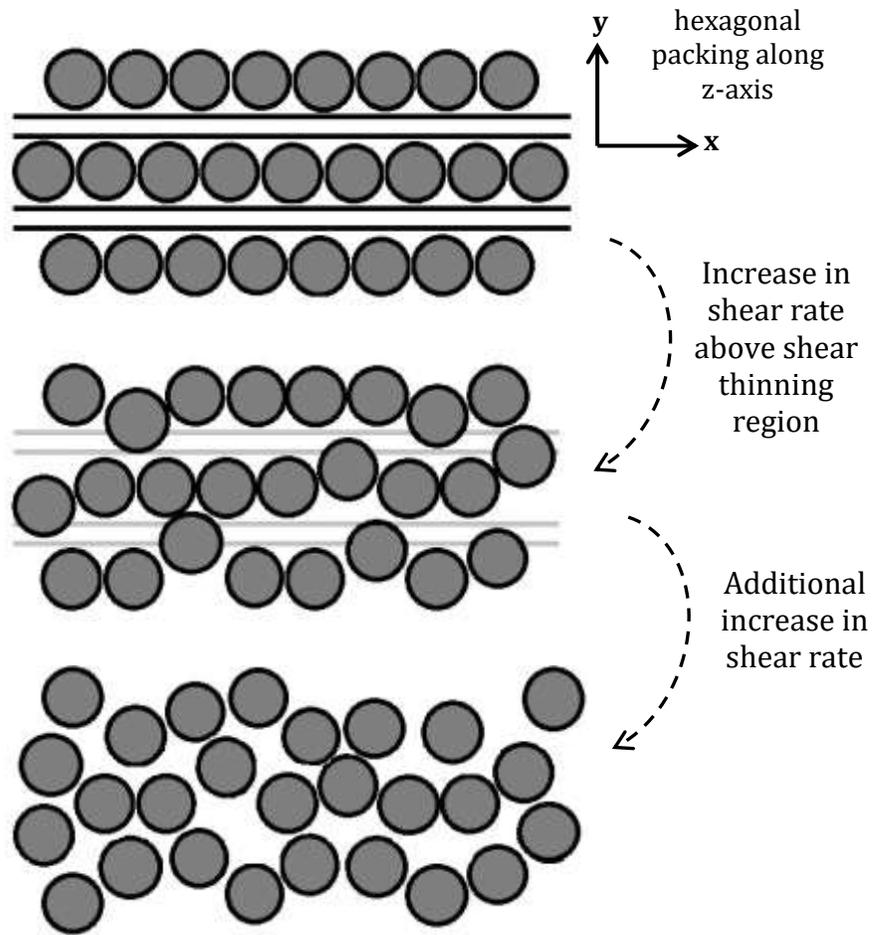


Figure 32. Particle structure schematic to demonstrate model proposed by Hoffman¹³. (A) hexagonally-packed layers, (B) particle jamming, and (C) total loss of particle order in system.

b) Repeatability

While batch viscosity is important to understand, arguably most important is sample repeatability. Without repeatability, a sample's viscosity has less meaning for rheological characterization. To illustrate repeatability as a function of analysis temperature and mixing time, the range (aka. scatter) of data collected among runs at each point was calculated. An equivalent value contour plot of this data range as a function of mixing time and analysis temperature can be found in Figure 33. As with the previously discussed plot of viscosity, this plot was produced using SigmaPlot's approximation plotting software.

As the range approaches zero, the repeatability and/or reliability of data increases. From Figure 33 it is seen that the ideal parameters to achieve near-to-zero scatter are a 32 minute mixing time with a rheological analysis temperature of 37°C. However, a large, more flexible window for good repeatability is apparent. By comparing the plots shown in Figure 29 and Figure 33 it can be concluded that a large region of low viscosity, specifically 5 to 10Pa.s in this batch, resulted in the greatest level of sample repeatability. The desired viscosity was achieved with an analysis temperature in the range of ~36-39°C for all mixing times less than or equal to ~32 minutes. As mixing time exceeds 32 minutes the temperature necessary to decrease scatter increases and has a narrower range than that of the lower mixing times.

At low temperatures, repeatability experiences dramatic fluctuations as a result of changes in mixing time. This demonstrates a greater dependence on mixing for lower temperature samples, and is indicative of the presence of an ideal mixing time. Greatest repeatability at low temperatures was achieved between 16 and 32 minutes of mixing, while poor repeatability was seen around 8 minutes and above 32 minutes. This indicates an optimum window of mixing time for low temperature analysis.

Overall, if used for injection molding, an optimum window for repeatability can be found between 16 and 32 minutes of mixing time (additional work necessary to determine exact range) using a minimum injection temperature of ~36°C to achieve

sufficient flow but not exceeding $\sim 39^{\circ}\text{C}$ in order to avoid the potential for curing due to the fact that the binder is a thermosetting polymer.

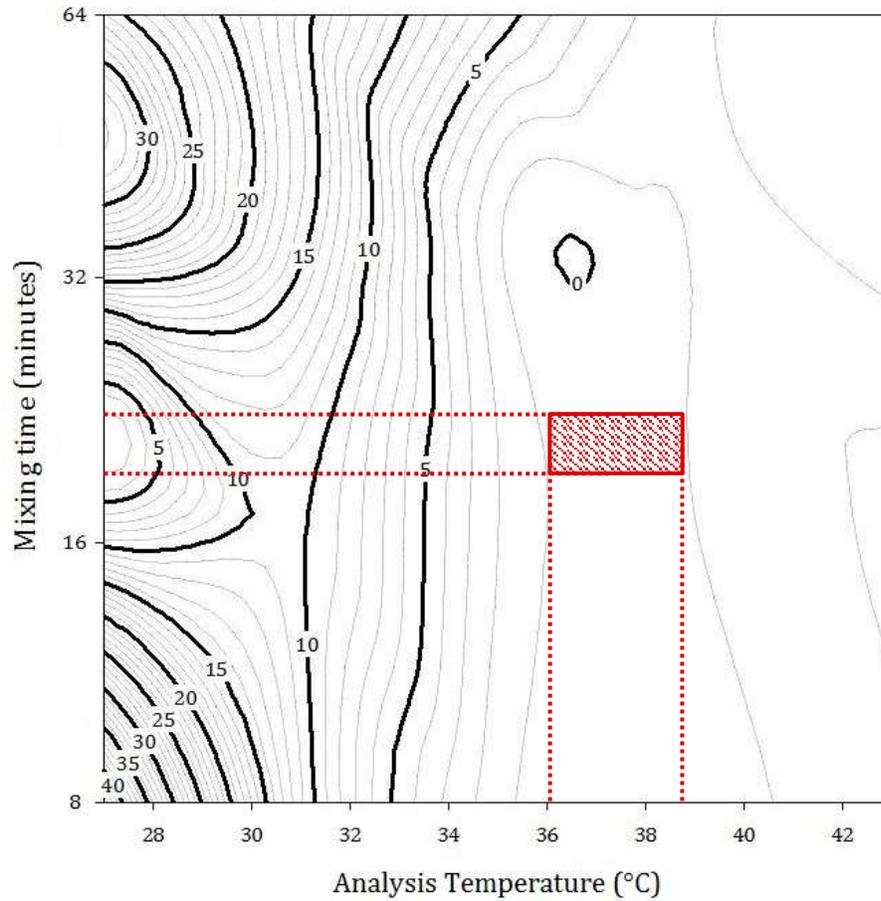


Figure 33. Plot illustrating the range in viscosity when four measurements are taken under the same conditions. An optimum window is shown.

C. CONCLUSIONS

Predictability of injection molding performance begins with the ability to make conclusions based off of rheological analysis of a batch. This study investigated the effect of two factors whose importance in injection molding were not previously well understood: mixing and batch temperature.

The criteria required for a viable injection molding batch included the following: thermosetting, flowability, strength in handling, and repeatability. Four different binder systems were tested as potential candidate systems for ceramic injection molding. These systems included TEOS, PMMA, PC-7, and polyester resin. Each system was tested to determine if it fulfilled the four aforementioned requirements. TEOS and PMMA samples were unable to be handled and thus were eliminated as they did not meet the strength criteria. PC-7 was able to obtain all requirements except repeatability, and was therefore discontinued. The final system utilized a polyester resin binder system, and also failed the repeatability requirements. Upon the marked "failure" of yet another system, it was then considered that perhaps differences in injection molding performance do not stem from variations in the batch and/or rheology, but rather that rheology is dictated by poor mixing and/or temperature control of the batch.

To test this hypothesis, samples were produced and underwent rheological analysis at four different mixing times as well as five different analysis temperatures. Contour plots were able to be produced to better illustrate the effect of these parameters on the final viscosity of the samples as well as the repeatability in data measurements. These contour plots illustrate a complex relationship between mixing time and temperature with sample viscosity and repeatability.

The greatest level of repeatability was seen when the viscosity was between 5 and 10Pa.s and 36-39°C for rheological analysis. Above 36°C sample repeatability was independent of mixing time. This trend, however, was not seen at lower analysis temperatures. As analysis temperature decreased away from 36°C, sample repeatability decreased as well. At the lowest temperature analyzed (27°C) a small

window of good repeatability was seen between 16 and 32 minutes of mixing. However, outside this small window repeatability was poor.

This study was able to provide a rudimentary yet novel insight into the critical effect of mixing as well as sample temperature in ceramic processing. Future work will allow for a deeper, more comprehensive interpretation of the vital role that these factors play in ceramic processing.

CONCLUSIONS

Nowadays, most industrial injection molding processes utilize thermoplastic binder systems. The use of thermosetting polymers has its advantages, but a greater understanding of their effect on the process is still necessary.

The development and analysis of four different binder systems has allowed for a greater understanding of the importance of both mixing and injection temperature in thermosetting injection molding bodies.

Slurry mixtures such as TEOS and PMMA produced parts with insufficient strength for handling and were too fluid for rheological analysis. Plastic mixtures including PC-7 and polyester resin resulted in pieces with acceptable strength and flowability, however repeatability was an ongoing issue.

Two equivalent value plots were produced allowing for a better predictability of rheology. These plots included both viscosity and range (or scatter) as a function of mixing temperature and analysis (or injection) temperature. An optimum window of repeatability was determined for the polyester resin sample by evaluating its behavior under numerous different mixing-temperature conditions. Repeatability increased as a function of time, independent of mixing time. However, as a function of temperature, samples with a mixing time between 16 and 32 minutes resulted in the best repeatability. The optimum window of repeatability was achieved when combining a mixing time between 16 and 32 minutes, and a temperature between 36 and 39°C. Additional work is necessary to narrow down an exact range of ideal mixing time.

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