

Development of Advanced Polymer-Soil Composites as High-Performance Construction Materials

by

Boris P. Nazareth

A thesis

presented to the University of Waterloo

in fulfillment of the

thesis requirement for the degree of

Master of Science

in

Chemistry

Waterloo, Ontario, Canada, 2023

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Authors Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

Construction using earth materials is an old building practice that can be traced back to approximately 10,000 BC. Costs for this type of construction are low because local materials are utilized, and structures are built with the simplistic technology available. More developed countries have moved on from earth materials to those such as concrete due to the better mechanical properties that they possess. However, the production of concrete has a detrimental impact on the environment as its production requires large amounts of energy, raw materials, and releases significant amounts of carbon dioxide. Polymer materials have been identified as useful soil-stabilizing additives because of their ability to fill voids between sand particles. Although polymers have been studied for their use in soil stabilization, they have not been explored as a potential substitute for concrete in construction. This research aimed to produce a composite building material with compressive strength values on par with that of concrete. In Chapter 2, the attempted functionalization of polymers was described to highlight methods capable of modifying polymers (plastics) for use. However, these experiments were paused to investigate the effectiveness of the highlighted functional group. A polymer solution was synthesized to exploit a covalent bond that forms between the polymer and the solid components of soil/sand. The production and compressive strengths of the formed polymer composites were outlined in Chapter 3. The results revealed the effectiveness of increasing amounts of the polymer solution. Variables that influenced the curing rate of the polymer composites were also investigated. This proof of concept study showed that polymer composites can be made to possess high compressive strength values.

Acknowledgments

When I started this degree, I was not sure what to expect. In the beginning, I was riddled with self-doubt and dead ends, but as I continued and leaned on my support group, I grew confident in my abilities and learned a lot about myself. I would like to thank all the amazing people in my life, without whom none of this would have been possible.

First, I would like to thank my family, my parents Laurita and Cavin Nazareth, my sister Lauren Nazareth, and our dog Chester. Thank you for always being there for me and for listening to me rant about things that sounded like gibberish. Mom and Dad, you have both done so much for me and I will never be able to repay you for all your sacrifices. You raised me to give my best in everything I do, and I hope I made you proud. Lauren, although we have not been together at the same school since St. Timothy's, with you going to Laurier we ended up as roommates for my final semester. Thank you for reminding me to take a break once in a while. Chester, Bark Bark Bark.

Next, I would like to thank Malvika Balaraj, my amazing girlfriend and best friend. Thank you for always believing in me and making me feel like I could do anything. With your help, I realized that I am capable of anything I set my mind to. Although we were separated by more than 3000 kilometers, with our constant facetime calls it always felt like you were close by. Thank you for being such a joy and I am excited to see where our future leads us.

Dr. Derek Schipper, thank you for being a great supervisor to me during my Chem 494 and throughout my master's degree. I remember when you pitched me the idea for this project; from that moment, I was all in. Although this project spanned many different fields, it taught me how to think like an entrepreneur and showed me that scientists have many different career paths beyond the bench.

I had the pleasure to work with so many kind people throughout my time in the Schipper lab. Dr. Parisa Ghods, you mentored me during my Chem 494 and helped convince me that I was smart enough to pursue a master's degree. Geoff Sinclair, I am so glad that you were my TA in undergrad, I look forward to watching a few more grand prix with you. Sarah Srokosz, thank you for helping create such a fun work environment, I still have my red hat from Oktoberfest and will cherish those memories forever. Jianan Wang, although we joked that you were a computer, I learned a lot from you. Thank you for always laughing at my jokes and please remember me when you make the Forbes list. Javan Buratynski, although our time as gym bros was short, you helped build the foundation of healthy living that I hope to continue. Thank you for all your help with the GPC. Mila Abaeva, we started grad school together and bonded over jokes with G-an. You are a great scientist, and I am happy I had the pleasure of sharing the lab aisle with you. Gigi Hu, you are a very hard-working person and were always there to lend a helping hand. Thank you for the many laughs, the beef shank you cooked me, and for showing me that naps can be taken anywhere. Luke Glofcheskie, thank you for teaching me about the rubber duck, you were always there when I needed to chat, and I am glad I had the pleasure of working with you. Scott McNeil, you are definitely the oldest person I know.

Thank you for pushing your retirement and deciding to bless all of us with your presence. Remember me when you win your Nobel prize. Mark Brutto, although you joined the lab recently, I was so happy that a fellow sports fan had joined the lab. I will see you at the parade when the Leafs win the cup. To the two undergrads, I had the pleasure of teaching, Jasmin Nazarali, and Zhaoxiang Liu, thank you for teaching me how to be a supervisor.

Julie Goll, I had the pleasure of working for you as a TA. Thank you for the many chats, you care a lot about the content that you teach your undergrads and had a huge impact on my organic chemistry education.

Thank you to my committee members for being a part of my master's degree journey. Dr. Chong and Dr. Duhamel, I learned a lot from both of your classes and during my 794.

Finally, I would like to thank all my friends that I have made along the way. Andrew Golabek, you were one of the first friends I made during undergrad and now you are like a brother. Thank you for all the carpool rides, being my fellow gym bro, and always being there. Andrew Bahlmann, "Physics Andrew", I enjoyed having you as my roommate for many years, and I look forward to reuniting over a plate of Schnitzel. Mike Tarasca and Fabio Cuzzucoli, thank you for the spro's, the laughs, and the many goofs and gaffs. The lads from Momoney Modiscord, thank you for inviting me into your gaming circle. Although I can still hear Louis sighing in my headset, I enjoyed every one of our games. Last but

not least, thank you to the Darko Jemima boys. Who knew that even after all these years a WhatsApp group chat would keep a group of high school friends so close.

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List of Abbreviations

1-oct	1-octanethiol
AA	Acrylic acid
AIBA	2,2'-Azobis(2-methylpropionamidine) dihydrochloride
ART	Alignment relay technique
ASTM	American society for testing and materials
CTA	Chain transfer agent
DI	Deionized
DMF	Dimethylformamide
DMVP	Dimethyl vinylphosphonate
EDTA	Ethylenediaminetetraacetic acid
ESI	Element specific imaging
GPC	Gel permeation chromatograph
ITO	Indium tin oxide
M_n	Number-average molecular weight
M_w	Weight-average molecular weight
M_v	Viscosity Average Molecular Weight
MSAM	Multi-Scale Additive Manufacturing Lab
OHS	Overhead stirrer
PAA	Poly(acrylic acid)
PDMVP	Poly(dimethyl vinylphosphonate)
PMAA	Poly(methacrylic acid)
PMA	Poly(methyl acrylate)

PVC	Poly(vinyl chloride)
PVPA	Poly(vinyl phosphonic acid)
PVPA-<i>co</i>-AA	Poly(vinylphosphonic acid – <i>co</i> – acrylic acid)
RAFT	Reversible addition–fragmentation chain-transfer
RBF	Round bottom flask
S-DEVP	Styrene-diethyl vinylphosphonate
SEC	Size exclusion chromatography
SLS	Static light scattering
SWNTs	Single-walled carbon nanotubes
TBAI	Tetrabutylammonium iodide
TBHP	tert-Butyl hydroperoxide
TEM	Transmission electron microscopy
THF	Tetrahydrofuran
TMP	Trimethyl phosphate
TMS-diazomethane	Trimethylsilyldiazomethane
UCS	Unconfined compressive strength
VBPA	Vinylbenzylphosphonic acid
VPA	Vinylphosphonic acid
XPS	X-ray photoelectron spectroscopy

Chapter 1: Construction Materials

1.1 Earth-Based Construction Materials

Construction using earth materials is an old building practice that can be traced back to approximately 10,000 BC.¹ Even today, structures made from earth materials house 30% of the world's population. For many of these inhabitants' construction using these materials is a necessity as they are usually found in developing countries where housing needs to be low-cost, materials need to be easily accessible, and built with the simplest technology available. Materials like mud and clay fit these criteria as they do not require any prior treatment before use as a construction material, and are only comprised of raw, sun-dried earth.



Figure 1: Traditional construction techniques using earth a) A cob wall constructed in Mount Pleasant Eco-Park, Cornwall (United Kingdom)² b) Unstabilized loadbearing rammed earth (Berlin)³ c) Wattle and Daub building (Venezuela)⁴

There are a variety of construction techniques that make use of earth materials such as cob, rammed earth, wattle and daub, and adobe.¹ Cob is the simplest of the techniques as it involves stacking earth (mud) mixed with straw and moulding the material to create walls. The rammed earth method is used in places with damp and humid climates.⁵ The technique involves taking a mixture of sand, gravel, and soil and

compacting it between forms made of wood. Once the mixture dries, the forms can be removed to reveal the finished structure. The wattle and daub technique is made up of two parts. The wattle is a woven structure made up of plant material held together by a frame.¹ The plant material can be made from reed, bamboo, and branches. The daub (or mud) is then smeared onto the wattle to cover the entire surface. This technique produces a very thin structural material, but the resulting structure is earthquake resistant compared to the previous techniques as it is extremely flexible.⁵ Finally, the last technique is adobe construction. Adobe bricks are made by mixing sand, silt, clay, and water which are shaped into bricks and dried in the sun.^{1,5} However, since these bricks are unfired and sun-dried, this technique is usually used in climates that allow for periods of dry weather. All these construction techniques share similar construction materials such as mud, sand, soil, etc. to build structures. However, the techniques in which the materials are used for varies depending on the needs of the final structure and the climate of the region.



Figure 2: Adobe bricks being made and left to dry (Ecuador)⁴

The adobe technique has seen a resurgence in interest and its mechanical properties are currently being studied as there is an increasing effort to preserve traditional earthen construction. Especially now, with increasing housing costs and the adverse environmental impact of modern construction techniques the traditional methods of using sustainable and locally sourced building materials could help solve these issues. The

reason more developed countries may have moved on from earth materials to those such as concrete is likely due to the increased compressive strength that they possess. Illampas *et al.* investigated adobe brick's ability to withstand compressive loading and found their cylindrical samples had compressive strength values ranging from 0.77 to 1.41 MPa.⁶ These values are quite weak when compared to structural concrete which has values in the range of 17 to 103 MPa.⁷ Therefore, the change in construction techniques from earth-based materials to those like concrete and cement is justified when comparing their mechanical properties.

1.2 Concrete

Although the terms concrete and cement are sometimes used interchangeably, they are not the same. Concrete is composed of a mixture of differently-sized aggregates, cement, and water.⁸ These ingredients form the world's most used building material and the second most consumed substance on earth after water.⁹ Cement's role in concrete production is to act as the binder, holding together the aggregate to form the composite material.⁸ Aggregates role in cement production is to provide strength, durability, and workability as well as reduce shrinkage. Since cement is the costliest ingredient in concrete production it makes sense that the aggregates constitute 60-80% of the final volume of concrete. These aggregates are of various shapes and sizes and range from small particles of sand to larger pieces of rock. The shapes and size ratios of the aggregates in the final concrete mixture are dictated by the desired properties and use of the hardened concrete.

If concrete is just a mixture of cement, water, and aggregate, why then, are there multiple articles that get published every year about its destructive impact on the environment? It is the production of cement that requires a large amount of energy, raw materials, and releases significant amounts of carbon dioxide. To understand why cement has this detrimental impact on the environment the way it is manufactured must be explained. First, to make cement, an intermediate material called clinker is produced. Clinker is a source of lime, calcium oxide, silica, alumina, and iron oxide.¹⁰ Production begins at a quarry where limestone, calcium carbonate, is extracted and crushed before being sent to a blending plant. The limestone is then ground and blended with shale, clay, sand, and iron ore to form a powder. The shale and clay are silicate minerals and are a source of alumina and iron, while the sand is a source of silica. The grinding of the materials is an important step in the process as the particle size of the materials has a significant effect on their amalgamation in the kiln. Variability in the amounts of each component and their size leads to inconsistencies in the chemistry that occurs in the kiln. This leads to variability in clinker quality which affects cement performance and consequently the strength of the concrete. The powdered mixture is then heated in a rotating cylindrical kiln that is held at an incline.¹¹ At the lower end of the kiln, a fuel is burned, and the heat produced is used to transform and combine the materials.

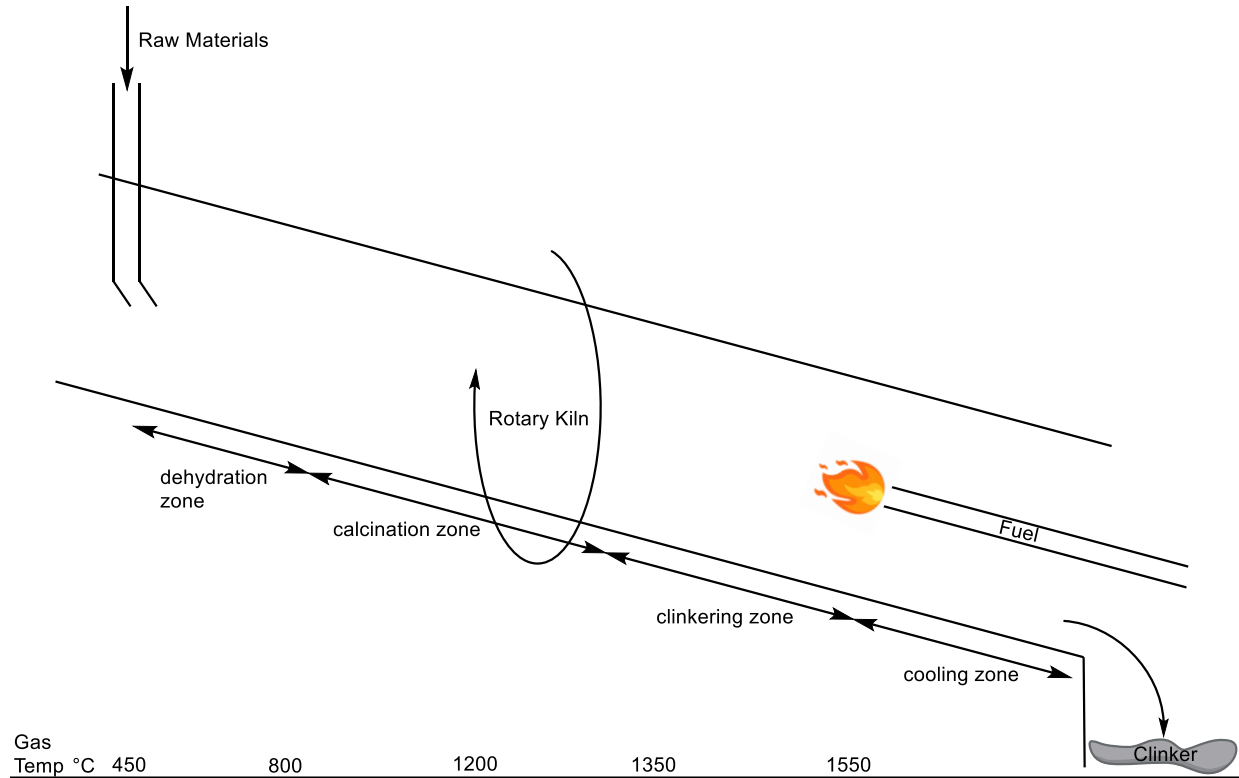
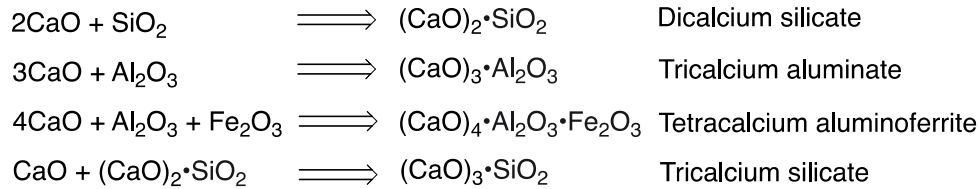


Figure 3: Diagram of rotary kiln

The time that the mixture spends in the kiln varies depending on the length of the kiln and the different production processes of each plant, but the science remains the same. As the mixture passes through the kiln, four stages of transformation occur which lead to the production of clinker. First, as the mixture enters the kiln any water present is lost to evaporation.^{10,12} Next, at approximately the 800 °C mark, CaCO_3 is broken down into CaO and CO_2 , through a process called calcination. As the temperature continues to rise chemical reactions that produce calcium silicates occur (Scheme 1). This process is called clinkering. Finally, cooling occurs which allows the produced marble-sized pieces of clinker to reach a safe temperature for grinding. After the clinker is cooled and ground, it is then mixed with gypsum to produce what is commonly known as Portland cement.



Scheme 1: Clinkering chemical reactions

As mentioned above concrete is made by mixing aggregates, cement, and water. Water is necessary for the production of concrete as the calcium silicate ingredients listed in Scheme 1, need water to hydrate and cure (harden). Concrete hardens through a process called hydration.¹⁰ During this process the calcium silicate ingredients and water react releasing calcium ions, hydroxide ions, and heat. The resulting calcium hydroxide and calcium silicate hydrate precipitate thereby accelerating the reaction (Le Chatelier's principle). Given time, more $\text{Ca}(\text{OH})_2$ and calcium silicate hydrates precipitate and harden filling the empty space between the grains of aggregate. This hydration chemistry is what provides strength to the concrete. It should be noted that this explanation of hydration chemistry is brief, in reality, the different ingredients listed in Scheme 1 would react with water at different rates alongside various other processes.

Water is an important ingredient in the production of concrete as it has a large effect on its strength and workability. During hydration only a specific amount of water is consumed, the rest is added so that the concrete can flow and remain workable; however, this negatively impacts the strength.⁸ The water not consumed by the hydration reactions is left to sit in the empty pore spaces of the concrete and does not help with forming calcium silicate hydrate bonds. This weakens the structure as these empty pore spaces do not contribute strength to the material. A low water-to-cement ratio leads to high

strength but poor workability, while a high water-to-cement ratio yields a low strength concrete with good workability. Finding the correct water-to-cement ratio, that yields the proper amount of strength but flows well, is key when working with concrete.

With some background on the production of cement, its harmful effect on the environment can be explained. Although all the processes described seem simple, it is the magnitude at which they occur that is the issue. Cement manufacturing is a billion-dollar industry and billions of metric tons are produced every year.¹³ The emissions start at the very beginning of production with the harvesting and transport of limestone from quarries.¹⁴ They then continue with the use of fossil fuels to heat the kilns which produce clinker. There has been ongoing research into the use of alternative fuel sources (used tires, animal residues, sewage sludges, etc.) to heat the kilns; however, these substitutes can influence the properties of the clinker produced. The differences in the way that the materials burn can affect the porosity and crystal sizes of the clinker and its reactivity. Simultaneously, when the calcination process occurs to produce CaO , the CO_2 that was once trapped in the limestone is now released into the atmosphere. To combat this, research continues on the topic of carbon capture and storage technology, however, these pose other challenges and added costs. Methods to produce cement have improved substantially through the use of more efficient technologies and the use of waste materials from other processes and industries. As the world's population continues to grow research will continue to be necessary to improve concretes sustainability. These methods will include the use of alternative raw materials, new fuel sources, and more

efficient kilns. However, the topic of sustainable construction has also sparked research into new types of aggregate binders and construction materials.

1.3 Soil Stabilization

Soil stabilization is a technique employed to improve the physical properties of soil. These properties include mechanical strength (shear and compressive strength), permeability, durability, and plasticity.¹⁵ The techniques used to improve these parameters can include physical, biological, and/or chemical methods.¹⁶ For chemical methods, the reagent employed to enhance soil stability can be mechanically mixed with the soil to form a homogenous mixture or can be sprayed onto the undisturbed soil surface and allowed to permeate. Traditional chemical stabilization methods include the use of additives like lime, cement, fly ash, and bituminous materials. However, as described in the concrete section above, the procurement of these cementitious additives is energy-intensive, costly, and contributes to CO₂ emissions.¹⁵

Other untraditional non-cementitious materials, like foams, enzymes, acids, and even polymers have been employed as soil stabilizers.^{17,18} Polymer materials have been identified as a useful stabilizing additive because of their ability to fill voids between sand particles. This stabilizes the soil by reducing permeability, increasing strength, and provides stability against contaminants. Furthermore, if the polymer additive is distributed in liquid form it can be sprayed onto the soil surface and removes the need for mechanical manipulation.¹⁶

Rezaeimalek *et al.* studied the stabilizing effect that a styrene-acrylic polymer has when mixed with poorly graded sand.^{17,18} A study was also conducted on the effect of different curing environments on the unconfined compressive strength (UCS) of the composites. Their results revealed that the UCS for the composite samples increased as the amount of polymer added increased. The styrene-acrylic stabilized composite samples typically took 28 days to fully cure in air (20 °C) and reach maximal strength. However, the researchers found that this curing time could be reduced to 1-2 days when the samples were cured using heat (100 °C), with negligible effect on the UCS of the samples. The highest UCS values from the researchers' experiments were 5.096 MPa and 7.077 MPa for sand and clay, respectively.

Similarly, Song *et al.* conducted laboratory and field experiments on the stabilizing effect of their vinyl acetate polymer on soil.¹⁹ They found that as the concentration of polymer solution sprayed onto the soil increased, the erosion resistance of the soil surface also increased. The UCS and the shear strength of the soil also increased with increasing polymer concentration. They mention that the carboxyl groups on the polymer chains form hydrogen bonds with the hydroxyl groups on the surface of the soil particles. With increasing polymer concentration, the amount of hydrogen bonding also increases, and this is what increases the soil's stability. The researchers then wanted to evaluate the effect that the polymer solution would have on seed growth. The results from this experiment indicated that the vinyl acetate polymer had no adverse effects on vegetation growth.

These studies provide proof-of-concept evidence for polymers as a viable replacement for cementitious soil stabilizers. Their ability to fill voids between the sand and soil particles gives the stabilized soil strength and improves resistance to weathering.¹⁷ Although polymers have been studied for their use in soil stabilization, they have not been explored as a potential substitute for concrete in construction. The results above show that the UCS of polymer composite samples must increase significantly to compete with concrete. If a polymer solution blended with sand/soil had compressive strength values on par with concrete, it could be the environmentally friendly material that replaces concrete.

Chapter 2: Phosphonylation of hydrocarbon polymers for metal oxide binding applications

2.1 Surface functionalization using a phosphorus – metal oxide bond

Surface modification chemistry is an area of research that is critical to the advancement of engineering and electronic applications.²⁰ This chemistry can be used to create protective coatings, biological microarrays, and analytical sensors. When small organic molecules are bonded as a thin layer onto a surface, the properties of the surface can be tuned and modified. In the past, these thin layers were applied to surfaces using polymer coatings or layer by layer deposition. More recently, research has shifted to modifying surfaces through grafting. Grafting makes use of functional groups that can chemically bond molecules onto a surface. This technique allows for better control of the surface properties. Functional groups like phosphonic acid and its derivatives have been used to modify metal oxide surfaces. As illustrated in **Figure 4**, this is accomplished through a condensation reaction between the P-OH or P-OR group of the functionalized molecule and the surface hydroxyl group. A water or alcohol molecule is also produced depending on whether the acid or phosphonate derivative was used as the anchor. A unique feature of the phosphonate functional group is that it has more than one potential binding site.^{20,21} Various coordination modes have been proposed for how the functionalized molecule could bind to a metal oxide surface, but this strongly depends on the reaction conditions and the type of metal surface.

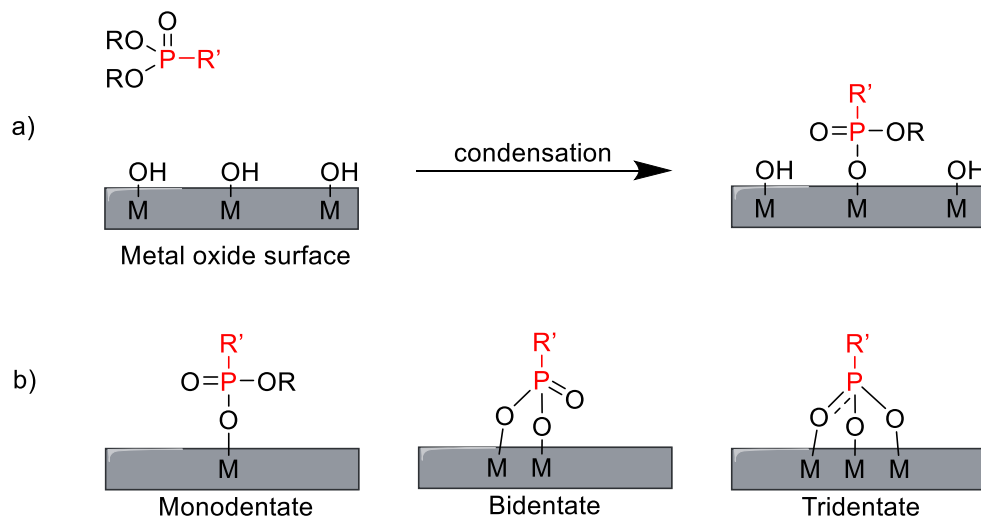


Figure 4: Phosphorus – metal oxide bond a) Condensation reaction between the phosphonate functionalized molecule and the metal oxide surface b) Proposed coordination modes when bonded to the surface

The use of this surface modification technique was demonstrated by Selmani and Schipper in 2018.²² The researchers functionalized small molecules and bonded them onto a metal oxide surface. The small molecules were then used to sort and align single-walled carbon nanotubes (SWNTs). An iptycene tweezer molecule (small molecule) was functionalized with two phosphonate ester groups, the molecule is illustrated in **Figure 5**. By binding two phosphonate groups onto the metal oxide surface, they prevented the rotation of their aligned functionalized iptycene tweezer molecule. The bond was achieved by dissolving the functionalized molecule in a liquid crystal solution. The solution was then deposited onto a liquid-crystal-alignment layer which induced alignment of the small molecules. The metal oxide surface (indium tin oxide, ITO) was then placed on top and pressed, squeezing the droplet into a thin film between the alignment layer and the metal oxide substrate. The functionalized iptycene molecules took 24 hours at room temperature to react with the ITO surface and form the covalent bond. It should be noted that this reaction was conducted without high temperatures or a catalyst, demonstrating

the simplicity of the reaction and the strength of the phosphorus-metal oxide bond. This technique for sorting and aligning SWNT's, dubbed the alignment relay technique (ART), was also completed using a silicon dioxide surface.²³

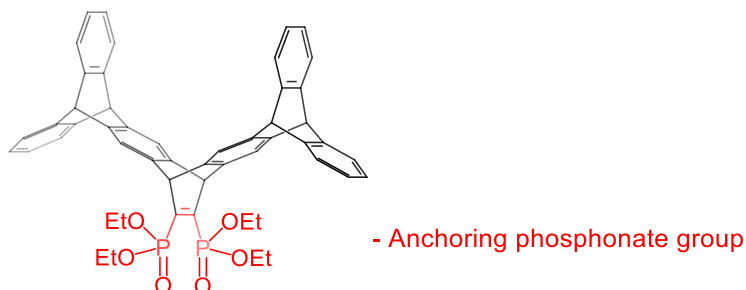
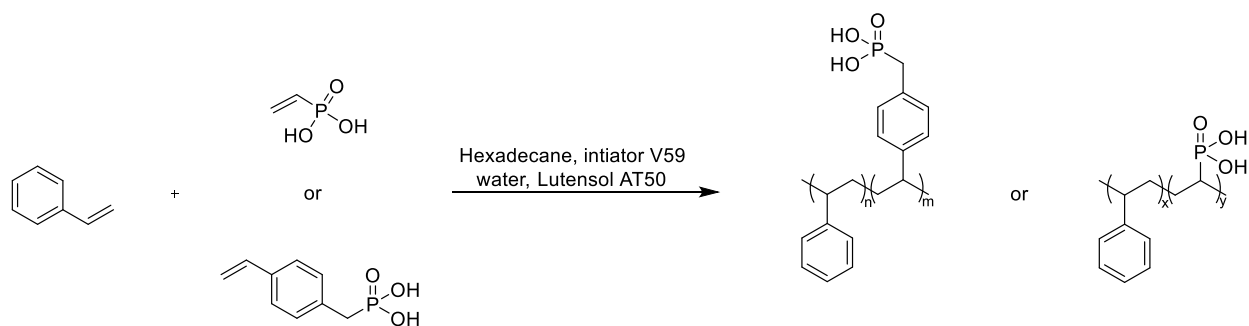


Figure 5: Functionalized iptycene tweezer molecule

Similarly, Thissen *et al.* researched a method to activate silicon oxide to deposit thin films, for further use as a semiconductor surface.²⁴ The primary molecules used to modify silicon dioxide (SiO_2) surfaces have been silanes. However, grafting using silanes is unreliable, as it is impacted by water contamination. This leads to a dense monolayer or a three-dimensional polysiloxane layer with lots of homocondensation.²¹ To bypass this issue, the researchers decided to use phosphonic acids to bond their small organic molecules, as homocondensation of P-O-H bonds to make P-O-P bonds only occurs at high temperatures.^{21,24} Still, the issue with using phosphonic acid as the grafting molecule is that the Si-O-P bond suffers from interface instability in water.²⁴ Thus, the silicon oxide surface needed to be modified so that once the thin films were deposited, it would be stable in an aqueous environment. This was accomplished by placing an aluminum oxide layer on top of the SiO_2 layer, by dipping the silicon oxide wafers in a solution of aluminum chloride, and rinsing with deionized (DI) water. The results established the validity of this method, as the phosphonic acid molecules under ambient conditions were not readily

reacting with the silicon oxide surface. However, once the aluminum oxide layer was applied, the phosphonic acids reacted under ambient conditions to provide a bond that was stable in aqueous environments. The stability was proven through static water contact angle measurements where the phosphonic acid functionalized molecule on aluminum oxide modified silicon oxide wafers showed constant values of 110-120° over the testing time. However, the phosphonic acid functionalized molecule on the unmodified silicon oxide wafers were hydrolyzed very easily. This research further demonstrated the thermodynamic stability of the phosphorus-metal oxide bond and its applicability to surface functionalization.



Scheme 2: Synthesis of phosphonate surface functionalized polystyrene nanoparticles

Zeller *et al.* introduced a unique use of the phosphorus-metal oxide bond, where they investigated the use of a phosphonic acid containing polymer nanoparticles, to bind bone implant material.²⁵ Titanium is typically used for bone replacement due to its high chemical stability in the body. The phosphonate surface functionalized polystyrene nanoparticles were synthesized by a free radical copolymerization of styrene and vinylphosphonic acid (VPA) or vinylbenzylphosphonic acid (VBPA) in a mini emulsion process (Scheme 2). Transmission electron microscopy (TEM) revealed that the synthesized nanoparticles were spherical in shape and homogenous in size. The

distribution of phosphorus in the nanoparticles were examined using element specific imaging (ESI). The ESI images verified a large concentration of phosphorus at the surface of the particles, where binding to the titanium surface would primarily occur.

Table 1: Adhesion forces determined by atomic force microscopy (AFM).²⁵

Anchor group	Tip material	Adhesion force (nN)
N/A	SiO ₂	12.5 ± 2.6
Phosphonic acid	SiO ₂	43.4 ± 3.6
N/A	TiO ₂	13.4 ± 0.9
Phosphonic acid	TiO ₂	63.9 ± 4.3

To determine the binding strength of the phosphonate surface functionalized polymer nanoparticles, the authors assessed the adhesion forces by AFM.²⁵ The AFM experiment measured the adhesion force between the atomic force microscope tips and nanoparticles that had adhered onto metal oxide wafers (silicon and titanium dioxide). The force necessary to pull the metal oxide tips from the nanoparticle coated surface is the measured adhesion force. The results summarized in Table 1 indicate that the introduction of the phosphonate groups led to a higher adhesion force than the unfunctionalized particles. The strongest adhesion force was observed with the titanium dioxide tip and the phosphonate containing particles. This observation was explained by the results of an X-ray photoelectron spectroscopy (XPS) experiment. XPS revealed the concentration of hydroxyl (-OH) groups on the two metal oxide surfaces differed. The

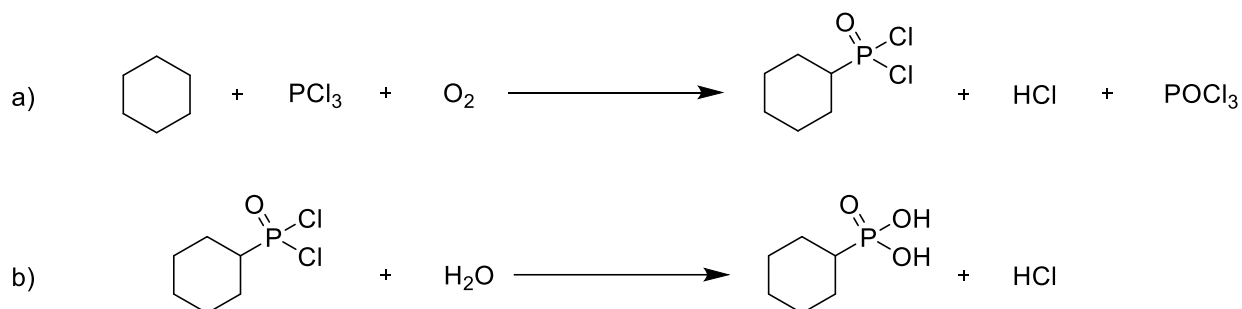
titanium dioxide and silicon surfaces had about eleven and eight -OH groups per nm², respectively. This difference in -OH group concentration was likely the cause of the stronger adhesion force when using titanium dioxide. The authors claimed that the strong adhesion forces demonstrated by the functionalized particles make them promising candidates for the functionalization of implant material. If polystyrene were substituted for a more biodegradable polymer, it could be bound to implant materials to release drugs or growth factors, that would help heal an injury. This research was interesting, as it demonstrated the wide variety of applications, that can employ the stable phosphorus-metal oxide bond.

This brief review has shown that a range of metal oxide surfaces can be modified through grafting to exhibit unique properties. Specifically, they displayed the strength and stability of the phosphorus-metal oxide bond. If a phosphonate group is bonded to a molecule, the molecule can then be chemically bound to metal oxides, which is of importance in a broad range of applications. The use of grafting molecules for other unique applications is an exciting area of research. However, to graft molecules onto unique metal oxide surfaces, methods to bond phosphonate groups onto a variety of molecules need to be discovered.

2.2 Hydrocarbons phosphonylated with phosphorus trichloride and oxygen

One of the fundamental elements of synthetic organic chemistry is to develop novel and creative methods towards new chemical scaffolds. In 1948, Clayton and Jenson accomplished this when they discovered a new method to bond phosphonyl dichloride

onto aliphatic hydrocarbons.²⁶ They recognized that when open chain or cyclic hydrocarbons are mixed with phosphorus trichloride (PCl_3), and oxygen is allowed to bubble through the reaction mixture, it produces a chlorophosphonylated product. When mixed with water, the phosphonyl dichloride group can then be hydrolyzed to produce a phosphonic acid (Scheme 3). The establishment of a method to attach a phosphonic acid/phosphonate group onto hydrocarbon chains is valuable because of the unique binding interactions phosphonates can impart.²⁰ As reviewed in the previous section, phosphonic acid and phosphonate groups readily react with a wide range of metal oxides and form stable covalent bonds. The ability to functionalize molecules with phosphonic acid groups, makes these molecules useful for chemistry that requires stable binding interactions.



Scheme 3: a) Synthesis of cyclohexanephosphonyl dichloride b) Hydrolyzation of the phosphonyl dichloride product to produce cyclohexanephosphonic acid

A few years after Clayton and Jenson's discovery, researchers Isbell and Wadsworth conducted a study on the factors that affect the yield of the chlorophosphonylation of hydrocarbons.²⁷ The study began with testing various catalytic agents to see whether the yield of the alkylphosphonyl dichloride product could be improved. They concluded that catalytic agents had no effect on the yield of the reaction. However, they did find that impurities like sulfur, rubber, iron powder, and boron trifluoride

inhibited the reaction completely. Next, they varied the reaction temperature to gauge the effect that it had on the final yield. They found that at reaction temperatures below -40°C , one of the by-products of the reaction, phosphoryl trichloride (POCl_3), was solidifying and plugging the oxygen inlet line, stopping the flow of oxygen that is necessary for the reaction. However, at temperatures between -40 and 70°C the reaction was able to be completed, and there was no significant change in the yield of the final product. These experiments demonstrated the robustness of the reaction, as it can take place over a wide temperature range with no need for a catalyst.

Next, Isbell and Wadsworth investigated the effect that dry air, as opposed to pure oxygen, would have on the reaction.²⁷ As illustrated in **Figure 6**, oxygen facilitates the radical mechanism, that is necessary for the reaction to go to completion. First, oxygen reacts with PCl_3 to create a PCl_3 -oxygen diradical. The oxy radical on this molecule then abstracts a hydrogen atom from cyclohexane. The cyclohexane radical and the $\cdot\text{PCl}_3\text{-O-}$ OH molecule combine to form a bond. A second equivalent of PCl_3 then attacks the peroxy group of the molecule in step 3, this results in the release of a chloride ion, and the formation of the cyclohexanephosphonyl dichloride product. The PCl_3 group with the bonded OH is then deprotonated by the chloride ion to form POCl_3 and hydrochloric acid (HCl). Therefore, it makes sense that the researchers found the reaction still took place when dry air was used. However, it had an extremely slow reaction rate when compared to the reaction rate that was observed with pure oxygen. Finally, Isbell and Wadsworth conducted a series of experiments varying the molar equivalents of cyclohexane (hydrocarbon) and PCl_3 in the reaction. They concluded that the best yield was obtained

with a 2:1 molar ratio of PCl_3 to cyclohexane. This can also be explained by the mechanism shown in **Figure 6**. In step 3 of the mechanism, a second equivalent of PCl_3 is necessary for the reaction to go to completion. Therefore, it is clear why the best yield was reported when the molar ratio was 2:1 PCl_3 to cyclohexane.

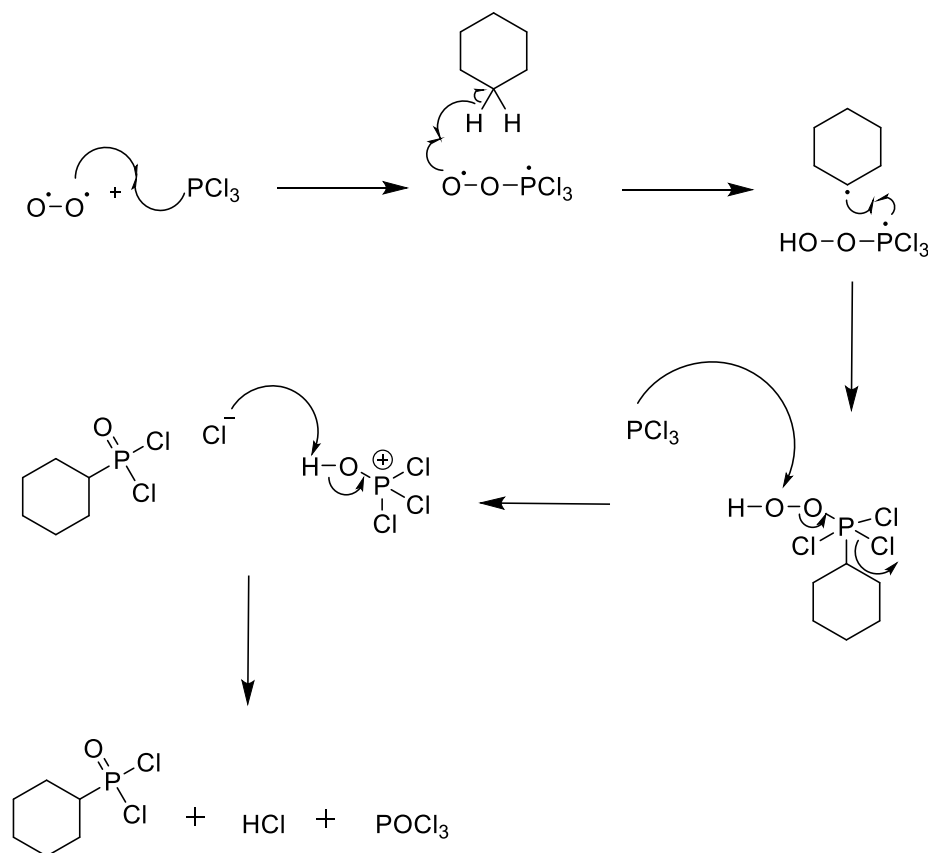


Figure 6: Mechanism for the reaction between cyclohexane, phosphorus trichloride, and oxygen.

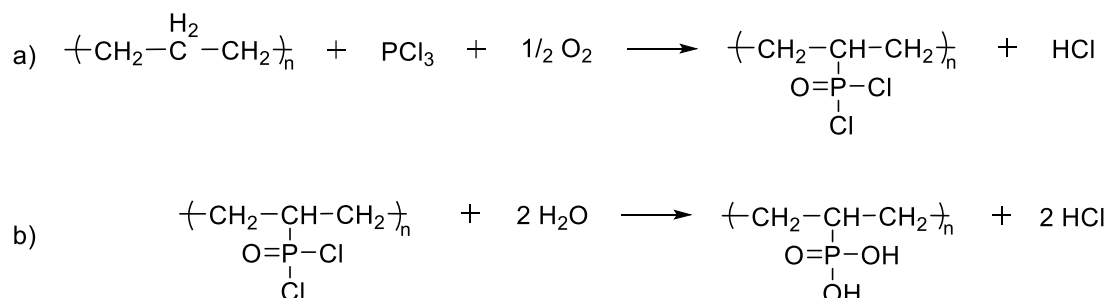
The two papers reviewed in this section are two of the oldest papers reporting on the preparation of phosphonyl dichloride functionalized hydrocarbons using PCl_3 and oxygen. Clayton and Jensen discovered the reaction method, and their work was the first to report the chlorophosphonylation of hydrocarbons using this process.²⁶ The work completed by Isbell and Wadsworth then elucidated the optimal reaction conditions that provide the greatest yield.²⁷ It should be noted that the chlorophosphonylation reaction is

not only limited to hydrocarbons, the reaction can also be used to bond phosphonyl dichloride groups on a variety of materials, including polymers.

2.3 Phosphonylation of polymers

2.3.1 Phosphonylation of polymers using phosphorus trichloride and oxygen

Once Clayton and Jenson had established that PCl_3 and oxygen could be used to place phosphonyl dichloride functional groups onto aliphatic hydrocarbons, researchers then explored other compounds that could be chlorophosphonated using this method.²⁶ In 1960, Schroeder and Sopchak recognized that the chlorophosphonylation of a high molecular weight polymer using PCl_3 and oxygen had not yet been conducted.²⁸ Thus, they began their study using a preliminary 2000 g/mol, polyethylene grease, to establish a background before moving to a higher molecular weight polymer. They completed the chlorophosphonylation reaction of polyethylene and subsequently hydrolyzed the polymer converting the phosphonyl dichloride groups to phosphonic acid groups (Scheme 4). The authors made note that the highly branched polyethylene contains primary, secondary, and tertiary carbons, all of which can be chlorophosphonylated. However, they did not report which carbon type was primarily chlorophosphonylated by the reaction.



Scheme 4: a) Chlorophosphonylation of polyethylene grease with phosphorus trichloride and oxygen b) Hydrolysis of the phosphonyl dichloride group to a phosphonic acid group

Prior to the chlorophosphonylation reaction, Schroeder and Sopchak, stated that the polyethylene grease was sticky and soluble in hot, non-polar solvents.²⁸ However, after chlorophosphonylation and hydrolysis, the properties of the polymer changed to a nontacky, rubbery resin that was insoluble in those same solvents. The solubility of the polymer was highly dependent on the percentage of phosphorus that it contained. The polymer containing 16% phosphorus was soluble in water, but those with 12% phosphorus or less were insoluble in water, but soluble in aqueous sodium hydroxide. However, all the variations of the phosphonic acid containing polymers were soluble in hot pyridine. This result indicated that the percentage of phosphorus that the polymer contains does affect the overall properties of the polymer.

To gain more information about the chlorophosphonylation reaction, Schroeder and Sopchak also studied the factors that affect the yield of the reaction between the polyethylene grease, PCl_3 , and oxygen. Like Isbell and Wadsworth, they also reported the production of POCl_3 as a by-product of the chlorophosphonylation reaction.^{27,28} However, their results differed as they identified an optimal reaction yield with a 20:1 molar ratio of PCl_3 to polyethylene. The large difference in optimal molar ratios is likely due to the large difference in molecular weight between polyethylene and cyclohexane. Using a ratio higher than 20:1 of PCl_3 to polyethylene did not improve the yield, but lower ratios decreased it.²⁸ Schroeder and Sopchak then conducted an experiment to determine the effect of temperature on the rate of the reaction. They conducted the reactions between 74 °C (reflux) and 20°C, and reported a sharp increase in the reaction rate when lowering the reaction temperature from 74 °C to 60 °C, and a gradual increase in the rate

from 60 °C to 20°C. They concluded that this trend was due to an increase in the concentration of dissolved oxygen as the reaction was lowered to 20 °C. Following this, they monitored the evolution of HCl gas from the reaction and found that it was constant when plotted against time. With this zero-order rate behavior and the effect of temperature on the rate of the reaction, they concluded that the reaction rate is determined by the concentration of dissolved oxygen. Isbell and Wadsworth arrived at the same conclusion when evaluating the effect that dry air versus pure oxygen had on the rate of the reaction.²⁷

Next, Schroeder and Sopchak reacted the chlorophosphonylated polyethylene with various other nucleophilic reagents to create a variety of phosphonate derivatives. The previously mentioned phosphonic acid derivative was produced by hydrolysis using water.²⁸ The ester derivative was made through the addition of an alcohol and the amide was produced through the addition of excess ammonia or amine. The authors also mentioned that when the derivatives were produced, their properties ranged from being highly flexible (ester derivative) to very stiff (unsubstituted amide derivative). This was an important observation because polymers containing different phosphonate derivatives could be used in distinct applications, depending on the properties required.

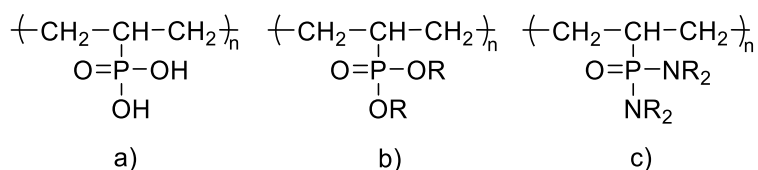


Figure 7: Phosphonyl derivatives produced after the chlorophosphonylation reaction. a) phosphonic acid produced through hydrolysis b) phosphonate ester produced by addition of an alcohol c) phosphonyl amide produced by addition of an amine

In addition to the difference in physical properties between the phosphonate polymer derivatives, Schroeder and Sopchak also reported a change in solubility.²⁸ As mentioned above, the phosphonic acid functionalized polymer was soluble in hot pyridine; however, when the ester and amide phosphonate polymer derivatives were dried, they became insoluble in a variety of solvents. The authors theorized that this may be due to cross-linking occurring between the phosphonyl groups on the polymers when being dried in the vacuum oven. Although they did not know how the cross-linking occurred, they hypothesized that phosphonic anhydride linkages may have been forming between the groups after partial hydrolysis. However, they later rejected this hypothesis, stating that crosslinking was not observed in the phosphonic acid functionalized polymer.

After completion of these background experiments using the polyethylene grease, Schroeder and Sopchak then conducted experiments using a higher molecular weight polymer. This study was conducted using polyethylene DYNH (commercial name), with an average molecular weight of 26,000 g/mol. They mentioned that chlorophosphonylation of this polymer was very similar to that of the polyethylene grease with a few exceptions.²⁸ The first exception was that when the reaction was run at temperatures below 55°C, the reaction rate was poor. This was attributed to the DYNH polymer separating into solid particles at those temperatures. However, the authors did find the reaction rate to be constant over a temperature range of 50-70°C. This finding conflicted with the results received for the polyethylene grease reactions, where the rate varied over this range. The variation in reaction rate due to temperature should be

carefully monitored when replicating this reaction with polymers of different molecular weights.

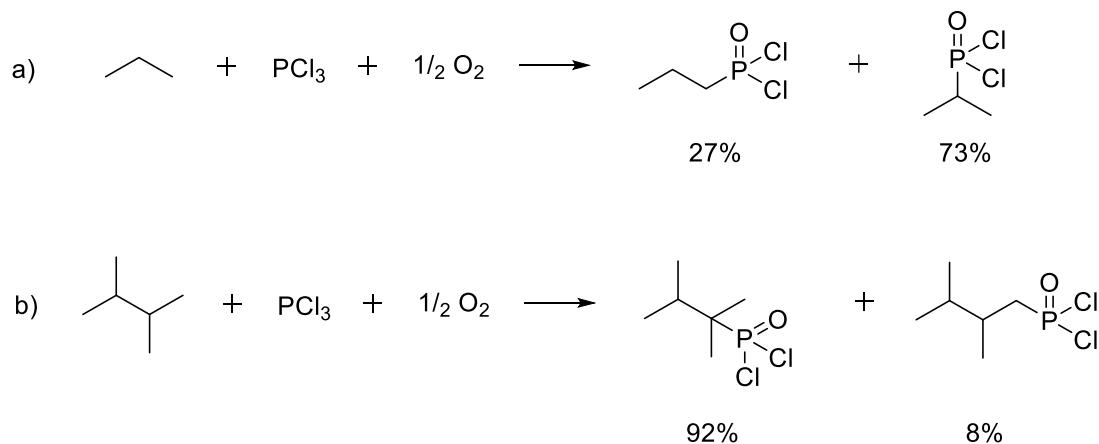
From the prior experiments with the preliminary polyethylene grease, Schroeder and Sopchak determined that the rate of reaction was dependent on the concentration of dissolved oxygen.²⁸ Using the higher molecular weight polymer, polyethylene DYNH, they conducted oxygen dependence experiments, where they varied the amount of oxygen that was allowed to be dissolved through the reaction mixture. With increasing dissolved oxygen concentration, the rate of reaction increased consistently, before eventually reaching a plateau. The dependence of the reaction rate on the concentration of dissolved oxygen is another important parameter to monitor when replicating this reaction with other polymers.

Again, like Isbell and Wadsworth, Schroeder and Sopchak also tested the catalytic effects of various reagents on the reaction. They found that additives like nickel, vanadium, silver, manganese, chromium, etc., increased the rate of the reaction, but also found these same compounds promoted side reactions.²⁸ This was evidenced by the phosphorus content of the generated polymers being lower than what was expected based on the amount of HCl gas produced. The authors also found that additives like iodine, sulfur, 1-octanethiol, phosphorus pentachloride, etc., inhibited the reaction completely. Through further investigation of the compounds that helped improve the reaction rate, they found that reproducibility was an issue. From this, they were able to

conclude that the compounds they initially thought were helping improve the reaction rate, were just scavengers for the inhibitory compounds and not catalysts.

Finally, Schroeder and Sopchak attempted the chlorophosphonylation reaction of other types of polymers. This included polystyrene, poly(methyl methacrylate), and polyisobutylene. They reported that the polymers degraded under these reaction conditions, as was evidenced by a sharp decrease in the molecular weight of the polymers.²⁸ However, this was not seen with the reactions using polyethylene, as there was no polymer degradation. These results suggested that another approach was needed to phosphonylate polymers, which degrade under these reaction conditions using PCl_3 and oxygen.

Another polymer that chemists attempted to chlorophosphonylate was atactic polypropylene. Belluš *et al.* studied the reaction conditions necessary to functionalize polypropylene with phosphonyl dichloride and phosphonic acid groups.²⁹ They also studied the properties of the polymer after it had been modified. Like Schroeder and Sopchak, Belluš *et al.* stated that the phosphonyl dichloride groups could bind to primary, secondary, and tertiary carbons.^{28,29} However, based on prior reactions with smaller organic hydrocarbons, propane, and 2,3-dimethylbutane, they assumed that the tertiary carbons of the polymer would be primarily phosphonylated (Scheme 5). Since the chlorophosphonylation reaction is radical in nature, the tertiary carbon being primarily phosphonylated is understandable, due to the stability of a tertiary radical.



Scheme 5: Chlorophosphonylation of propane and 2,3-dimethylbutane a)
 Functionalization occurred primarily on the secondary carbon of propane b)
 Functionalization occurred primarily on the tertiary carbon of 2,3-dimethylbutane

The method applied by Belluš *et al.* to conduct their chlorophosphonylation was like those mentioned previously. The reaction was completed by dissolving the atactic polypropylene in phosphorus trichloride, and oxygen was allowed to bubble through the reaction mixture.²⁹ In order to gain a better control on the degree of chlorophosphonylation, they kept the reaction conditions the same for each of the reactions. With constant molar ratios, oxygen flow, stirring, and temperature, they were able to control the degree of chlorophosphonylation through variation in reaction time. They noted that as the phosphorus content of the functionalized polypropylene increased, the polymer changed from being sticky to hard and rigid. The degree of phosphonylation also affected the solubility of the polymer. The polymers functionalized with the phosphonic acid groups were more polar than the non-functionalized ones. Therefore, they had an increased solubility in polar or basic organic solvents in comparison to the non-functionalized polymer. Interestingly, Belluš *et al.* reported that after hydrolysis of the phosphonyl dichloride groups to phosphonic acid, the polymer remained completely

soluble in toluene at 20°C. However, after the polymer was dried, the solubility in toluene was significantly reduced. They reported that this was due to partial anhydride formation between the phosphonic acid groups, as shown in **Figure 7**. However, this result contradicted the conclusions reached by Schroeder and Sopchak, as they mentioned that partial anhydride formation was not seen in their polymer functionalized with phosphonic acid groups.²⁸ The extent of partial anhydride formation is important to assess for future applications with the polymer. If the polymer were not being immediately used in a reaction, it could be stored in another more stable form to prevent anhydride formation which would affect solubility.

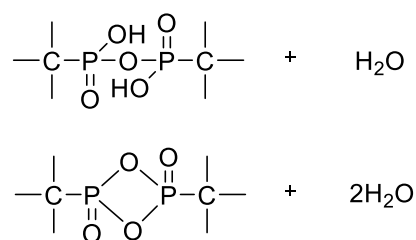


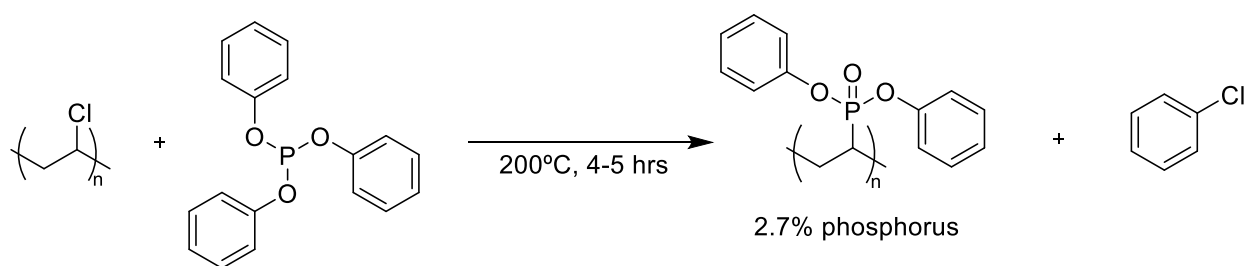
Figure 7: Anhydride formation due to the phosphonic acid groups contained within the polymer after drying

The papers reviewed in this section highlighted different attempts and studies of the chlorophosphonylation of various polymers. Schroeder and Sopchak conducted preliminary experiments using a polyethylene grease before studying the reaction using a higher molecular weight polymer, polyethylene DYNH.²⁸ They also attempted the reaction using polystyrene, poly(methyl methacrylate), and polyisobutylene but these polymers degraded under the reaction conditions. Through the review process, many key details were uncovered about the chlorophosphonylation reaction. It was important to note specifics, such as the dependence of reaction rate on the concentration of dissolved oxygen, or side reactions like partial anhydride formation. Chlorophosphonylation was

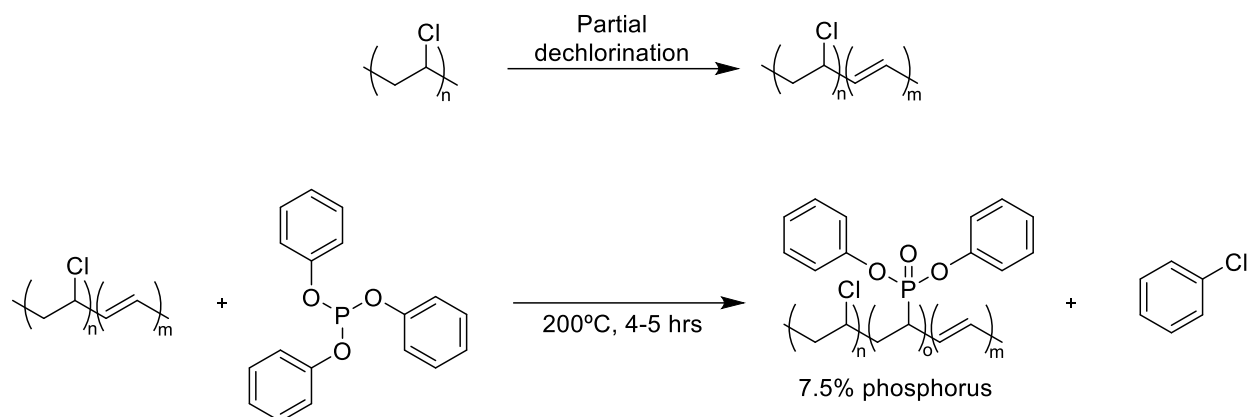
thoroughly reviewed in the previous sections because of the ability that phosphonates have to bind metal oxides. However, there are other methods to bond phosphonate groups onto molecules.

2.3.2 Phosphonylation of polymers using organophosphites

Another method that researchers have investigated to phosphonylate polymers is through a reaction with phosphites. Zil'berman *et al.* reported a method to functionalize poly(vinyl chloride) (PVC) with phosphorus through an Arbuzov rearrangement.³⁰ By heating a solution of triphenyl phosphite at 200 °C for 4-5 hours with PVC, they obtained a polymer after precipitation from dimethylformamide (DMF) or tetrahydrofuran (THF) that contained 2.7% phosphorus (Scheme 6). An infrared spectrum confirmed functionalization of the polymer as absorption bands with frequencies of 1600, 1500 cm^{-1} (aromatic ring stretch) and 1200 cm^{-1} (P=O stretch) were observed, even after repeated precipitation of the polymer.



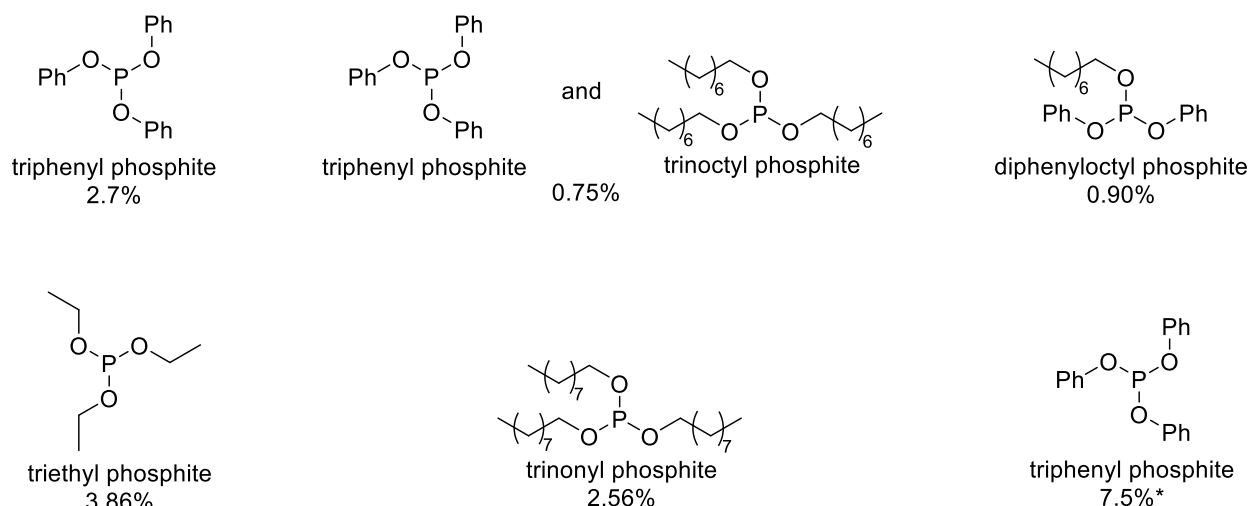
Scheme 6: Phosphonylation of PVC using phosphorus trichloride



Scheme 7: Partial dichlorination of PVC prior to phosphonylation using phosphorus trichloride

Interestingly, Zil'berman *et al.* noted that under these same reaction conditions, the reaction does not occur with secondary alkyl halides.³⁰ They stated that it is the labile PVC chlorine atoms placed beside an allyl group that helps this reaction occur. The bimolecular transition state of this reaction is stabilized by hyperconjugation between the orbital of the phosphorus and the conjugated pi bond of the allyl group. To prove this reactivity, they ran two experiments. First, they repeated the reaction using PVC of increasing molecular weights and found that as the molecular weight of the PVC increased, there was a decrease in the phosphorus content of the final polymer. This can be explained due to the decrease in the amount of olefin (allyl) end groups in the longer polymers. Simultaneously, PVC with higher molecular weights are obtained by running the polymerization reaction at lower temperatures. However, this also causes less branching in the longer chained PVC and is, therefore, another reason for the lesser amount of olefin end groups. Secondly, they conducted the reaction using PVC in which HCl had already been partially removed. This increased the number of allyl groups in the polymer prior to reacting it with the organic phosphite. Therefore, the final partially

dechlorinated polymer contained 7.5% phosphorus compared to 2.7% phosphorus when hydrogen chloride was not partially removed (Scheme 7).



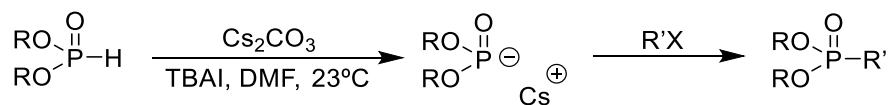
*PVC, hydrogen chloride partially removed (Cl, 39.9%)

Figure 8: Organic phosphites used in the phosphonylation of PVC along with the phosphorus content of the PVC post functionalization

The authors also found that the thermal stability of the functionalized PVC also increased after the phosphonylation reaction. **Figure 8**, contains the phosphites that were used to functionalize the PVC, as well as the phosphorus content after functionalization. Intriguingly, Zil'berman *et al.* found the thermal stability of PVC functionalized only with triphenyl phosphite was lower than that of PVC functionalized using a mixture of triphenyl and trialkyl or a mixed phosphite (triarylalkyl phosphite). The authors state that this is understandable because the rearrangement takes place more easily with a smaller R group (alkyl) bound to the phosphorus as opposed to the phenyl group.

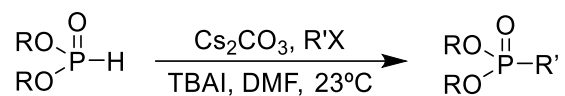
2.3.3 Phosphonylation by cesium carbonate (Cs₂CO₃) – promoted synthesis

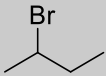
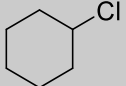
Finally, this last method reported by Cohen *et al.* is a mild reaction using cesium carbonate (Cs₂CO₃), tetrabutylammonium iodide (TBAI), and DMF as the solvent to functionalize alkyl halides at room temperature (Scheme 8).³¹ The reaction mechanism involves generating the phosphonate anion from a dialkyl phosphite. The phosphonate anion then attacks the alkyl halide generating the phosphonate functionalized molecule. The authors screened a variety of bases including DBU, triethylamine, and a variety of other alkali metal carbonate bases but they were not as effective as Cs₂CO₃. Next, they assessed the effect that TBAI had on the reaction. TBAI was used as a phase transfer catalyst, and it had a significant effect on the reaction yield. When TBAI was omitted from the reaction, the yield decreased from 97% to 31% overall.



Scheme 8: Synthesis of phosphonates using cesium carbonate, tetrabutylammonium iodide, and DMF at room temperature

Table 2: Secondary alkyl halides phosphonated through the cesium carbonate promoted synthesis



R'X	Time (hrs)	Yield (%)
 2-bromobutane	66	75
 2-iodopropane	40	55
 cyclohexyl chloride	70	47

The authors scoped a wide variety of alkyl halides for their ability to be phosphonylated using this reaction method. These included sterically demanding secondary alkyl halides like 2-bromobutane, 2-iodopropane, and cyclohexyl chloride. Given the reaction's mild and efficient method to phosphonylate these compounds, the hypothesis was to use this same reaction to attempt the phosphonylation of PVC. Since PVC is composed of repeating units of secondary alkyl halides, the idea was that this simple method could be employed as a phosphonylation technique.

2.4 Proposed Research

Thus far, this chapter has reviewed two different types of seemingly unrelated reactions. Section 1 of this chapter highlighted the use of the phosphorus-metal oxide bond as a method to functionalize surfaces. Generally, surface functionalization chemistry

is used by the electronics industry to enhance the properties of high-performance devices.²⁰ The ability to place nanoscale layers on surfaces using small organic molecules enables one to tune and modify the properties of the surface to improve device performance. Concomitantly, the chlorophosphonylation method discovered by Clayton and Jensen produced a straightforward approach to bond phosphonyl dichloride functional groups onto hydrocarbons.²⁶ The chlorophosphonylation reaction and other methods to functionalize polymers and small molecules were then reviewed. Researchers studied the effects that these phosphorus groups had on the properties of the polymers, as well as the parameters that affected yield. While these two topics seem unrelated, the proposed research aimed to combine these reactions to synthesize a new type of construction material with desirable properties.

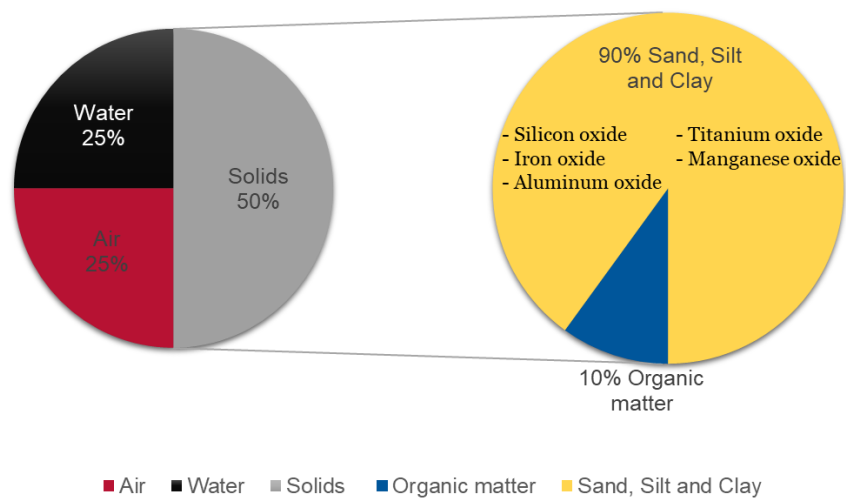


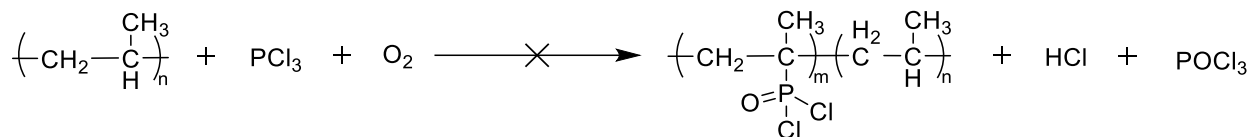
Figure 9: Approximate composition of soil

The goal of this research was to functionalize a variety of polymers (polypropylene, polyethylene, etc.) with phosphonate groups using the methods outlined above. The

phosphonylated polymers were then going to be mixed with soil so that the phosphonate groups would bond with the metal oxide particles found in soil. By volume, soil is composed of water, air, and solids.³² The solids are comprised of sand, silt, clay, and organic matter, and most soils vary by the quantity of sand, silt, and clay that they contain. Sand, silt, and clay are all metal oxides of different sizes and crystal structures.³³ As highlighted in **Figure 9**, since many of the metal oxides in soil overlap with those used in surface functionalization chemistry the hypothesis was that the same covalent bond would form between the functionalized polymers and metal oxide particles to create a robust composite material.

2.5 Results

The project began with conducting the chlorophosphonylation reaction using PCl_3 and oxygen. Although the reviewed papers were quite thorough in their experiments and optimization of the reaction, they were not very explicit on the reaction set-up. As such, cyclohexane was used as the preliminary substrate to evaluate the effectiveness of the reaction setup and to see if the chlorophosphonylation was successful. After reviewing the literature, the bubbling of oxygen was deemed to be important to the success of the reaction. For this reason, oxygen was bubbled through the reaction mixture using a glass pipette that was passed through a septum and inserted below the surface of the liquid reaction mixture. Using this reaction setup the cyclohexyl phosphonyl dichloride product was made. ^1H and ^{31}P NMR spectra were acquired and the chemical shifts obtained for the synthesized product matched the values reported in literature.³⁴



Scheme 9: Unsuccessful chlorophosphonylation reaction of amorphous polypropylene

Next, the reaction was attempted on amorphous polypropylene pellets that were acquired from Sigma Aldrich. The pellets were a cloudy white to off-white in colour, rubbery and about 0.75 cm in diameter. Unfortunately, the documents provided by Sigma Aldrich did not report a molecular weight value for the polymer. Following the reaction procedure set by Belluš *et al.*, the chlorophosphonylation of the amorphous polypropylene should have dissolved in phosphorus trichloride. However, solubility issues were immediately recognized as the polymer failed to dissolve in the PCl_3 solution. To help the polymer dissolve, the pellets were flattened and cut into pieces before being added to the reaction mixture. Still, the polymer was not dissolving in PCl_3 as mentioned in the literature. It should also be noted that although the polymer pellets were a cloudy white colour, once they were added to the PCl_3 solution they became clear. This made it difficult to tell whether the polymer pieces had truly dissolved. The stirring time of the polymer in the PCl_3 solution was also increased prior to bubbling oxygen through the reaction mixture. This was done to try and help the polymer dissolve without evaporating the PCl_3 or producing POCl_3 , but this was not successful.



Figure 10: Attempted chlorophosphonylation of amorphous polypropylene

Another issue that was encountered when conducting the reaction using the polypropylene polymer was the evaporation of the PCl_3 solvent. Since the reaction was being heated at $55\text{ }^\circ\text{C}$ and had oxygen bubbling through the reaction mixture, when left for 3 hours the PCl_3 evaporated completely. The ^{31}P NMR for the resulting brown/ black residue revealed that the expected chlorophosphonylated polymer was not being made. However, the NMR did contain the spectral values for PCl_3 and the oxidized POCl_3 .

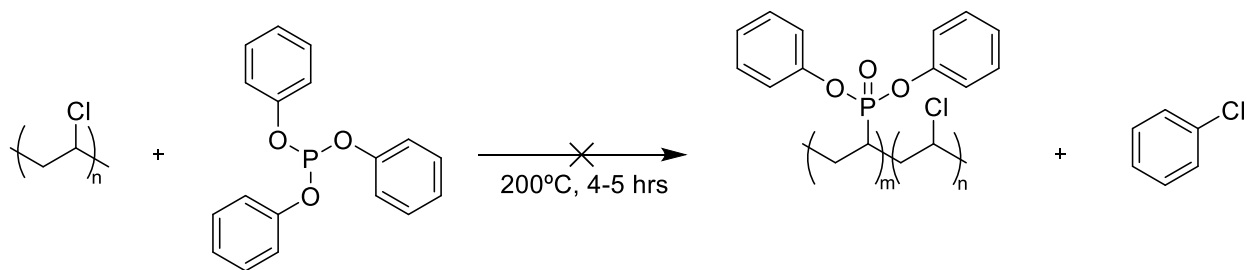
As shown in **Figure 10**, the experimental setup had inlet and outlet tubes that carried the gases required and produced (O_2 and HCl) by the reaction. The silicone tubing used as the outlet tube for the reaction continuously degraded due to the HCl gas that evolved as part of the reaction. This necessitated multiple attempts at building the reaction setup. Attention was then turned to see if there was a simpler method by which the reaction could be conducted to produce the chlorophosphonylated product. Instead of bubbling oxygen through the reaction mixture, a needle going through the septa into

the reaction vessel was capped with an oxygen-filled balloon and the reaction mixture was left to stir vigorously. Again, this new reaction setup was evaluated using cyclohexane as the preliminary substrate, and the formation of the chlorophosphonylated product was confirmed by the acquired ^1H and ^{31}P NMR spectra. This new reaction set up with an oxygen-filled balloon was then attempted on polypropylene. It is worth noting that because the reaction set-up with the reflux condenser was abandoned, the reactions using just the oxygen-containing balloon were conducted at room temperature. Unfortunately, the acquired ^{31}P NMR spectra only revealed the presence of PCl_3 and POCl_3 , and none of the expected chlorophosphonylated products. It was suspected that the reaction continuously failed due to the polymer not dissolving in the PCl_3 solution. An attempt was then made to dissolve the polymer in benzene prior to adding PCl_3 and oxygen. After 10 minutes of stirring and 20 minutes of sonicating, the polymer pieces looked to have gotten smaller and partially dissolved. Once again, however, the ^{31}P NMR spectra acquired after the reaction was deemed complete only revealed the presence of PCl_3 and POCl_3 .

After not being able to produce the chlorophosphonylated polypropylene product, the reaction was attempted on polystyrene. This was prior to reviewing the research conducted by Schroeder and Sopchak, where they mentioned that polystyrene degrades under these reaction conditions using PCl_3 and oxygen.²⁸ However, the results they reported can be confirmed because when the PCl_3 was added to the polystyrene, it appeared as though the polystyrene had dissolved. From the acquired ^{31}P NMR it was

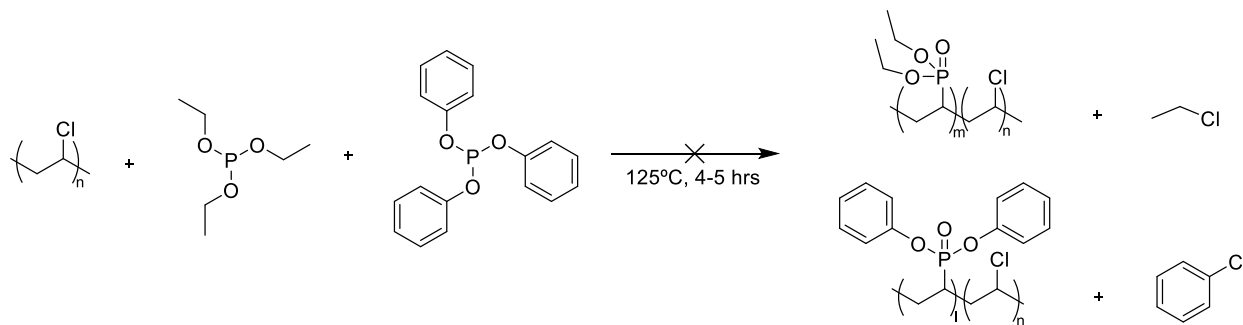
inferred that the chlorophosphonylated product was not made and what was thought to have been polystyrene dissolving may have been the polymer degrading.

A new substrate, paraffin candle wax, was then acquired to attempt the chlorophosphonylation reaction. Since paraffin wax has a similar structure to polyethylene it was assumed that it would be a good model substrate to evaluate the feasibility of the reaction. The reaction was run using the different methods highlighted above (room temp with an oxygen-filled balloon, heating at 55 °C with oxygen bubbling through the reaction mixture, and using benzene to dissolve the candle wax prior to adding PCl_3 and oxygen). When a ^{31}P NMR spectrum was acquired for the reactions run using these methods, it revealed a new peak at ~60 ppm. However, there were no literature papers available to indeed confirm that the wax had been chlorophosphonylated. The ^{31}P NMR peak for cyclohexyl phosphonyl dichloride appeared at 57 ppm.³⁴ Based on the proximity of the peaks the candle wax may have been chlorophosphonylated. However, a mixture of peaks was also expected based on the many sites that paraffin wax has for chlorophosphonylation. Therefore, the results of the chlorophosphonylation of the paraffin wax were inconclusive. This method for the chlorophosphonylation of polymers was then abandoned.



Scheme 10: Unsuccessful phosphonylation reaction of PVC using triphenyl phosphite

After the failed attempts to chlorophosphonylate the polymers using PCl_3 and oxygen, PVC was then acquired from Sigma Aldrich. The acquired PVC was a white powder, with an average M_w of $\sim 43,000$ and an average M_n of $\sim 22,000$. The PVC was acquired so that phosphonylation using organophosphites could be attempted. The reaction conditions were followed as outlined by Zil'berman *et al.* PVC was added to a microwave vial along with a stir bar and triphenyl phosphite, this was set to react in the microwave reactor at $200\text{ }^\circ\text{C}$ for 5 hours. However, the reaction had to be stopped early because of pressure building in the microwave reactor. After dissolving the reaction mixture in DMF and precipitating using methanol, ^1H and ^{31}P NMR were acquired. The acquired ^{31}P NMR had no peaks, signifying the product had not been made.

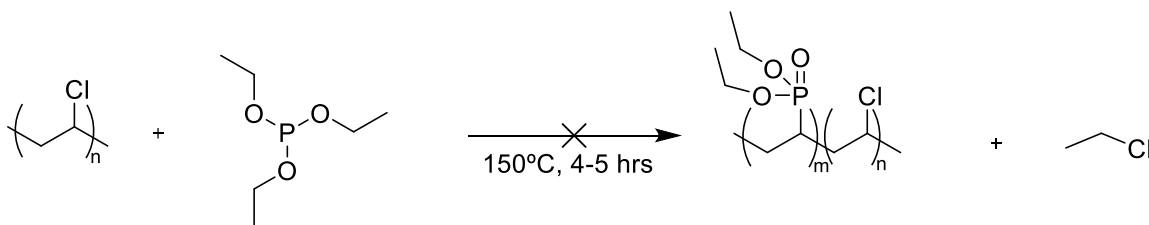


Scheme 11: Unsuccessful phosphonylation reaction of PVC using triphenyl phosphite and triethyl phosphite



Figure 11: Product of the attempted phosphonylation of PVC using triphenyl and triethyl phosphite

The reaction was then repeated with a mixture of triphenyl and triethyl phosphite at 125 °C instead of 200 °C to help keep the pressure in the reaction mixture within the instrument limits. As seen in **Figure 11**, a colour change occurred as the reaction mixture went from clear to orange. However, the solids in the reaction mixture were not soluble in DMF as outlined by the literature. Acetone, chloroform, dichloromethane (DCM), THF, methanol, acetonitrile, ethyl acetate, benzene, and dimethyl sulfoxide (DMSO) were also used to attempt to dissolve the solid contents, but none were successful.

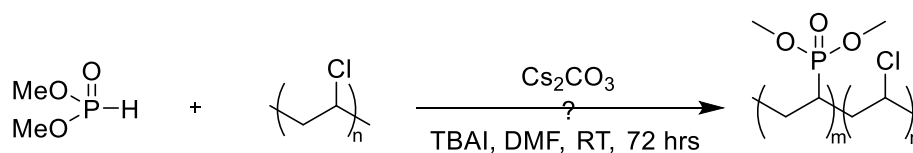


Scheme 12: Unsuccessful phosphonylation reaction of PVC using triethyl phosphite



Figure 12: Product of the attempted phosphonylation of PVC using triethyl phosphite

Finally, the reaction was attempted using triethyl phosphite at 150 °C for 5 hours. Again, the pressure inside the vial reached the maximum allowed by the microwave reactor, and the reaction vessel needed to be vented manually. The product received from the reaction was a circular ball. When the ball was cracked open using a mortar and pestle it was black (burnt) on the inside. A few more attempts with the reaction method using organophosphites and PVC were attempted, but none were successful. Infrared spectroscopy was also employed to help elucidate whether the phosphonylated product was made, but it was also inconclusive.



Scheme 13: Attempted phosphonylation reaction of PVC using the Cs_2CO_3 – promoted synthesis



Figure 13: Product of the attempted phosphonylation reaction of PVC using the Cs_2CO_3 – promoted synthesis

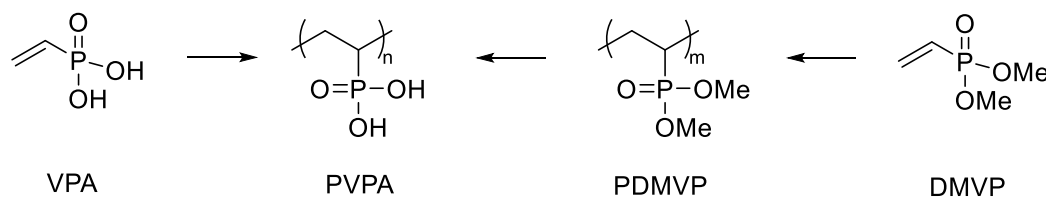
Lastly, the Cs_2CO_3 – promoted synthesis of phosphonates was attempted with the acquired PVC powder. The reaction was set up using the same method outlined by Cohen *et al.* The reaction time was even increased to 72 hours to match the reaction time of cyclohexyl chloride which the authors allowed to react for 70 hours. A colour change occurred for the resulting product as the white PVC powder became a brown paste, shown in **Figure 12**. The obtained ^{31}P NMR spectra had small peaks at 33 and 40 ppm. However, the ^1H NMR spectra was not valuable due to the large solvent peaks. Additional drying (high vacuum) also was not useful as the paste was so thick that the solvent was not being removed. Infrared spectroscopy was then used to try and elucidate whether the phosphonylated product was made, but it was also inconclusive. After this, the characterization of this product was stopped. When presenting the proposal for this project to committee members, it was decided that the project should first attempt to validate whether the phosphonate-metal oxide bond can occur with soil/sand. To do this,

instead of phosphorylating existing polymers, the project evolved into making our own polymers with phosphonate groups built into the polymer chain.

Chapter 3: Water-soluble PVPA-co-AA polymer solution

3.1 Poly(vinylphosphonic acid)

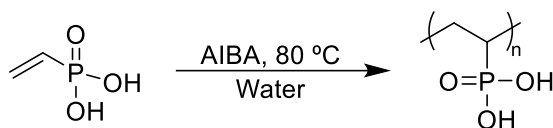
Poly(vinylphosphonic acid) (PVPA) is a polyelectrolyte synthesized via free radical polymerization of vinylphosphonic acid (VPA).³⁵ PVPA can also be made by the polymerization of vinylphosphonate ester derivatives followed by hydrolysis of the ester groups, as shown in Scheme 14.^{35,36} Phosphonic acid containing polymers and their derivatives have found applications in corrosion-resistant coatings,³⁷ fuel cell development,³⁸ and even as dental cements.³⁹ Since PVPA contains the phosphonic acid group as a part of its polymer backbone, the experiments to place phosphonate groups onto polymer chains would not need to be conducted. As such, PVPA synthesis and its properties were investigated.



Scheme 14: Synthesis of PVPA directly from VPA monomer (left); Synthesis of PVPA from the polymerization of dimethyl vinylphosphonate (DMVP), followed by the hydrolysis of poly(dimethyl vinylphosphonate) (PDMVP) (right)

A thorough study on the free radical polymerization of VPA was conducted by Bingöl *et al.*, where they uncovered the reaction mechanism for the polymerization. To synthesize their polymer, VPA and 2,2'-azobis(2-methylpropionamidine) dihydrochloride (AIBA), a water-soluble azo initiator, were dissolved in water and allowed to polymerize at 80 °C for 3 hours.³⁵ The resulting polymer was purified and isolated using a cellulose dialysis membrane. They reported that the molecular weight of the polymer was 62,000

Da which they determined using static light scattering (SLS). The SLS experiment was conducted in a 5 g L⁻¹ aqueous solution of NaH₂PO₄.



Scheme 15: PVPA synthesis using the AIBA radical initiator

Through analysis of ¹H and ¹³C NMR spectra, Bingöl *et al.* realized that PVPA is synthesized through a cyclopolymerization mechanism that begins with the formation of VPA anhydride.³⁵ When comparing the ¹³C NMR spectra for PVPA synthesized directly from VPA and the PVPA synthesized through hydrolysis of PDMVP, they noticed that they were significantly different. This implied that the polymerization mechanism between the two polymers was also different. The ¹H NMR spectra for PVPA obtained through the hydrolysis of PDMVP was consistent with that of an atactic polymer made from head-to-tail linked monomer units. However, the signals and intensities of the ¹H NMR spectra for PVPA synthesized by radical polymerization of VPA were consistent with an atactic polymer with many head-to-head and tail-to-tail linked monomer units. From this observation, they rationalized that it is not the VPA monomers that undergo polymerization, but rather it is the anhydride. The mechanism they proposed is illustrated in **Figure 14**.³⁵ VPA anhydride is formed in equilibrium with the free vinylphosphonic acid. The anhydrides are then polymerized via a five- or six-membered ring transition state. The five-membered ring transition state yields a head-to-head linkage with a methyne radical while the six-membered ring transition state produces a head-to-tail linkage with a methylenic radical. The authors stated that when the polymer is placed in a dilute aqueous solution at room temperature, the anhydride structures disappear, and the only

evidence of this mechanistic pathway is through the signals in the NMR spectra. Finally, Bingöl *et al.* also collected titration curve data on the synthesized PVPA in comparison to the VPA monomer. The VPA monomer is a diprotic acid with pK_{a_s} of 2.74 and 7.34, however, PVPA acted like a monoprotic acid and the second proton of the phosphonic acid groups were not removable. They hypothesized that due to electrostatic reasons, PVPA behaves like a monoprotic acid. The charge density of the fully ionized PVPA chain was likely too high to allow for the removal of the second proton.^{35,40,41}

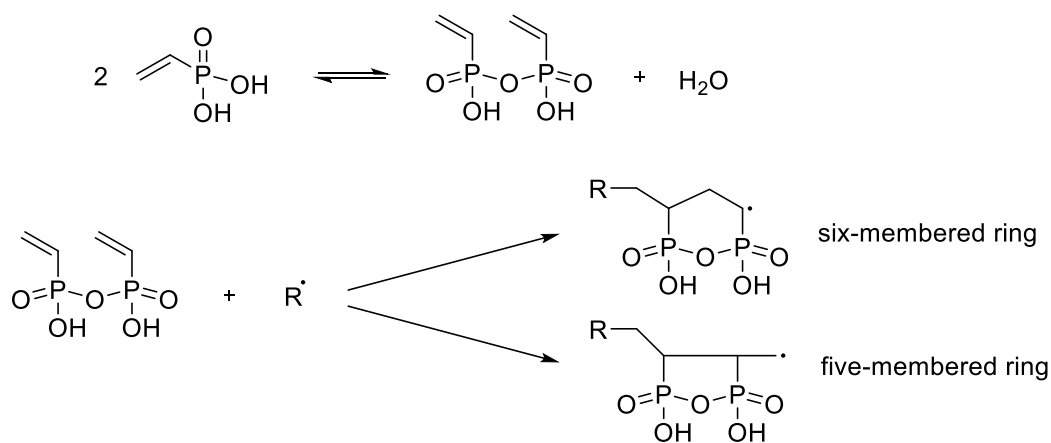


Figure 14: Proposed mechanism of cyclopolymerization via VPA anhydride.³⁵

Although PVPA contains the phosphonate groups that the project intended to use when creating the polymer–soil composites, the cyclopolymerization mechanism prevents the formation of high molecular-weight polymers.⁴¹ It was hypothesized that the presence of the phosphonate groups and the length of the polymers would both influence the properties of the polymer–soil composites. In addition, the cost of VPA monomer is high and if the polymer solution were going to be used as a composite building material it would not be feasible in terms of cost (VPA \$259.00 for 25 grams, Sigma Aldrich). However, a novel phosphonate containing polymer, poly(vinylphosphonic acid) – co –

acrylic acid (PVPA-co-AA) was then found. Using this copolymer, the ratio of phosphonate in the polymer would be able to be modified and would help validate whether the phosphonate-metal oxide bond can occur with soil/sand.

3.2 Poly(vinylphosphonic acid) – co – acrylic acid

The phosphonate containing polymer, PVPA-co-AA has been identified as a potential candidate in bone tissue engineering. The polymer is theorized to mimic bisphosphonate drugs that are used to treat osteoporosis.^{41,42} The phosphonate groups on PVPA-co-AA are structurally similar to bisphosphonates, and the negative charge on the phosphonate groups allows them to chelate Ca^{2+} ions. PVPA-co-AA is made from two monomers, VPA and acrylic acid (AA). As such, it contains both phosphonic acid and carboxylic acid functional groups. Both functional groups can chelate Ca^{2+} and have been used previously in bone tissue scaffolds.⁴² Dey *et al.* synthesized and characterized a range of PVPA-co-AA with varying compositions of both monomers (VPA: AA) to study their effect in bone tissue scaffolds.⁴¹

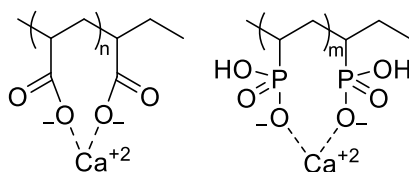
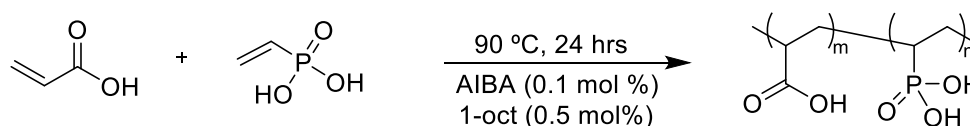


Figure 15: Calcium chelating ability of PAA and PVPA

The authors highlighted a few differences between the VPA and AA monomers. Firstly, they noted that the reactivity ratios of AA (r_1) and VPA (r_2) were 4.09 and 0.042, respectively.⁴¹ The large difference in the reactivity ratios, where $r_1 \gg 1 \gg r_2$, might cause composition drift, where the composition of the copolymer changes as the polymerization

continues. The lower reactivity ratio of VPA can be explained by the polymerization mechanism discovered by Bingöl *et al.*³⁵ The mechanism which starts with the formation of VPA anhydride likely lowers the reactivity of VPA and slows the rate of reaction.^{35,41} Secondly, they stated that the main difference between the two monomers is the ease at which the acids are deprotonated when in solution. Bingöl *et al.* found that the pK_a values of VPA were 2.74 and 7.34,³⁵ while AA has a pK_a of 4.26.⁴³ This means that VPA is likely to be deprotonated in solution versus the AA monomer, this would increase electrostatic forces between the growing polymer chain and the monomer and likely contributes to its low reactivity ratio.^{41,44}



Scheme 16: Optimized free radical polymerization of AA and PVPA conducted by Dey *et al.*⁴¹

To synthesize the range of PVPA-co-AA polymers with different ratios of VPA to AA, Dey *et al.* repeated the same procedure but modified the molar ratios of VPA to AA, as necessary.⁴¹ VPA was dissolved in water and added to a flask that had been purged with nitrogen, this was left to stir at 90 °C for 30 minutes. AA, AIBA, and 1-octanethiol (1-oct) were all separately dissolved in water and were added to the reaction flask in equal portions every 30 minutes over the course of 6 hours. Finally, after the last addition of AA, AIBA, and 1-oct, the reaction was left to stir for 18 hours. The reason AA and the initiator were added to the reaction vessel in a semi-batch process, was to allow VPA to be incorporated into the polymer chain. As mentioned above, since the reactivity ratio of AA is much higher than VPA, VPA is likely only added to the polymer chain once the

concentration of AA has decreased. Therefore, to prevent the formation of polymer chains that were entirely polyacrylic acid (PAA), AA was added slowly over time to the reaction mixture that contained a higher concentration of VPA.⁴⁴ The semi-batch addition of the initiator, AIBA, was to ensure that propagating polymer chains were always present in the reaction mixture as AA was being added.

In an effort to gain insights into the compositions of the various PVPA-co-AA samples produced, Dey *et al.* also developed a new method to quantitatively determine the copolymer composition using ³¹P NMR spectroscopy. The ³¹P NMR spectra were recorded in solution (5 wt% in D₂O) and were referenced to trimethyl phosphate (TMP) ($\delta(^{31}\text{P}) = 2.8$ ppm).⁴¹ 1.5 wt% of TMP was added to the NMR sample containing PVPA-co-AA and D₂O. The moles per integral of TMP were calculated using eq.1:

$$n_{TMP} = \frac{m_{TMP}}{M_{TMP} \times \int TMP} \quad (1)$$

where n_{TMP} is the number of moles of TMP, m_{TMP} is the mass of TMP added to the NMR sample, M_{TMP} is the molar mass of TMP and $\int TMP$ is the area under the peak for TMP. This value was then used to calculate the number of moles of VPA, n_{VPA} , in the NMR sample, using eq. 2:

$$n_{VPA} = n_{TMP} \times \int VPA \quad (2)$$

The $\int VPA$ is the integral under the peak for O=P(OH)₂ polymer at 29-32 ppm. The moles of VPA, the total mass of the polymer sample, $m_{PVPA-co-AA}$, and the molar masses of

VPA and AA, M_{VPA} and M_{AA} , respectively, were used in eq. 3 to calculate the number of moles of AA, n_{AA} .

$$n_{AA} = \frac{(m_{PVPA-co-AA} - (n_{VPA} \times M_{VPA}))}{M_{AA}} \quad (3)$$

Finally, the mol % VPA in the copolymer sample could be calculated, using eq. 4:

$$mol \% VPA = \frac{n_{VPA}}{n_{VPA} + n_{AA}} \quad (4)$$

This method was developed because although the monomer feed ratio could be calculated and added to the reaction vessel accurately, the copolymer compositions varied greatly. The difference in copolymer compositions and feed composition was likely caused by the large difference in reactivity ratios between VPA and AA.

Similar to Bingöl *et al.*, Dey *et al.* also conducted titration experiments on the PVPA homopolymer and their copolymers. The titration data they collected matched that of Bingöl *et al.* where the VPA monomer demonstrated the two dissociation steps, while PVPA behaved as a monoprotic acid.^{35,41} Interestingly, the titration curves of the PVPA-co-AA copolymers showed two neutralization steps. The authors attributed the first step to VPA and the second step to AA.⁴¹ However, they also made note that these steps were not very distinct.

Finally, Dey *et al.* performed calcium chelation experiments to quantify the calcium chelation capacities of the different PVPA-co-AA polymers. They conducted the experiment at pH 7.3 and 9.0, with copolymers compositions ranging from 0 to 100 mol % VPA.⁴¹ The calcium chelation capacities of the polymers were all higher at the higher pH of 9.0. This was expected since at the more basic pH, the acid groups are increasingly deprotonated. The increased deprotonation leads to intramolecular repulsion and the polymer chain expands creating more available binding sites for the Ca^{2+} ions. As the mol % VPA of the copolymers increased so did their calcium chelating ability, until it reached a maximum of ~30 mol % VPA. After that, there was a steady decrease in the calcium chelation ability of the copolymers. The authors expected that the calcium chelating ability of the copolymers should have increased linearly with increasing VPA content. This was because of the lower pK_a of VPA and the increased dissociation of its acid groups. However, the authors noted that at mol % VPA values greater than 60% there were significant decreases in the polymer's molar masses. They hypothesized that these results are caused by VPA hindering the production of high molecular weight polymers and the unknown distribution of phosphonic acid groups throughout the polymer chain, which may also play a role in the polymers ability to chelate Ca^{2+} ions.

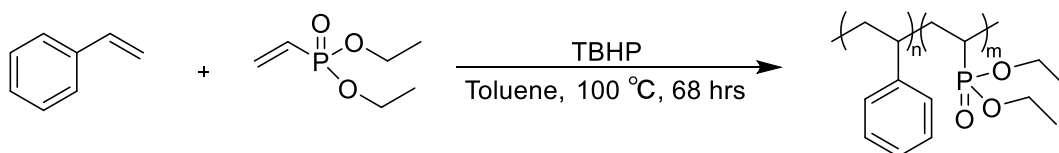
The work conducted by Dey *et al.* on the calcium chelating ability of their series of PVPA-co-AA polymers gave insight into the polymers potential use in bone tissue engineering. The binding ability of both monomer groups to chelate Ca^{+2} made this copolymer appealing for their bone scaffold applications. Given the results of this study and the potential to alter the feed composition of the polymer, it was decided that the

production of our polymer composites would begin with the production of PVPA-co-AA. The ability to have phosphonate groups within the polymer backbone and the cost of AA (AA \$24.00 for 25 grams, TCI Chemicals) being substantially lower than VPA, made it a cost-effective choice. Therefore, work began on the production of a series of PVPA-co-AA polymers.

3.3 Composite results

3.3.1 Compression testing

The first composite samples produced from this part of the project were made from a styrene-diethyl vinylphosphonate (S-DEVP) copolymer. This was the first polymer made as part of the project that incorporated a phosphonate group directly into the polymer backbone. Due to supply chain issues of the VPA and AA monomers, it was decided that this phosphonate containing polymer would be a good starting point. The procedure outlined by Banks *et al.* was used to make the S-DEVP polymer.⁴⁵ The styrene and DEVP monomers were added to a dry round bottom flask (RBF) that had been purged with argon, toluene was used as the solvent and tert-butyl hydroperoxide (TBHP) as the initiator. The reaction was then left to stir at 100 °C for 68 hours. The polymer was isolated through precipitation in cold methanol and dried under a vacuum. The ³¹P NMR spectra that was acquired had two peaks, the peak at ~17 ppm was assigned to residual DEVP monomer and the peak at ~35 ppm was consistent with a polymer containing DEVP.⁴⁶



Scheme 17: Synthesis of styrene – diethyl vinylphosphonate



Figure 16: The first composite samples made with S-DEVP and various substrates

The first composite samples produced using this copolymer were made by mixing equal parts polymer and substrates by weight, using chloroform to dissolve S-DEVP. The substrates employed were aluminum oxide, silica, sand, titanium oxide, and magnesium oxide. The substrate – polymer mixtures were then left to dry in the fume hood for 3 days under ambient conditions. After drying, a scoopula was used in an attempt to puncture the samples. However, they were quite strong and resistant to being pierced. This was seen as a good sign since these were the first composite samples produced with a phosphonate containing polymer and they showed some indication of strength. However, it was decided that research on this copolymer's ability to produce composite samples would not continue further. It was realized that this polymer's solubility in organic solvents would not be scalable if it were to be used as a construction material. Attention was then given to PVPA as it is a water-soluble polymer, and it contained the wanted phosphonate group.

The polymerization of VPA was done following the procedure set by Bingöl *et al.* The polymer solution was dissolved in D₂O, and the acquired ³¹P NMR spectra helped confirm the production of PVPA as a peak was seen at 31 ppm, consistent with a PO₃H₂ group of PVPA in D₂O.⁴⁷ The first real composite sample was made using this PVPA

solution and S25-3 sand from Sigma Aldrich that is typically used to pack chromatography columns. It should be noted that the composites made with S-DEVP were made in glass vials, these were not removable without having to break the glass. As such, a new method for creating the polymer composites had to be conceived. It was decided that a mould would have to be created so that once the composites were added and dried, they could be removed easily. The first moulds were small 2-inch PVC pipes with threaded ends that could be capped with a metal nut or vial caps, shown in **Figure 17**. These were chosen as our first moulds as they produced samples that were assumed to be large enough for compression testing while using minimal amounts of product.

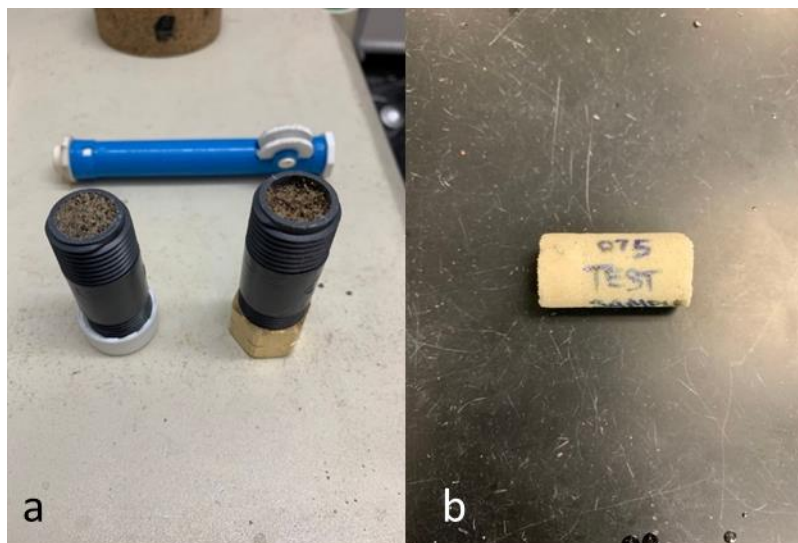


Figure 17: Preparation of the first composite samples. a) 2-inch PVC pipes as moulds for the first composite samples b) first composite sample produced using PVPA and sand

The compression testing of the composite samples produced made this project multifaceted. Compression testing was decided as the property that would be used to directly compare our polymer composites strength to concrete. To conduct the compression testing, technical staff from the department of civil and environmental

engineering were contacted and the early-stage samples produced were submitted for analysis. Once the project gained traction and samples were being produced regularly, the Multi-Scale Additive Manufacturing Lab (MSAM) allowed access to their universal mechanical testing system.

The technical staff from the department of civil and environmental engineering recommended that moulds of a bigger size be used to make the composites being submitted for compression testing. Issues with cracks and shape are amplified when collecting data with smaller sized samples. This is why in most testing studies, guidelines set by the American Society for Testing and Materials (ASTM) are typically followed. In the case of assessing the compressive strength of concrete, ASTM C39 guidelines require the concrete being tested to be 4 x 8 or 6 x 12-inch cylinders.⁴⁸ It was decided that the preparation of samples this large would be too costly at this stage of the research. Therefore, moulds were made from centrifuge tubes cut in half which produced approximately 1 x 2-inch cylindrical composites (more information about sample preparation in the supporting information section). It should be noted that the composites produced using this mould were not perfect cylinders. As shown in **Figure 18**, there is a slight taper to the samples, and they get skinnier as they get to the top. However, this was the best solution to produce samples without having to order custom made moulds.



Figure 18: Samples made in the centrifuge tube moulds containing the slight taper in diameter towards the top

The first composite sample **1** (refer to supporting information, composite samples produced), formed using the centrifuge tube mould was made using the PVPA polymer solution and the S25-3 sand. The polymer solutions used to make the composite samples were used without any purification directly after polymerization. In the text, when a mL amount of polymer solution is mentioned, it is being added directly from the reaction vessel. To prepare the sample, 0.6 mL of the polymer solution was mixed with 10 mL of DI water and was poured into a mould containing the sand, before being left to dry overnight. The next day the mould containing the sample was placed in a vacuum oven at 45 °C for 4 hours. The sample was then removed from the mould and dried in an oven at 150 °C for 2 hours. After drying, the sample was sent for compression testing where the maximum stress was calculated to be 0.60 (0.86%) MPa (Note: The polymer-to-sand weight percentage will be highlighted in brackets beside the compressive strength value for each composite sample). The vacuum oven was employed for the production of the first few composite samples to help dry the samples quickly. However, this procedure was

later stopped because the vacuum was pulling the polymer solution out of the mould along with some of the sand. Instead, the method outlined in the supporting information became the standard. Although the first sample made using the new mould was with PVPA, this was also stopped due to the cost of the VPA monomer mentioned in the previous sections. The polymer composites were then produced using PVPA-co-AA.

The PVPA-co-AA polymer was made following the procedure set by Dey *et al.*, where VPA was dissolved in water and added to the reaction vessel. The chain transfer agent (CTA), AA, and AIBA were all dissolved in water separately and added to the reaction vessel every 30 minutes over 6 hours.⁴¹ The polymer was made with and without the CTA, 1-octanethiol, to assess its effect on the compressive strength of the produced composite samples. Variations of the copolymer were also made with the feed composition varying from 70:30 to 99:1, AA to VPA. The polymer was confirmed to have been made using ³¹P NMR, where the acquired spectra for the sample dissolved in D₂O had a peak at ~30 ppm, matching the spectra acquired by Dey *et al.*⁴¹ However, residual monomer peaks for VPA were also present at ~15 ppm.

The first composite experiment using a PVPA-co-AA polymer was done to evaluate the method of pouring the polymer solution into a mould containing the sand versus mixing the polymer solution and sand prior to adding it to the mould. These early experiments were conducted to assess different methods of examining the composite samples so that a consistent method of preparation could be finalized. For sample **2**, 0.6 mL of the PVPA-co-AA (CTA) (30:70) (naming convention: CTA in brackets signifies that

CTA was used in the polymer synthesis, the ratio in brackets highlights the feed ratio when synthesizing the polymer) polymer solution was mixed with 9 mL of DI water and poured into a mould that contained sand. When preparing sample **3**, 0.6 mL of polymer solution and 9 mL of DI water were mixed with the sand and then placed in the mould to dry. The compressive strength values for samples **2** and **3** were 0.70 (0.54%) and 0.94 (0.53%) MPa, respectively. The difference when comparing the two samples although not large is expected. When pouring the polymer solution from the top of the mould, the polymer would not be able to pass through to the bottom sand particles and bind them to provide strength. However, when thoroughly mixed, the polymer would have been homogeneously spread throughout the composite sample and is able to provide the increased strength. Following these results for the remainder of the polymer composites, the polymer was mixed with the sand prior to adding the mixture to the mould.

Next, the effect of not adding water to the polymer mixture was investigated. Water was being added to the polymer mixture because it was hypothesized that adding water would allow for better mixability when making the composite samples. Sample **4** was made using 1 mL of PVPA-co-AA (CTA) (10:90) and 8 mL of DI water. While sample **5** was made using 1 mL of PVPA-co-AA (CTA) (10:90) and no water. Both samples were made by blending the solution with the sand prior to adding them to the mould. After 6 days of drying open to air in the fume hood, sample **4** was still wet at the bottom and had to be placed in the oven at 52 °C for 6 hours before the water could be removed from the mould. However, sample **5** was dry and popped out of the mould with no issue. Both samples once out of the moulds were placed in the oven at 150 °C for 22 hours. Samples

4 and **5** had compressive strength values of 1.8 (0.81%) and 5.4 (0.81%) MPa, respectively. The sample with no added water showed a better compressive strength value than the sample with added water. Following this result, the addition of water to the polymer mixtures was stopped and just the polymer solution was used to make the polymer composites.

Next, a set of composite samples was made using increasing amounts of the polymer solution. PVPA-co-AA (CTA) (10:90) was used to make samples **6**, **7**, and **8**, with 1, 2, and 3 mL of the polymer solution, respectively. As illustrated in **Figure 19**, the compressive strengths of the polymer composites increased linearly, from 3.4 (0.86%) to 22.1 (2.57%) MPa. This trend was expected as the increased amounts of polymer binding to the sand particles should impart greater compressive strength to the composite samples. This experiment was then repeated with a PAA polymer solution to assess if the phosphonate group in the copolymers were having any effect on bettering the compressive strength of the produced samples.

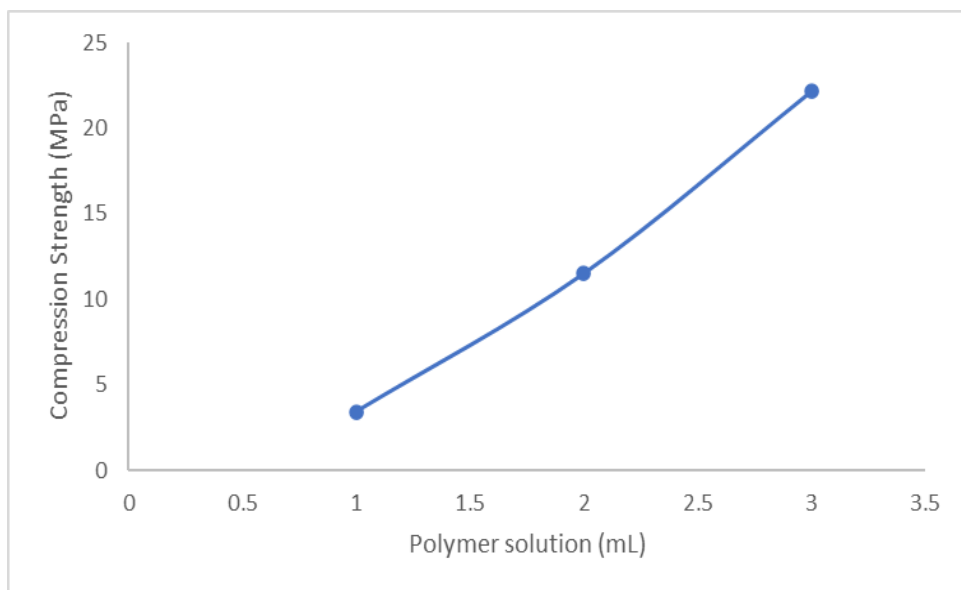


Figure 19: Compressive strength of PVPA-co-AA (CTA) (30:70) polymer composites increased with greater amounts of added polymer solution

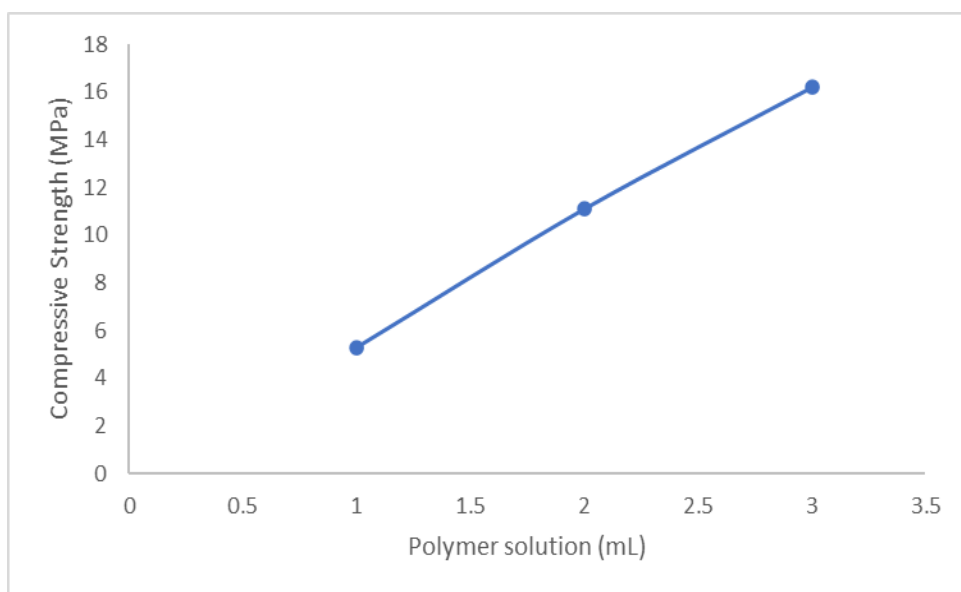


Figure 20: Compressive strength of PAA (CTA) polymer composites increased with greater amounts of added polymer solution

Table 3: Comparing the compressive strength value of polymer composites made with PVPA-co-AA (CTA) (30:70) and PAA (CTA)

	Polymer composites and Compressive strength (MPa)	
Polymer amount (mL)	PVPA-co-AA (CTA) (30:70)	Polyacrylic acid (CTA)
1	3.4 (0.86%)	5.3 (0.81%)
2	11.5 (1.72%)	11.1 (1.62%)
3	22.1 (2.57%)	16.2 (2.44%)

The polyacrylic acid samples, **9**, **10**, and **11**, were made using the same method as the previous experiment with increasing amounts of the polymer solution. The same linear trend was seen where the compressive strength values of the composites increased with the amount of added polymer solution. When comparing the compressive strength values of both composite sets, the PAA 1 mL sample was stronger than the corresponding PVPA-co-AA 1 mL sample. However, for the samples made with 3 mL of polymer solution the PVPA-co-AA sample was significantly stronger (Table 3). Given these results, it was not possible to say with certainty whether the phosphonate groups in the PVPA-co-AA polymer, were imparting any increased strength compared to PAA.

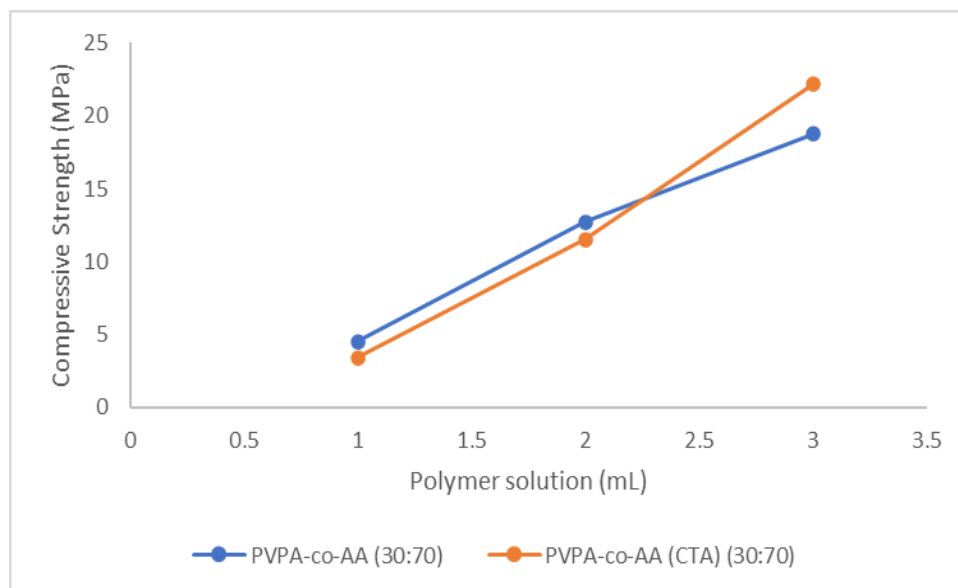


Figure 21: The effect of CTA on PVPA-co-AA (30:70) polymer composites

Subsequently, the addition of chain transfer agent, 1-octanethiol, was investigated to see its effect on the strength of the produced composite samples. Given that PVPA-co-AA (CTA) (30:70) polymer had already been made with CTA, producing samples **6**, **7**, and **8**, a PVPA-co-AA (30:70) polymer was synthesized without the addition of CTA. However, the water that the CTA was usually dissolved in prior to adding it to the reaction vessel, was still added. This was done to keep the amount of polymer in the volume measurements (assuming complete polymerization) consistent when making the polymer composites. The composites, **12**, **13**, and **14**, made with PVPA-co-AA (30:70) were created following the previous method of incremental 1 mL amounts. As highlighted in **Figure 21**, the two polymer composite sets were not vastly different in their compressive strength.

The experiment was then repeated with PVPA-co-AA (10:90) polymers with and without CTA. The composites without CTA were samples **15**, **16**, and **17**, while the composites with CTA were **18**, **19** and **20*** (Note: This sample was too strong and exceeded the capacity of the frame it was being tested with, the sample is likely stronger). The compressive strength results for this experiment as shown in **Figure 22**, were quite different. In this experiment, the polymer composites made with the polymer solution containing CTA were stronger than those without. After a literature search, it was found that PAA is branched when produced by radical polymerization.⁴⁹ Chain transfer agents like 1-octanethiol, are found to reduce the degree of branching when present among the polymer reactants. CTA's work through a "patching" reaction, where a mid-chain radical that would usually lead to a branched polymer, abstracts a hydrogen atom from the CTA and this prevents branching. Dey *et al.* also added CTA when the VPA: AA feed ratio was under 40:60 (VPA content <40%), and much of the copolymer would have been composed of AA monomer units.⁴¹ At the same time the authors stated that copolymers with high VPA contents (>60%) had much lower molar masses. This could be the reason that the CTA had such a large effect on the PVPA-co-AA (10:90) composites. The (10:90) samples with CTA, likely had a lesser degree of branching and so the polymer chains were longer. While without the added CTA, branching was allowed to occur producing shorter, branched polymer chains. These shorter branched polymers were not able to bind as many sand particles and caused the lower compressive strength. The degree of branching had a greater effect on the (10:90) polymer samples because this copolymer had a large amount of AA and mimics PAA. However, the (30:70) samples may have had a smaller difference between the polymers with and without CTA, because of the effect

that VPA has on producing higher molecular weight polymers. Therefore, the branching effect was negligible between the two polymer composite sets. Additionally, the polymer solutions containing CTA were less viscous than their counterparts. This made them easier to use when making the composite samples. Based on these results and the ease of use that the added CTA provided, CTA (1-octanethiol) was added for the subsequent polymerizations.

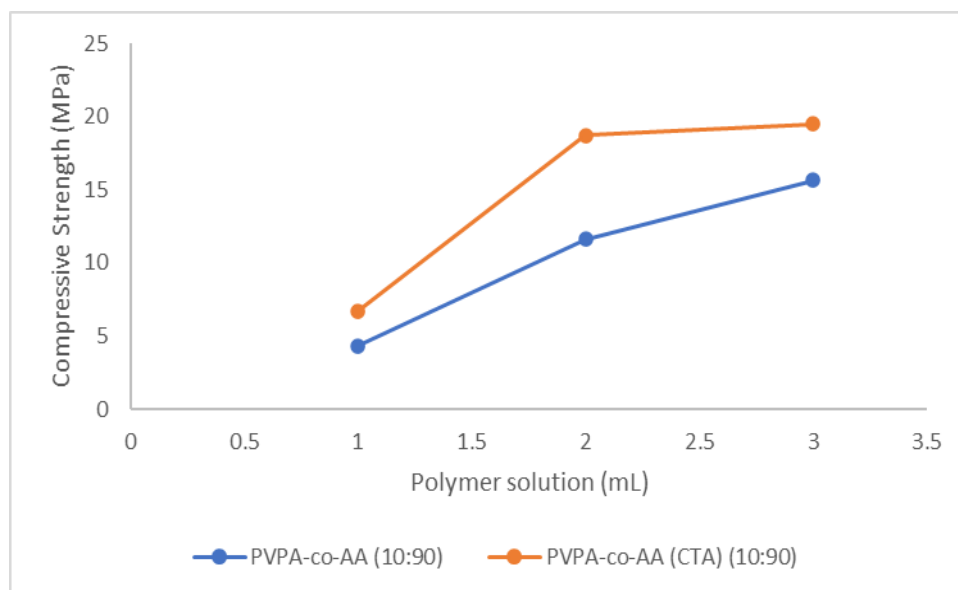


Figure 22: The effect of CTA on PVPA-co-AA (10:90) polymer composites

*Note: The PVPA-co-AA (CTA) (10:90) sample with 3 mL of polymer, exceeded the capacity of the frame it was being tested with, the sample is likely stronger

The next experiment conducted made use of isolated PVPA-co-AA (CTA) (30:70) polymer. Dey *et al.* isolated their polymers using dialysis, and the resulting polymer was dried at 55 °C.⁴¹ Our method of isolating the polymer involved precipitation in acetone. This mixture was centrifuged and formed a pellet, after decanting the water/acetone mixture, additional acetone was added. This was shaken and centrifuged until the pellet changed from clear to white in colour. After drying using the high vacuum, a ³¹P NMR

spectrum was acquired and confirmed the isolation of the polymer through the disappearance of the monomer VPA peak. Two composite samples were made using PVPA-co-AA (CTA) (30:70). Sample **21** was made by mixing 1 mL of the polymer solution with sand, using the same procedure outlined previously. Sample **22** was made using 0.3708 g of the dry isolated polymer dissolved in 1.5 mL of DI water. This mixture was then blended with the sand and added to the mould. After 6 days of air drying in the fume hood and 4 hours in the oven at 150 °C, the samples were sent for compression testing. The compressive strength for sample **21** was 3.3 (0.86%) MPa, while sample **22** was 4.7 (0.86%) MPa. The difference between these two composite samples is quite large, however, the result is understandable. Although the polymer/sand and VPA/sand ratios are the same, the polymer in solution assumed that a complete polymerization had occurred. However, this is not the case as is evident through the ^{31}P NMR of the polymer solution where the monomer peaks for VPA are still visible.

Table 4: Testing the effect of additional water on the compressive strength values of polymer composites

Amounts of polymer and water used to make the composite samples		Polymer composites and Compressive strength (MPa)	
Polymer amount (mL)	Water amount (mL)	PVPA-co-AA (CTA) (2:98)	Polyacrylic acid (CTA) (1:99)
3	-	18.5 (2.41%) (23)	19.2 (2.39%) (26)
3	3	20.5 (2.37%) (24)	22.2 (2.41%) (27)
1.5	1.5	11.9 (1.21%) (25)	11.9 (1.20%) (28)

Once more, the effect of adding water to the polymer and sand prior to adding the mixture to the mould was investigated to see if the additional water helped with mixability. However, on this occasion instead of a 1:8 mL polymer solution to water ratio, the experiment was repeated with 1:1 mL polymer solution and water quantities. This was compared to a control sample that had no additional water added. Samples **23**, **24**, and **25** were made with a PVPA-co-AA (CTA) (2:98) polymer, and samples **26**, **27**, and **28** were made with a PVPA-co-AA (CTA) (1:99) polymer. Samples **23** and **26** were the control samples with no additional water, samples **24** and **27** were made with 3 mL of polymer solution and 3 mL of water, while samples **25** and **28** were made with 1.5 mL of polymer solution and 1.5 mL of water. The results for both sample sets were almost identical, the samples with 3 mL of polymer and water (**24** and **27**) were stronger than the control samples with no additional water (**23** and **26**). The samples with 1.5 mL of polymer

and water (**25** and **28**) were about half as strong as the 3 mL polymer and water samples (**24** and **27**). The additional water helped with the mixability when making the composite samples and also yielded better compressive strength results. However, the excess of water made handling the composite samples more difficult. The samples required additional days to dry in the fume hood, or needed to be carefully handled before placing them in the oven to dry at 150 °C. Many samples broke at this step as they were quite soft until the water had evaporated. Therefore, although the additional water may have contributed greater strength, this was not investigated further, however, due to the improvement in compressive strength it may be worthwhile revisiting water added samples in the future.

The next polymer characteristic that was investigated was molecular weight. However, for this experiment, the PVPA-co-AA copolymers were not used. Instead, PAA powder of various molecular weights was ordered from polysciences. Polymers of approximately 450,000, 1,000,000, and 4,000,000 weight average molecular weight (M_w) were ordered for this experiment. Two sets of polymer composites were made with these PAA powders. For the first set of samples (**29**, **30**, and **31**) the dry polymer powder was mixed with the sand and then 3 mL of water was added before blending and putting the mixtures into the mould. The amount of dry polymer was approximately 1.04 g, this was done to stay consistent with the quantity of polymer in approximately 3 mL of polymer solution assuming a complete polymerization. For the second set of samples (**32**, **33**, and **34**), the polymer powders were dissolved in 3 mL of water before being mixed with the sand. The compressive strength of the first set of samples were 11.5 (2.42%), 9.0

(2.45%), and 7.1 (2.41%) MPa for samples **29**, **30** and **31**, respectively. The compressive strength of these samples showed that the sample made with the lowest molecular weight polymer (450,000 M_w) was the strongest, and as the polymers got bigger the strength decreased. However, the compressive strengths did not vary as much as they did for the second set of polymers. Again, with the second set of samples the lowest molecular weight polymer **32** ($\sim 450,000 M_w$) was the strongest, with a compressive strength value of 12.6 (2.42%) MPa. However, the samples **33** ($\sim 1,000,000 M_w$) and **34** ($\sim 4,000,000 M_w$) had compressive strength values of 1.3 (2.42%) and 1.6 (2.42%) MPa, respectively. These results were quite different from those in the first sample set. The pictures in **Figure 23** can explain this finding. When comparing the mixability of the three samples, the 450,000 M_w polymer powder dissolved the best in the water creating a paste. However, as the molecular weight of the polymer powders increased, the mixability decreased, and this is likely what caused the resulting composites to have such low compressive strength values.

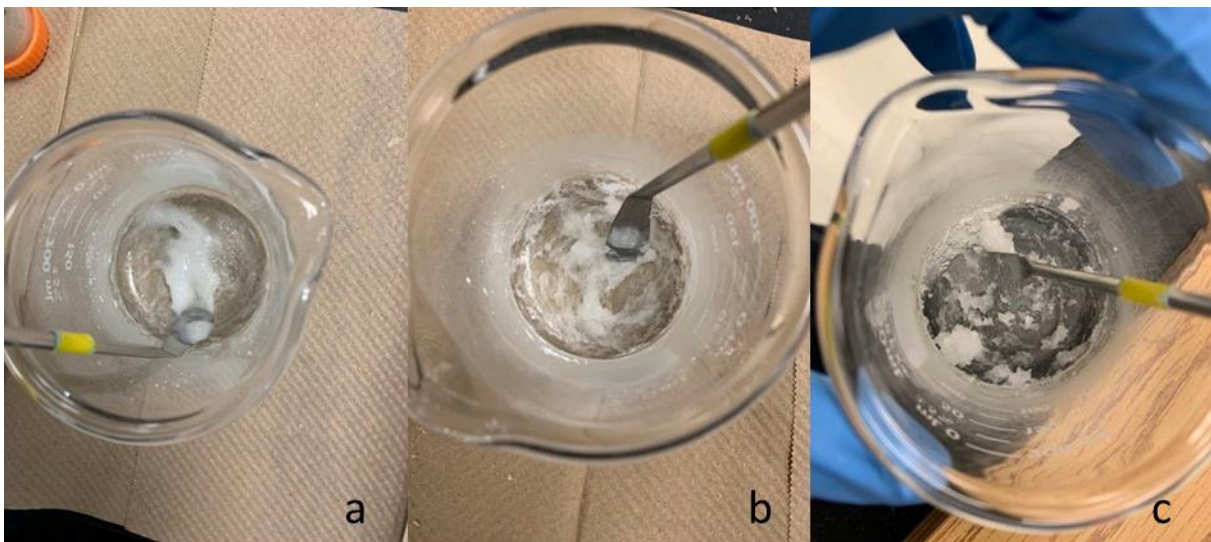


Figure 23: Polymer powders dissolved in water prior to being mixed with sand. a) 450,000 M_w b) 1,000,000 M_w c) 4,000,000 M_w

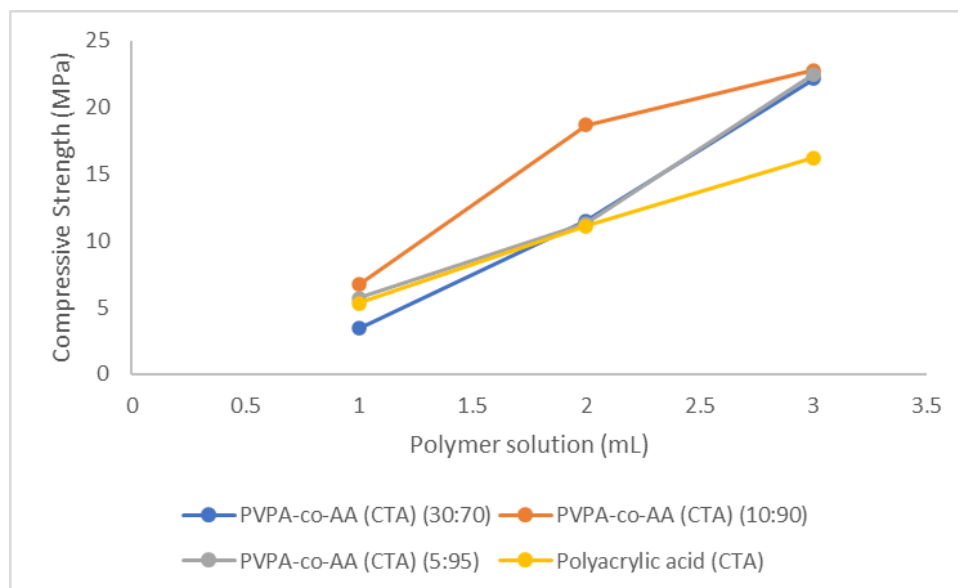


Figure 24: Composite strength comparison of PVPA-co-AA copolymers with varying feed ratios

Finally, a PVPA-co-AA (CTA) (5:95) copolymer was synthesized and composite samples were made following the same method as before. This was done to complete a set of polymers with varying feed ratios, to assess whether the addition of the phosphonate group was having any effect on producing stronger composite samples. As shown in **Figure 24**, there was no trend seen in the compressive strength data. Based on the initial hypothesis, if the phosphonate group were imparting strength to the composite samples, the expected trend would be that the compressive strength increases from PAA to the PVPA-co-AA (CTA) (70:30) polymer composites. It was then speculated based on the experiments with the PAA powder of varying molecular weights, that the molecular weight of the polymers might be causing the lack of a compressive strength trend.

The determination of molecular weight of the PVPA-co-AA and PAA polymers was more difficult than expected. These polymers are all water-soluble and therefore needed

to be analyzed on a gel permeation chromatograph (GPC) that had an aqueous mobile phase. However, after contacting multiple labs on campus, there were no labs with a functioning aqueous GPC. Polymer testing companies were then contacted to see if the polymers could be sent for analysis. However, this did not pan out as the cost per sample analysis was not feasible at this point in the research process. Therefore, alternate methods of determining the polymer molecular weights needed to be employed.

$$[\eta] = KM^a$$

(5)

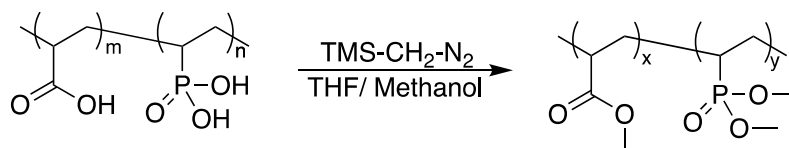
A literature search revealed a paper by Braybrook and Nicholson, where they were investigating the use of crosslinking agents and PVPA to improve the compressive strength of their glass-polyalkenoate cements.⁵⁰ The authors went on to state that they used Ostwald viscometry to determine the relative molar masses of the sodium salts of the polymers. The intrinsic viscosity, $[\eta]$, of the polymer was determined by plotting the viscosity of the polymer in solution at various concentrations and determining the y-axis (viscosity) intercept. The Mark-Houwink equation (5), along with the Mark-Houwink parameters, a and K , for PAA were used to estimate the relative molar masses of their PVPA.

Since the molecular weights of the polymers being used to make the composite samples, just needed to be compared to each other, this method of molecular weight determination was attempted. However, after a few attempts of elucidating the viscosity average molecular weight (M_v), this method of molecular weight determination was stopped. When plotting the reduced viscosity against the concentration, a linear plot with

a positive slope was expected. However, when the reduced viscosity was plotted against concentration for the PVPA-co-AA polymer, the plot was not linear. After a literature search it was found that our PVPA-co-AA polymer, was exhibiting a phenomenon dubbed the “polyelectrolyte effect”.⁵¹ Normally, the reduced viscosity of a neutral polymer decreases as the solution is diluted. However, PVPA-co-AA is a polyelectrolyte, and the reduced viscosities of polyelectrolytes increase as the solution is diluted. Researchers have found that as a polyelectrolyte solution is made more dilute, strong intra-chain repulsion occurs which causes chain extension. As the polymer chains are extended, they cause an increase in the reduced viscosity. The polyelectrolyte effect was not investigated further as a new method for determining the relative molar weight of the polymers became known.

A study was conducted by Lacík *et al.* on size-exclusion chromatography (SEC) analysis of PAA and poly(methacrylic acid) (PMAA).⁵² Focusing on PAA, the authors employed two SEC methods to investigate if they were in close agreement. The first method was direct aqueous-phase SEC on PAA and the second was THF-based SEC after esterification of PAA to the methyl ester, poly(methyl acrylate) (PMA). Esterification of the PAA polymer was done using the methylation agent, trimethylsilyldiazomethane (TMS-diazomethane). Similarly, Komber *et al.* methylated PVPA using TMS-diazomethane for their NMR study on PVPA and its dimethyl ester.⁵³ The methylated polymer was confirmed to have been made by the ppm shift in the ³¹P NMR for the phosphonate group. The signal for the O=P(OH)₂ group for PVPA is usually in the 29-32 ppm range.⁴¹ However, the methylated O=P(OMe)₂ group shows a signal at 35-38 ppm.⁵³

Lacík *et al.* found that for PAA (prepared by reversible addition–fragmentation chain-transfer (RAFT) polymerization), the two SEC methods were only in close agreement with weight average molar masses between 80,000 and 145,000 g mol⁻¹.⁵² While for PAA standards with higher molar masses or their pulsed-laser polymerization (PLP) prepared PAA, the values from the THF-based SEC method were approximately 40% below the molar masses that were determined by the aqueous-phase SEC. The authors stated that this difference might be due to branching or degradation of branched PAA during methylation. Although the methylation of PAA was not accurate when comparing the aqueous SEC data to the THF SEC data, since our study needed to compare the range of polymers to each other, this method of analysis was employed. Furthermore, seeing that the methylation using TMS-diazomethane was also conducted on PVPA, highlighted that our PVPA-co-AA polymers should be able to be methylated using the same method.



Scheme 18: Synthesis of the methylated PVPA-co-AA polymer

The methylation technique utilized by Lacík *et al.* was used to methylate our polymers. However, instead of a THF/H₂O mixture, the polymers were dissolved in THF/methanol as it was easier to remove these two solvents. TMS-diazomethane was added in excess to ensure complete methylation of the polymer. Upon dropwise addition of TMS-diazomethane, bubbles of nitrogen evolved from the reaction. The methylating agent was added until nitrogen production stopped, and the reaction maintained a yellow colour. The reaction was stirred overnight, and the next day a stream of air was used to

blow off the remaining solvent, leaving a polymeric film. The acquired ^{31}P NMR spectrum in CDCl_3 had a peak at ~ 35 ppm, and the original $\text{O}=\text{P}(\text{OH})_2$ peak at ~ 30 ppm was not visible. The corresponding ^1H NMR spectra had a new peak at ~ 3.6 ppm, which was assigned to the methyl group, replacing the $-\text{OH}$ group of the PAA units and forming the ester.⁵⁴ Finally, the polymers dissolving in the chloroform and THF solvents when prior to methylation they were insoluble, was further proof that the methylation was successful.

Table 5: Molecular weight data for the polymers synthesized using a stir bar. Analyzed by Franklin Frasca from the Duhamel group.

Polymer	M_w (daltons)	M_n (daltons)	PDI
PAA (CTA)	110,000	49,000	2.2
PVPA-co-AA (CTA) (30:70)	395,000	195,000	2.0
PVPA-co-AA (CTA) (10:90)	285,000	68,000	4.2
PVPA-co-AA (CTA) (5:95)	264,000	62,000	4.2
PVPA-co-AA (CTA) (2:98)	444,000	139,000	3.2
PVPA-co-AA (CTA) (1:99)	505,000	171,000	2.9

Following the methylation of the polymers, the number-average (M_n) and weight-average (M_w) molecular weights were determined by size exclusion chromatography using a Viscotek GPCmax VE2001. Chromatography experiments were performed by Franklin Frasca, and the results of the analysis are shown in Table 5. The trend that was expected was increasing molecular weights corresponding to a decrease in the polymer

VPA feed ratios. However, when these molecular weights were plotted against the polymer VPA feed ratio there was no trend (**Figures 25, 26, and 27**).

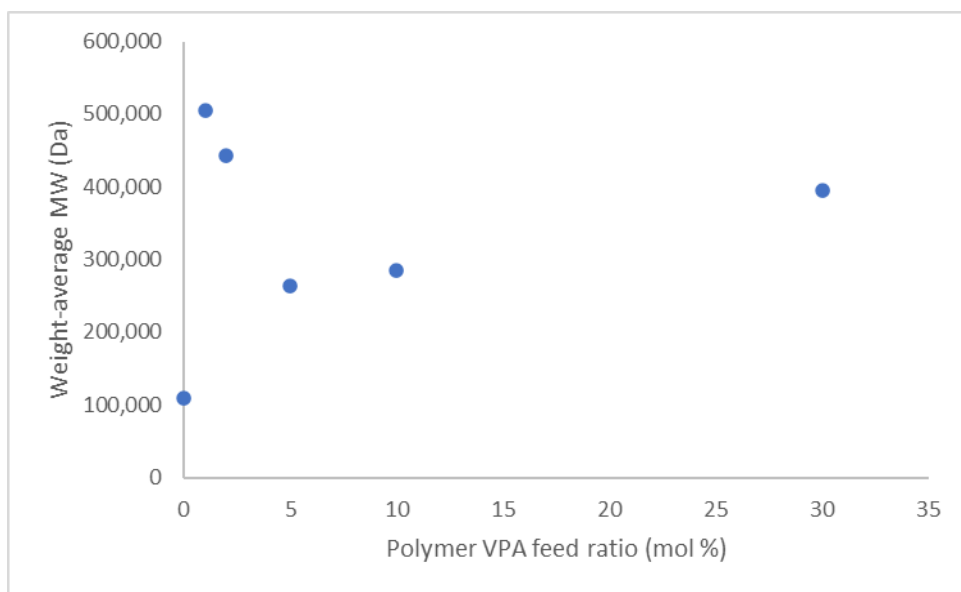


Figure 25: The weight—average molecular weight of the polymers plotted against the polymer VPA feed ratios

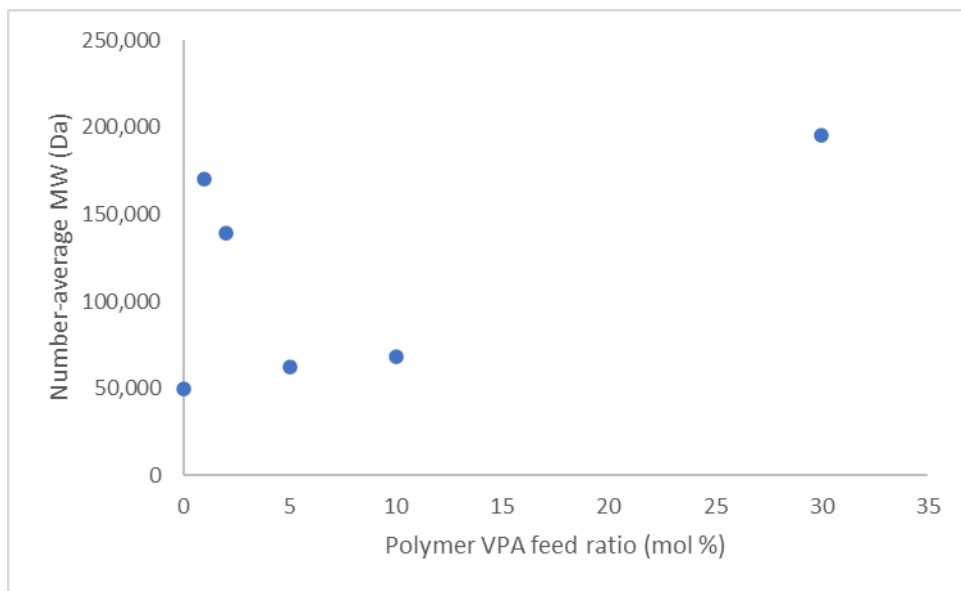


Figure 26: The number—average molecular weight of the polymers plotted against the polymer VPA feed ratios

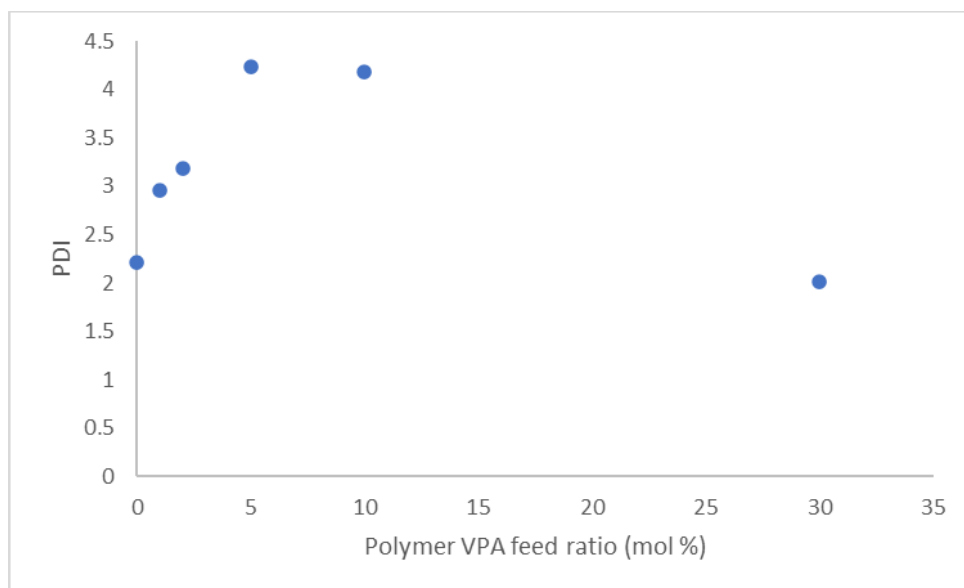


Figure 27: The PDI of the polymers plotted against the polymer VPA feed ratios

In light of these results, the synthesis and compressive testing methods were examined to see if there were any variables that might have been causing the lack of a trend. One variable that was thought of was the use of a magnetic stir bar when making the polymer solutions. When synthesizing the polymers, sometimes the reaction mixtures became so thick that the stir bar would stop stirring and would start vibrating back and forth, extremely slowly. This resulted in a hard polymer “cap” sometimes covering the polymer solutions underneath. The polymer cap was pure PAA as it was not being mixed with the VPA in solution and was just sitting on top of the reaction mixture when being added over the 6 hours. To solve this issue an overhead mechanical stirrer was acquired, and the range of PVPA-co-AA polymers with varying feed ratios was remade. After looking at the compression testing method, it was realized that there were also inconsistent drying times for the composite samples. When checking the literature for concrete testing, all the methods had a consistent 28-day drying period. This variable was also thought to have been causing issues with the lack of a trend for the compressive

strength data. The MSAM lab was then contacted, and they allowed access to their universal mechanical testing system. With access to conduct the compressive strength testing on our samples, the drying times of the composite samples were then kept to a consistent 7 days. After 7 days of drying in the fume hood, the composites were removed from the mould and baked for 4 hours at 150 °C. They were then placed in a desiccator overnight and the compressive strength was assessed the next day.

Table 6: Composite samples made with the polymers synthesized with the overhead stirrer (OHS)

Polymer	Composite Samples
PAA (CTA)	39, 40, 41, 42
PVPA-co-AA (CTA) (30:70)	43, 44 ,45, 46
PVPA-co-AA (CTA) (10:90)	47, 48, 49, 50, 51
PVPA-co-AA (CTA) (5:95)	52, 53, 54, 55
PVPA-co-AA (CTA) (2:98)	56, 57, 58, 59
PVPA-co-AA (CTA) (1:99)	60, 61, 62, 63

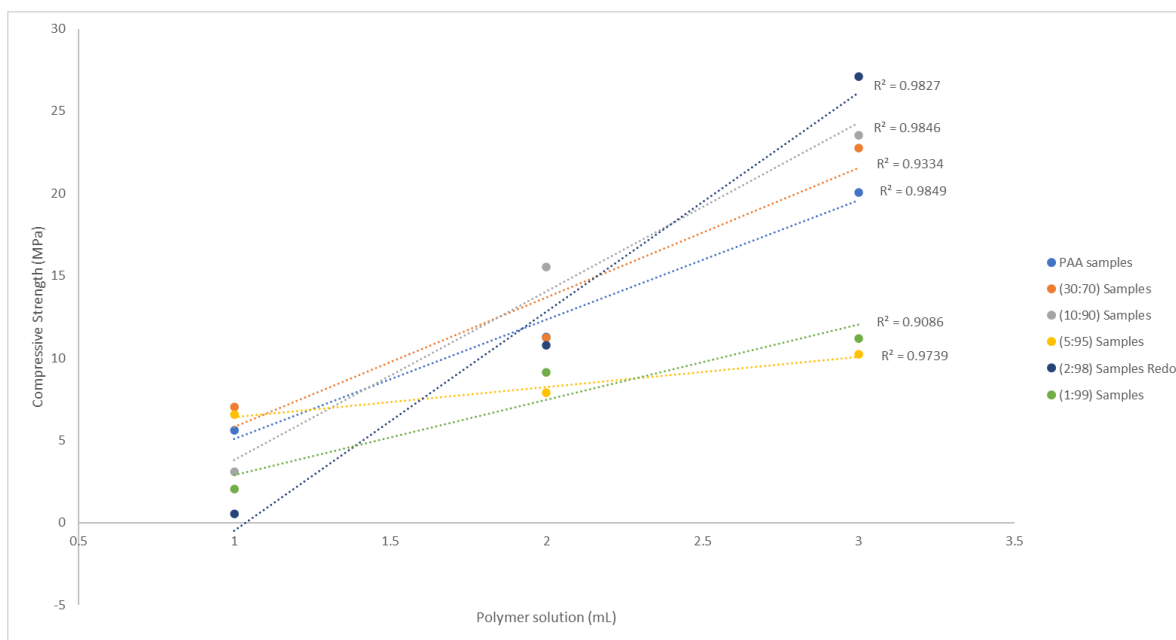


Figure 28: Composite strength comparison of PVPA-co-AA with varying feed ratios copolymers synthesized using the OHS

The newly synthesized PVPA-co-AA (CTA) (OHS) samples were prepared in sets every week. Each composite set was comprised of a 1-, 2- and 3-mL polymer-containing sample, along with an additional sample evaluating a curing technique. Table 6 contains the composite samples made with each polymer and more information can be found in the supporting information section – 5 composite samples produced. As shown in **Figure 28**, when the compressive strengths for each data set was plotted, a trend was again not seen. However, the polymer solutions made with the overhead stirrer were homogenous in their consistency compared to the stir bar produced samples. The polymers were once again methylated so that the THF-based GPC could be used to elucidate the molecular weights.

Table 7: Molecular weight data for the polymers synthesized using the overhead stirrer.
Analyzed by Franklin Frasca from the Duhamel group.

Polymer	M _w (daltons)	M _n (daltons)	PDI
PAA (CTA) (OHS)	300,000	215,000	1.4
PVPA-co-AA (CTA) (OHS) (30:70)	430,000	383,000	1.1
PVPA-co-AA (CTA) (OHS) (10:90)	1,052,000	691,000	1.5
PVPA-co-AA (CTA) (OHS) (5:95)	905,000	431,000	2.1
PVPA-co-AA (CTA) (OHS) (2:98)	704,000	346,000	2.0
PVPA-co-AA (CTA) (OHS) (1:99)	1,500,000	826,000	1.8

Once more, following the methylation of the polymers, the M_n and M_w were determined by size exclusion chromatography. The samples were run by Franklin Frasca, and the results of the analysis are shown in Table 6. Unfortunately, when the molecular weights were plotted against the polymer VPA feed ratio there was still no trend (**Figure 29, 30 and 31**). Additionally, when looking at the molecular weights of these polymers and comparing them to the corresponding PDI's they seemed to be lower than they should have been. Typically, polymers of such large masses are associated with larger PDI values.

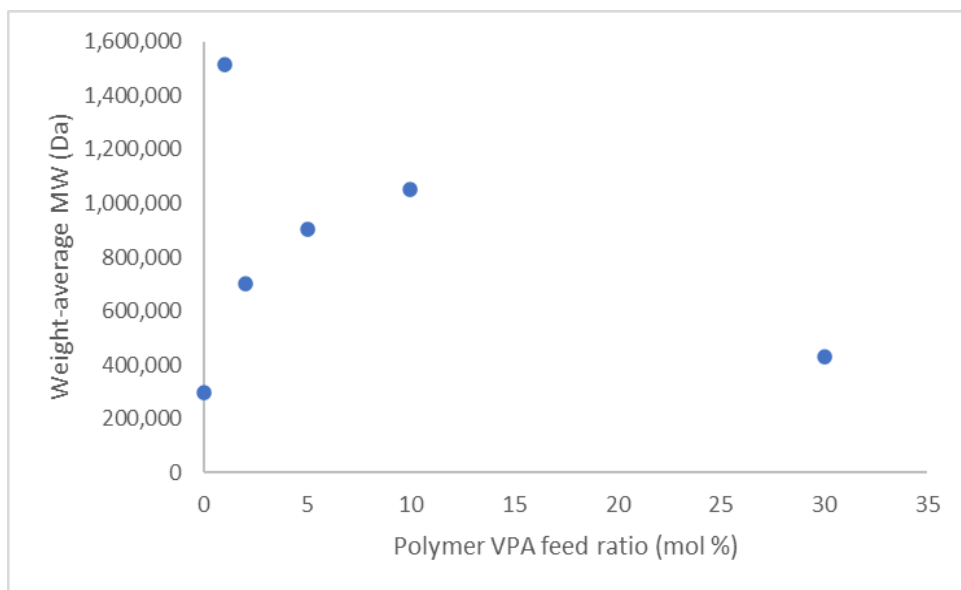


Figure 29: The weight—average molecular weight of the OHS polymers plotted against the polymer VPA feed ratios

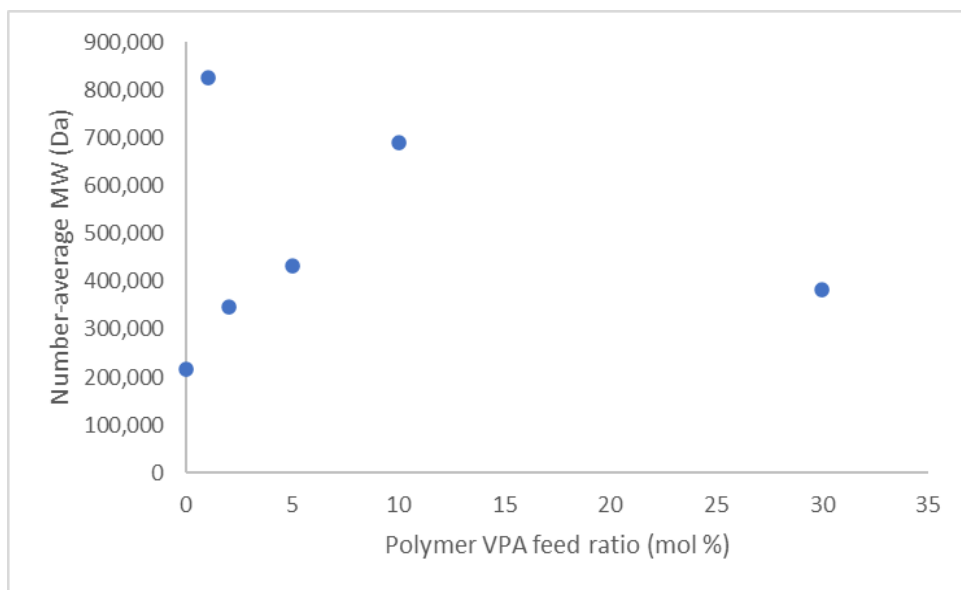


Figure 30: The number—average molecular weight of the OHS polymers plotted against the polymer VPA feed ratios

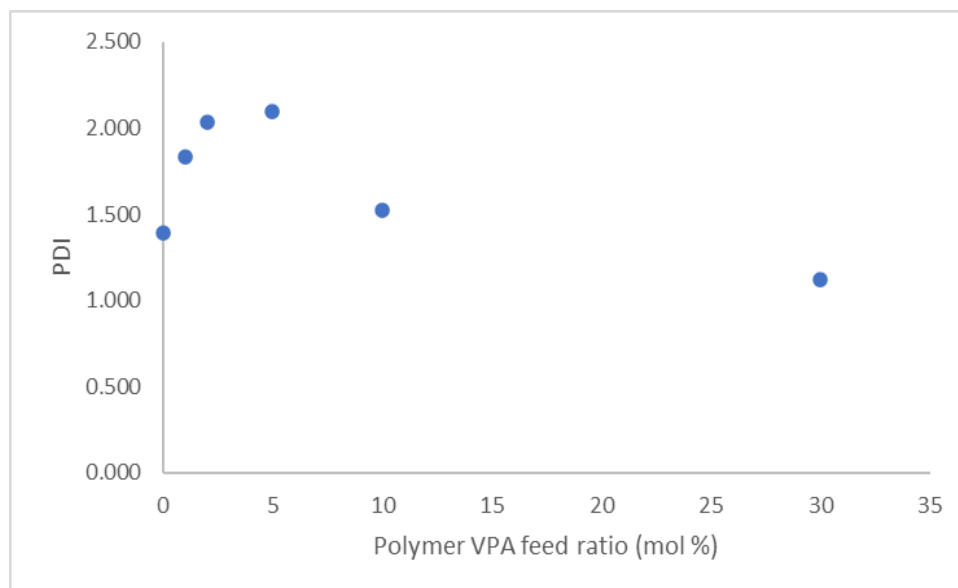


Figure 31: The PDI of the polymers plotted against the polymer VPA feed ratios

Although a trend in the data was not seen, a few extra experiments were also conducted with this set of OHS copolymers and composite samples. PVPA-co-AA (CTA) (OHS) (10:90) used to make samples **47-51**, included a sample with 4 mL of the polymer solution. As shown in **Figure 32**, a linear trend of compressive strength increasing with increased amounts of the polymer solution was still seen. Sample **51** also had one of the highest compressive strengths of all the composite samples with a value of 30.0 (3.24%) MPa. Additionally, the data in **Figure 32** looked like it was about to plateau. However, the polymer batch used to make these composite samples had run out. Therefore, another batch of PVPA-co-AA (CTA) (OHS) (10:90) polymer and composite samples were made with 4-, 5-, and 6-mL of the polymer solution. As shown in **Figure 33**, the compressive strength of the 4 mL composite did not match that of the previous batch (20.0 vs. 24.0 MPa). Still, the 5 mL composite sample **65** had the highest compressive strength out of all the composite samples produced with 39.8 (4.06%) MPa (*Note: The mechanical

testing stopped mid-run; this sample may be stronger). The second batch of PVPA-co-AA (CTA) (OHS) (10:90) polymer was also precipitated and methylated so that its molecular weight could be compared to the previous polymer. When comparing the M_w and M_n , it was significantly different. Where the first batch had a 1,052,000 Da M_w and a 691,000 Da M_n . The second batch had a 701,000 Da M_w and a 446,000 Da M_n . The difference in the molecular weight and the compressive strength of the 4 mL containing polymer composite samples indicated that there are still inconsistencies in the synthesis of the polymers and production of the composite samples.

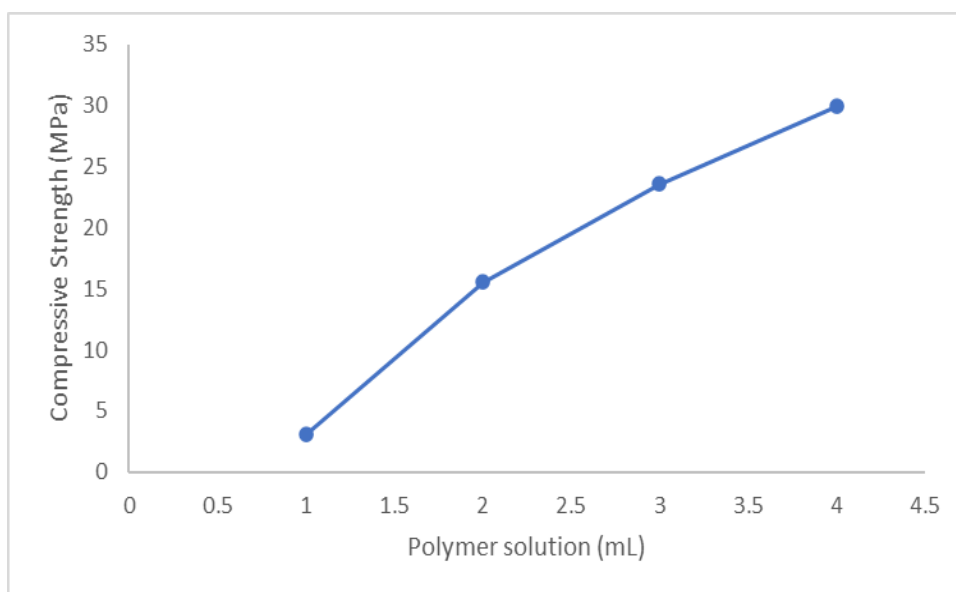


Figure 32: Compressive strength of PVPA-co-AA (CTA) (OHS) (10:90) polymer composites increased with greater amounts of added polymer

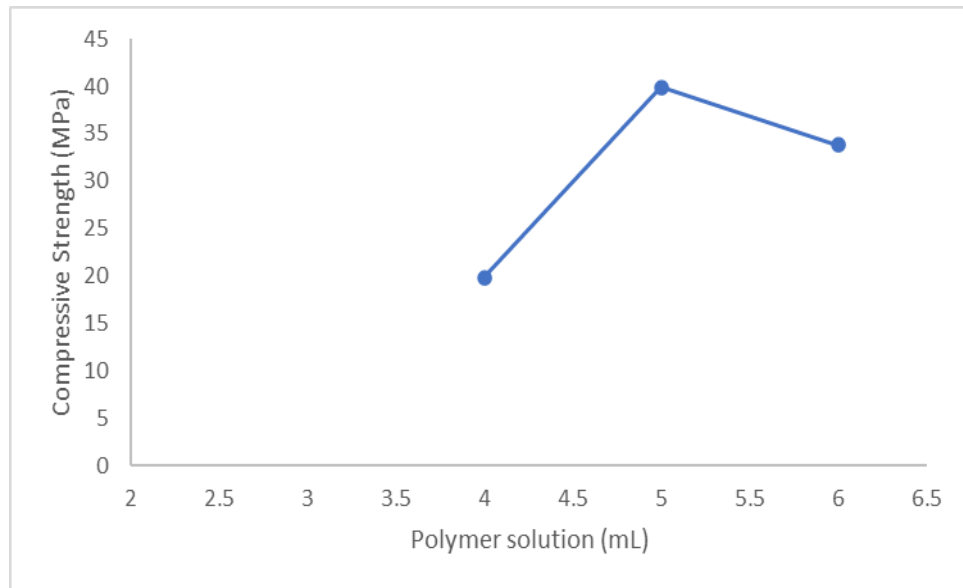


Figure 33: Compressive strength of the second batch of PVPA-co-AA (CTA) (OHS) (10:90) polymer composites

3.3.2 Curing

If the PVPA-co-AA copolymer were to be used as a composite material in construction, compressive strength would not be the only important variable that would need to be assessed. When conducting the compression testing experiments, once the polymer sand mixtures were added to the mould, they were allowed to air dry for 7 days. After the 7 days, they were strong enough to be removed from the mould without being severely damaged and were hardened completely in the oven at 150 °C. This method of curing and hardening of the composite samples is slow and would not meet the expectations of a construction material. Therefore, factors that affected the curing time of the composite materials were investigated so that they could be improved. The end goal for this part of the project was to deduce a method of improving the curing time in a cost-effective manner.

In order to stay consistent with the method being used for compression testing, the samples made for the curing experiments were made using the same polymer-to-sand ratios. Approximately, 3 mL of the polymer solution was thoroughly mixed with ~43 g of sand until a homogenous mixture was produced. When solid reagents were added to the blend, they were first ground into fine powders and then added on a percent weight basis by weight of the sand. The centrifuge tube moulds were also used for the curing experiments, but they were cut to produce approximately 1 x 1-inch cylindrical composites. This was done so that a second composite sample containing the same material could be used for testing when the first sample became damaged.

A Shore durometer was used to monitor the hardness of the samples surface at consistent time intervals over the course of a few hours. The durometers have a tip that converts the depth of indentation allowed by the material to relative hardness values. Although this method of measurement is not necessarily repeatable by any ASTM standards, it did serve for comparative purposes. Since each sample was being pierced by the tip of the durometer, after each measurement the surface of the sample was damaged. The time intervals were set so that enough data points could be collected before the surface of the samples were too damaged, and the measurements were stopped after they were completely damaged. Two types of durometers were used for these experiments, type A and type D. The type A durometer was used when testing the curing time of materials that were soft, while the type D durometer was used for the harder samples. The tip of the type A durometer is blunt compared to the type D durometer which had a sharp point and so it caused less damage to the samples. However, the hardness

values of the type A durometer also maxed out more quickly than the type D durometer. Generally, type A was used when the samples were soft so that surface damage could be minimized, once the detection limit of type A was reached the type D durometer was used.

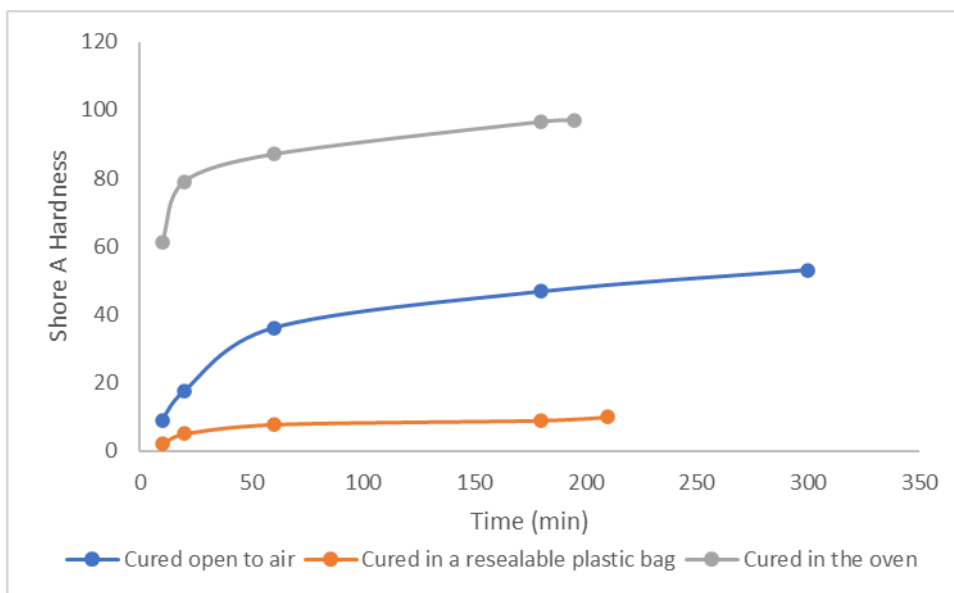


Figure 34: Composite samples cured in different environments

Based on the compressive strength experiments, it was hypothesized that the rate of water evaporation was a variable that would improve the curing time of the composite samples. As such, a PVPA-co-AA (CTA) (10:90) polymer solution was used to make three composite samples. The three samples were allowed to cure in three different environments, open to air, in a resealable plastic bag, and in an 80 °C oven. The resealable plastic bag was used to simulate a closed environment where the water would slowly evaporate, while the oven was used to speed up the evaporation process. As shown in **Figure 34**, the rate of curing differed significantly in the three environments. The sample in the resealable plastic bag had nearly no improvement, while the sample placed

in the oven hardened the fastest. Additionally, the resealable plastic bag containing the sample had droplets of water on its walls at the end of the experiment. These results showed that the rate of water evaporation had an impact on the hardening of the composite samples.

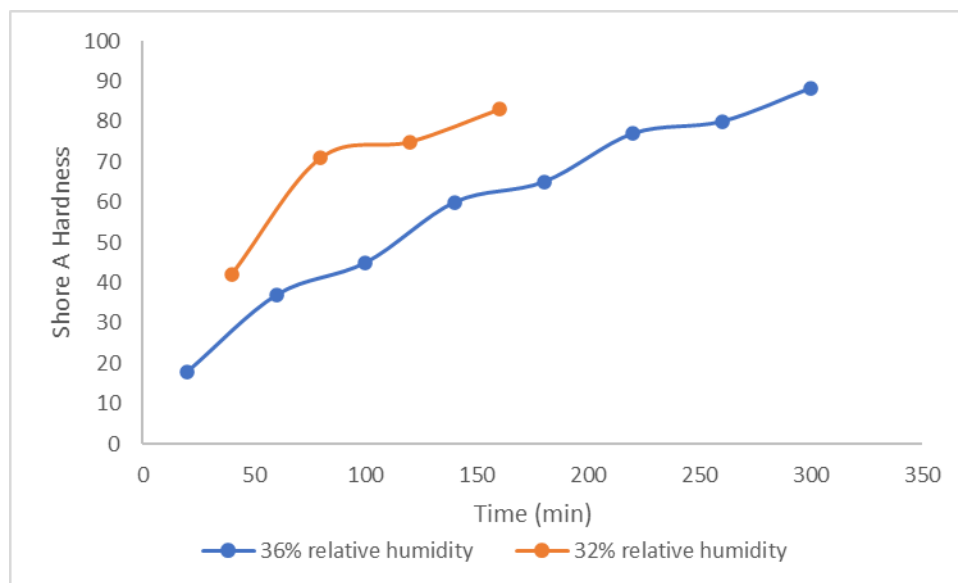


Figure 35: Effect of relative humidity on the curing of the composite samples

Simultaneously, when conducting the compressive strength experiments over the summer months, it was noticed that the humidity of the lab was extremely variable. On days that it rained, the lab would feel humid and wet. To test this, a thermometer was ordered that had a meter that measured the relative humidity. A curing experiment was then conducted to gauge the effect that the humidity in the lab was having on the curing rate of the samples. The same batch of PVPA-co-AA (CTA) (10:90) polymer solution was used to make the composite samples for the two different days with different relative humidities. As shown in **Figure 35**, the composite sample made on the day with 36% relative humidity needed almost twice the amount of time to cure to the same hardness as the sample cured at 32% relative humidity. These results concluded that the composite

samples used in the curing experiments could only be compared to samples made and tested on the same day, due to the variability in humidity.

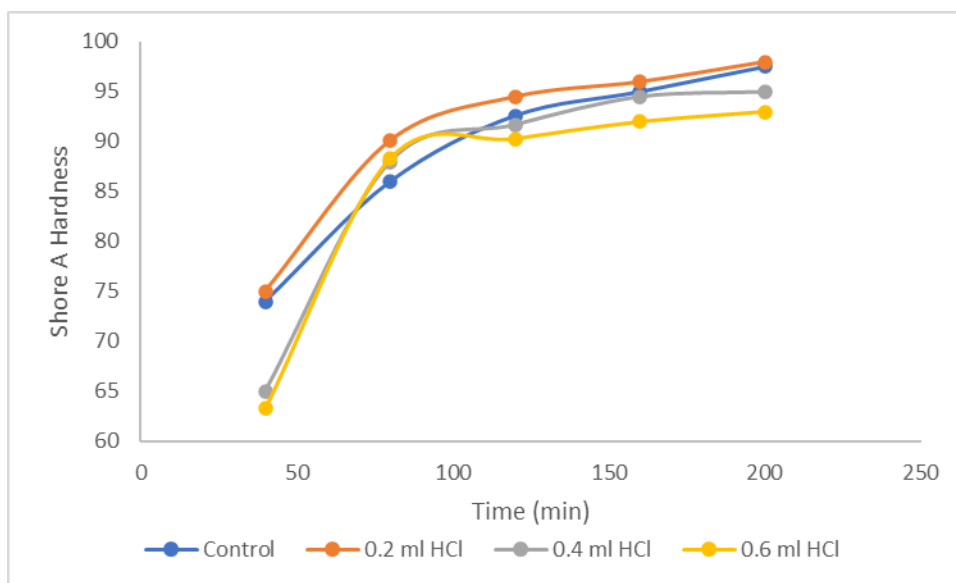


Figure 36: Effect of dosing hydrochloric acid on the curing of the composite samples

The next experiment was conducted to investigate the influence that an inorganic acid would have on the curing of the composite samples. The samples in this composite set were mixed with increasing amounts of 12 M HCl along with a control sample. **Figure 36** shows the rate of curing of each of the samples. The two samples with 0.4- and 0.6- mL had low hardness levels to start, this was likely caused by the extra liquid in the sample mixtures. However, after 1.5 hours all the samples cured at relatively the same rate as the control and reached a similar hardness after 3 hours. Therefore, the addition of acid did not have any effect on the rate of curing.

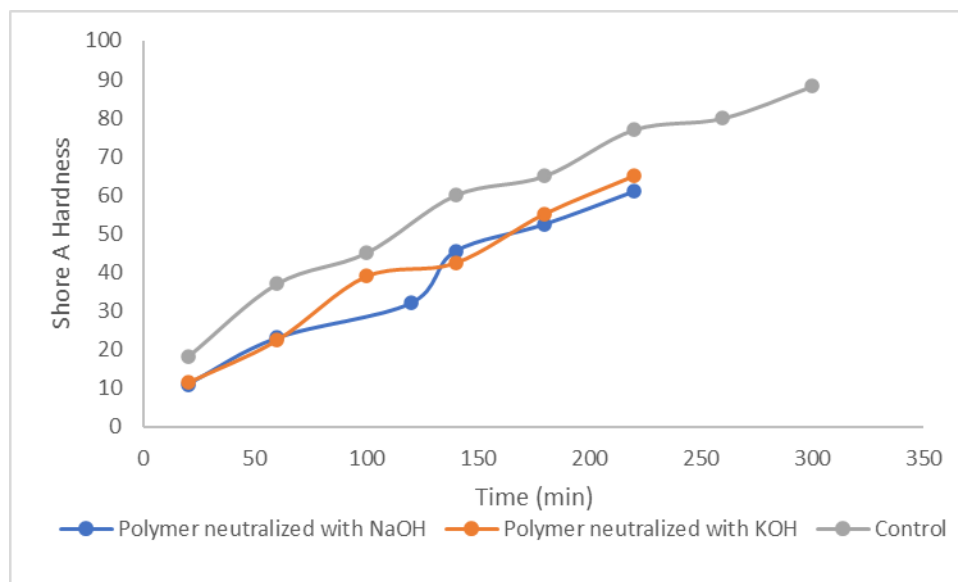


Figure 37: Effect of neutralising the polymer solution with various bases on the curing of the composite samples

Inorganic bases, potassium hydroxide (KOH), and sodium hydroxide (NaOH) were then used to neutralize the polymer solution. The powdered bases were added to the polymer solution and mixed until the solution was homogenous. As expected, the acid-base reaction radiated heat but after the polymer solution cooled down, it was used to make the composite samples. The neutralized polymer solutions were not found to improve the rate of curing as shown in **Figure 37**. It was hypothesized that the sodium and potassium ions may have been interacting with the phosphonate and acrylic acid groups of the polymer chain and hindering the reaction with the surface of the sand particles. Compression testing was also done using the neutralized polymer solutions and a control. The control sample **67** (23.2 (2.48%) MPa) was stronger than the two neutralized polymer containing samples. However, it should be noted that the compressive strength of the KOH neutralized sample **69** (18.1 (2.47%) MPa) was significantly stronger than the NaOH neutralized sample **68** (9.3 (2.48%) MPa).

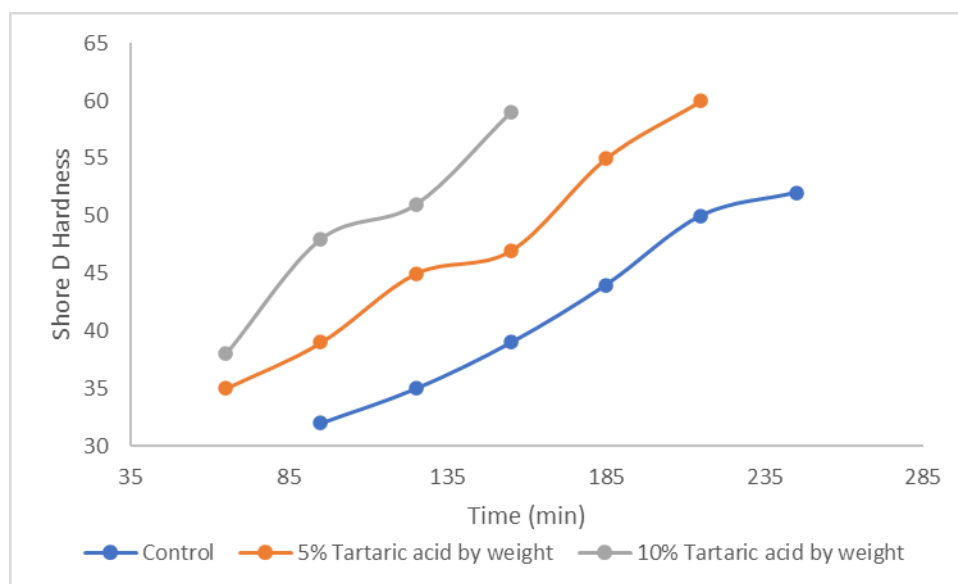


Figure 38: Rate of curing for polymer composites made with tartaric acid additive

As mentioned in the introduction of poly(vinylphosphonic acid), PVPA and its derivatives had been identified for their use in dental cements.³⁹ For dentists, there are three characteristics that are important for a dental cement: manipulation time, setting time, and strength post set.⁵⁵ Thus, dentistry papers were found that examined chelating agents and their ability to harden the dental cements. In 1976, Wilson *et al.* identified tartaric acid for its ability to help improve the curing time of their PAA-based dental cements.⁵⁵ The authors stated that the structure of the molecule allows it to bridge metal ions and links the nearby polyanionic chains. Since the PVPA-co-AA copolymers in this study were composed of a significant amount of AA, this additive was investigated. Tartaric acid was added in 5 and 10 % by weight of sand to examine its effect on the rate of curing. As shown in **Figure 38**, adding tartaric acid accelerated the rate of curing. Both the 5 and 10% tartaric acid containing samples hardened faster than the control. Therefore, tartaric acid could be an effective additive to accelerate the curing process of the composite samples. Additionally, compression testing was also done on sample **71**

dosed with 10% tartaric acid by weight and was compared to control sample **70**. The addition of the tartaric acid did not seem to lower the compressive strength compared to the control. The compressive strength values were 16.4 (2.49%) and 16.9 (2.48%) MPa, for the control and 10% tartaric acid containing sample, respectively.

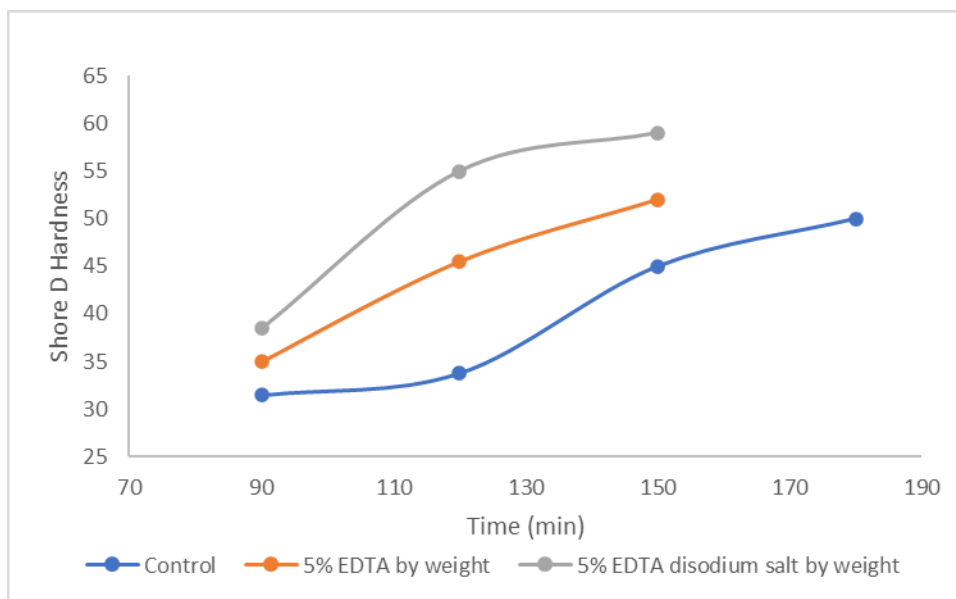


Figure 39: Rate of curing for polymer composites made with EDTA and EDTA disodium salt additive

Unfortunately, since this project was set with the goal of making a new composite material for construction, one of the variables that also needs to be considered is cost. Tartaric acid was found to be more expensive when compared to other common chelating agents like ethylenediaminetetraacetic acid (EDTA) or its disodium salt. Therefore, the experiment was repeated with EDTA and EDTA disodium salt. As shown in **Figure 39**, both additives accelerated the curing process, with the EDTA disodium salt being the most effective additive. Once EDTA disodium salt was found to be an effective curing agent, composite samples with varying amounts of the additive were screened, as shown in **Figure 40**. The EDTA disodium salt was found to be an effective curing agent, and the

rate of curing increased with increasing amounts of the EDTA salt. Compression testing was also done with the set of polymer OHS samples dosed with 5% EDTA disodium salt by weight. However, when comparing the control samples to the additive containing samples, the compressive strength of the additive containing samples were almost always weaker (Table 8). Although the curing rate was improving when the EDTA salt was added, the extra amount of total substrate might have been causing the decreased compressive strength.

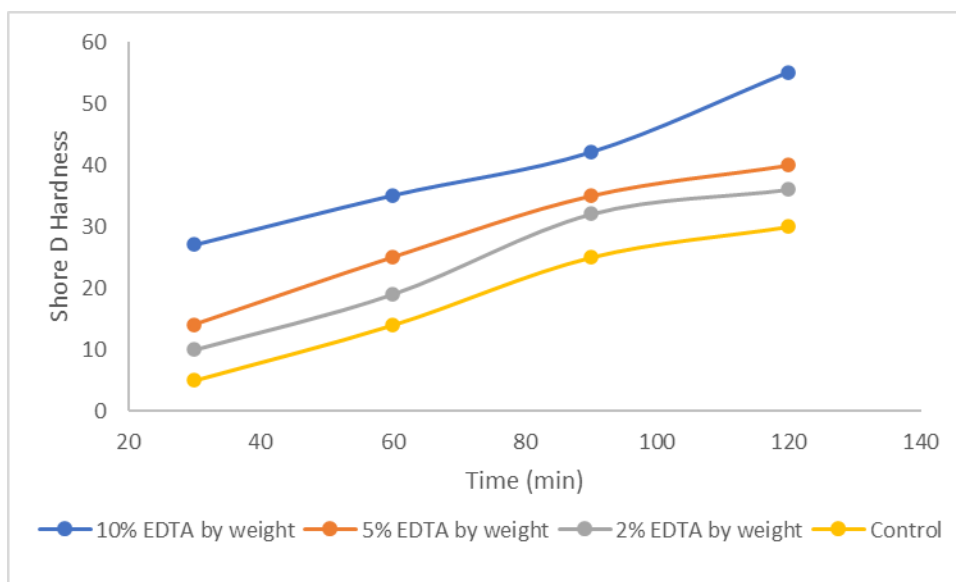


Figure 40: Rate of curing for polymer composites dosed with varying amounts of EDTA disodium salt additive

Table 8: Compressive strength of polymer composite control samples versus those dosed with EDTA disodium salt additive

Polymer	Control (MPa)	5% EDTA salt by weight (MPa)
PAA (CTA) (OHS)	20.1 (2.44%)	13.6 (2.43%)
PVPA-co-AA (CTA) (OHS) (30:70)	22.7 (2.57%)	13.1 (2.59%)
PVPA-co-AA (CTA) (OHS) (10:90)	23.6 (2.44%)	15.6 (2.43%)
PVPA-co-AA (CTA) (OHS) (5:95)	10.2 (2.40%)	12.1 (2.40%)
PVPA-co-AA (CTA) (OHS) (2:98)	27.1 (2.37%)	10.4 (2.37%)
PVPA-co-AA (CTA) (OHS) (1:99)	11.2 (2.37%)	11.5 (2.36%)

3.3.3 Different soil samples

Lastly, as mentioned in the proposed research section, the goal of this project was to create a composite building material that was able to be made by blending different sand/ soils and the polymer solution. Therefore, a few different substrates were tested for their ability to bind with the polymer solution and produce a composite sample with strength. The first substrate used was masonry sand acquired from the technical staff from the department of civil and environmental engineering. The masonry sand was composed of pieces of gravel, sand, etc. of various sizes, and is typically used to make mortar. The sample made with these randomly sized pieces broke immediately as there was too much space between the pieces. After using a 50 mesh sieve to isolate smaller

pieces only one sample **72** was able to be made with a PVPA-co-AA (CTA) (30:70) polymer. However, it was quite weak with a compressive strength of only 0.30 (2.51%) MPa. After reading through the literature, it was found that masonry sand is usually washed prior to using it to make mortar. If not, the cement does not bind to the aggregate very well.⁸ The masonry sand used to make the composite samples was not washed and was very dusty. This could be a reason why the samples failed and had such a low compressive strength.

Another interesting aggregate that is sometimes used in the production of concrete is recycled glass. Crushed recycled glass used as sandblasting media was ordered to see if it could be used as a substrate with our polymer solution. The composite samples were produced using a 10:90 **73** and 30:70 **74** PVPA-co-AA (CTA) polymer. The compressive strengths of the samples were 12.1 (2.94%) and 9.2 (3.16%) MPa, for the 10:90 and 30:70 polymers, respectively. Although these polymer composites were not as strong as those towards the end of the study it showed that depending on the required compressive strength the polymer glass composites could be useful.

Finally, the last two substrates used were from Canoe Cove, PEI, and Greenwich beach, PEI. The Canoe Cove soil was extremely fine, and the produced composite sample broke when being removed from the mould. The Greenwich beach sand formed a polymer composite sample **75**, which was similar to the regular S25-3 sand. Using this sand, the polymer composite had a compressive strength value of 24.4 (2.41%) MPa.

3.4 Future considerations

Given the highest compressive strength value that was reached, there is still lots of potential for this project. However, since a trend was not observed, it can be concluded that this investigation did not prove the effectiveness of the phosphonate group on the compressive strength of the polymer composites. An additional experiment that should be conducted to verify the effectiveness of the phosphonate group is the elucidation of the actual copolymer composition using the method developed by Dey *et al.*⁴¹ After examining the supplementary information provided by the authors, it was found that the copolymer composition varied significantly from the feed composition. Therefore, it is highly likely that although the feed compositions differed between our polymers, the actual copolymer compositions may be similar.

Additionally, the method in which the polymers were synthesized could be improved. When the CTA, AA, and initiator were added incrementally over the 6 hours, these additions were done by hand, and not through the use of a syringe pump. An automated syringe pump should be used for future reactions as it would allow for more accurate incremental additions over the reaction window. The moulds used in the next progression of this project should also be more aligned with that of an ASTM method. This proof of concept study showed that polymer composites with high compressive strengths can be made. The use of a more ASTM regulated testing method would allow for direct comparisons to other materials like concrete.

Finally, although the PVPA-co-AA copolymer was used in this study to elucidate the effectiveness of the phosphonate group in providing strength, because it is a water-soluble polymer it cannot be used as a construction material. The project should take the next step forward in creating more water-resistant polymer composites. Interesting research by Rezaeimalek *et al.* has shown the use styrene–acrylic polymer dispersion, as a polymer soil stabilizer.^{17,18} Their polymer composites had lower compressive strengths than the ones in our study. However, their study included subjecting the composite samples to 24 wet–dry cycles, where the samples were submerged in water for 24 hours and were then dried for 48 hours at temperatures under 100 °C. The compressive strengths of the samples subjected to the wet – dry cycles were 60% of their original strength. The PVPA-co-AA polymer composites, however, would have completely disintegrated. The incorporation of phosphonate groups into styrene–acrylic polymer dispersion might prove beneficial in improving the composites compressive strength.

Conclusion

The production of a robust composite material produced from a blend of functionalized polymer and sand/ soil was attempted. This project took inspiration from the traditional earth-based construction materials and looked to improve their mechanical properties. Enhancing these sustainable construction methods could help produce an environmentally friendly material that replaces concrete. The project began with the attempted phosphonylation of various polymers. The goal was to utilize the phosphorus-metal oxide bond that is used in surface functionalization chemistry to create the composite material. The phosphonylated polymers were then going to be mixed with soil so that the phosphonate groups would bond with the metal oxide particles found in soil. Unfortunately, the functionalization of the polymers was unsuccessful. However, after consultation with committee members, it was decided that the project should first attempt to validate whether the phosphonate-metal oxide bond can occur with soil/sand. To do this, instead of phosphonylating existing polymers, the project evolved into making our own polymers with phosphonate groups built into the polymer chain.

Various PVPA-co-AA polymers of varying feed ratios were made in an attempt to gauge whether the phosphonate groups were contributing to the compressive strength of the polymer composites. A trend was found where the compressive strength of the polymer composites increased linearly with the increase of the amount of added polymer solution. The polymers also had to be methylated so that they could be analyzed using a THF-based GPC to determine their molecular weight. Sadly, there was no trend seen for increasing compressive strength with increasing amounts of VPA in the feed composition.

The acquired molecular weight also had no trend when being compared to the VPA feed ratios. This highlighted potential sources of error in the synthesis of the polymers and the production of the polymer composites. However, the polymer composites reached a compressive strength value of 39.8 MPa. Concrete of this compressive strength is typically used for the production of structural beams and columns.⁷ This proof-of-concept project also investigated methods to improve the curing rate of the composite samples. The evaporation of water was found to be vital in the hardening of the composite samples while the addition of additives like EDTA disodium salt, helped speed up the curing rate. Based on these results, the project should move forward to create more water resistant polymer composites in order to elucidate the effectiveness of the added phosphonate groups.

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Appendix

1 General Considerations

1.1 Materials & Instrumentation

All chemicals were used without further purification unless otherwise stated. Vinylphosphonic acid (VPA) (>95%) and 1-octanethiol (1-Oct) (>98%) were purchased from TCI Ltd. Acrylic acid (AA) (99%) and 2,2'-azobis(2-methylpropionamidine) dihydrochloride (AIBA) (97%) were purchased from Sigma-Aldrich Ltd. Trimethylsilyldiazomethane, 10% in hexane (TMS-diazomethane) was purchased from Oakwood Products, Inc.

^1H -NMR spectra were recorded on a Brüker AVANCE300 (300 MHz) or Brüker AC300 (300 MHz) NMR spectrometer. ^{31}P -NMR spectra were broadband decoupled and recorded on a Brüker AC300 (121.4 MHz) NMR spectrometer with phosphoric acid in water as the external reference. The following abbreviations are used for NMR peak multiplicities: s, singlet; t, triplet; dd, doublet of doublets; m, multiplet; br., broad. Chemical shifts are reported in parts per million (ppm) relative to water (δ 4.79) or chloroform (δ 7.26) for ^1H -NMR and phosphoric acid in water (δ 0.00) for ^{31}P -NMR.

The first set of polymers number-average (M_n) and weight-average (M_w) molecular weights were determined by size exclusion chromatography using a Viscotek GPCmax VE2001 at 35 °C equipped with a DRI and PAS-103, PAS-104, and PAS-105 Styrene-Divinylbenzene gel columns. The flow rate was fixed at 1.0 mL/min using tetrahydrofuran (THF) as the eluent. All molecular weights are relative to a polystyrene calibration curve.

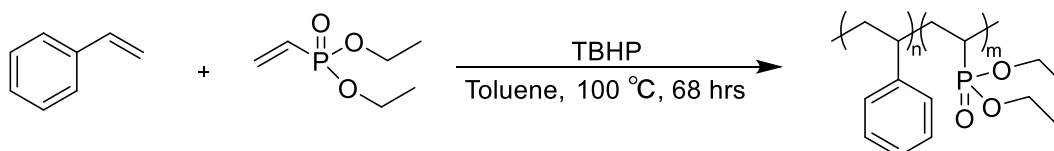
All GPC samples were prepared nominally at 1 mg/mL in THF and filtered through a 0.22 μ M PTFE filter into a 1 mL chromatography vial.

The second set of polymers absolute number-average (M_n) and weight-average (M_w) molecular weights were determined by size exclusion chromatography using a Viscotek GPCmax VE2001 at 35 °C equipped with a 305 TDA (triple detector array: DRI, LS, Visc.) and PAS-103, PAS-104, and PAS-105 Styrene-Divinylbenzene gel columns. The flow rate was fixed at 1.0 mL/min using tetrahydrofuran (THF) as the eluent. All GPC samples were prepared nominally at 1 mg/mL in THF and filtered through a 0.22 μ M PTFE filter into a 1 mL chromatography vial.

Unconfined compression tests were conducted using a universal mechanical testing system (MTS Model 43).

2 Experimental procedures

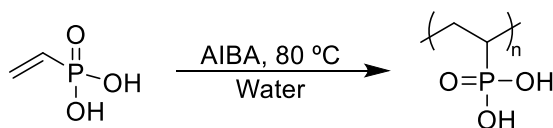
2.1 Synthesis of styrene-co-DEVP



Styrene (2.5 g, 0.024 mol) was passed through an Al₂O₃ pipette column to remove the 4-tert-butylcatechol inhibitor and added to a dry 25 mL RBF that had been purged with argon. 4 mL of dry toluene, DEVP (1 g, 6.1x10⁻³ mol), and 4.4M TBHP in isooctane (0.046 g, 5.1x10⁻⁴ mol) were then added. The reaction was heated at 100 °C and left to stir for 68 hours. The polymer was then isolated by precipitation in cold methanol. ¹H NMR

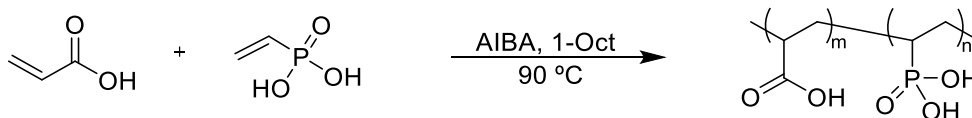
(300 MHz, CDCl₃) 7.25-6.57 (styryl aromatic peaks), 4.09 (*app.* p, $J = 7.2$ Hz, DEVP), 1.80 – 1.00 (aliphatic peaks), 1.33 (t, $J = 7.1$ Hz, DEVP). ³¹P NMR (121.4 MHz, CDCl₃) 35.14, 34.65.

2.2 Synthesis of PVPA



AIBA (2.5 mg, 9.26x10⁻³ mmol) was added to a clean microwave tube that had been purged with argon gas. Deionized water (0.5 mL), and vinylphosphonic acid (1.00 g, 9.256 mmol) were added to the tube and it was placed in a heating block at 80 °C for 3 hours. Unless otherwise stated the polymer solution was not purified prior to preparing the polymer composite samples. ¹H NMR (300 MHz, D₂O) 2.39 (CH-P), 2.11-1.46 (CH₂). ³¹P NMR (121.4 MHz, CDCl₃) 31.16.

2.3 Synthesis of PVPA-co-AA

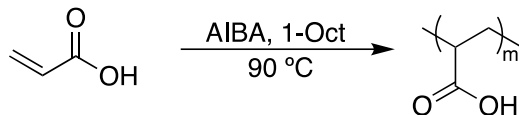


The following method details the synthesis of the 10:90 PVPA-co-AA polymer solution. A variety of polymer solutions with different molar ratios of VPA: AA were produced; however, the total moles of monomer was kept consistent. Vinylphosphonic acid (2.57 g, 23.8 mmol) was dissolved in deionized water (7.5 mL) and added to a dry 100 mL three-neck round bottom flask equipped with a mechanical stirrer that had been

purged with argon gas. The solution was heated in an oil bath to 90 °C and left to stir for 30 minutes. Acrylic acid (15.45 g, 214.4 mmol) was dissolved in deionized water (8 mL), AIBA (64.5 mg, 0.24 mmol) was dissolved in deionized water (8 mL), and 1-octanethiol (174.5 mg, 1.19 mmol) was dissolved in deionized water (10 mL). These were added to the reaction vessel in equal portions, every 30 minutes, for 6 hours. After the last addition, the solution was left to stir at 90 °C for 18 hours. Unless otherwise stated the polymer solution was not purified or isolated and was used directly to prepare the polymer composite samples. The polymer solution used in milliliter amounts and was used directly from the reaction vessel in which the reaction was conducted.

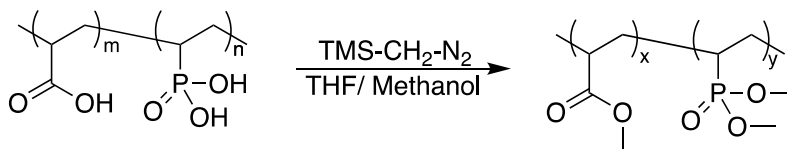
When polymer isolation was required for complete characterization the polymer was isolated by precipitation in acetone and centrifuged at 10,000 rpm (4 °C) to form a pellet. After decanting the water/acetone mixture, additional acetone was added. This was shaken and centrifuged, these steps were repeated until the pellet changed from clear to white in colour. After drying using the high vacuum, a ^{31}P NMR was acquired and used to confirm isolation of the polymer through the disappearance of the monomer VPA peak. ^1H NMR (300 MHz, D_2O) 4.38 (OH), 2.78-2.44 (CH), 2.01-1.67 (CH_2). ^{31}P NMR (121.4 MHz, CDCl_3) 29.63.

2.4 Synthesis of Polyacrylic acid



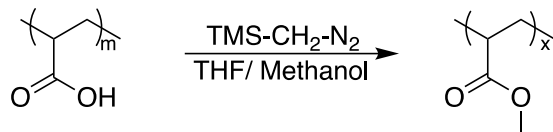
AIBA (0.039 g, 0.144 mmol) was added to a clean 100 mL two-neck round bottom flask equipped with a mechanical stirrer. The apparatus was then capped and purged with argon gas. Deionized water (19.33 mL), 1-octanethiol (0.1056 g, 0.722 mmol), and acrylic acid (10.4 g, 144.32 mmol) were added to the flask and placed in an oil bath heated at $90\text{ }^\circ\text{C}$ for 3 hours. ^1H NMR (300 MHz, D_2O) 4.38 (OH), 2.78-2.45 (CH), 1.98-1.68 (CH_2).

2.5 Synthesis of Methylated PVPA-co-AA



PVPA-co-AA copolymer was dissolved in a 1:1 v/v THF/ methanol solution for a concentration of 5 mg mL^{-1} . The yellow solution of TMS-diazomethane was added dropwise, which resulted in nitrogen bubbling and decolouration. After approximately 2 mL of the methylation agent was added the reaction mixture held its yellow colour and was allowed to stir overnight. The next day the reaction mixture was still slightly yellow, although the volume of liquid had decreased. A stream of air was used to blow off the remaining solvent and the reacted polymer was left in the reaction vessel. ^1H NMR (300 MHz, CDCl_3) 3.64 (OMe), 2.27 (CH), 2.03-1.65 (CH_2). ^{31}P NMR (121.4 MHz, CDCl_3) 34.86.

2.6 Synthesis of Poly(methyl acrylate)



PAA was dissolved in a 1:1 v/v THF/ methanol solution for a concentration of 5 mg mL⁻¹. The yellow solution of TMS-diazomethane was added dropwise, which resulted in nitrogen bubbling and decolouration. After approximately 2 mL of the methylation agent was added the reaction mixture held its yellow colour and was allowed to stir overnight. The next day the reaction mixture was still slightly yellow, although the volume of liquid had decreased. A stream of air was used to blow off the remaining solvent and the reacted polymer was left in the reaction vessel. ¹H NMR (300 MHz, CDCl₃) 3.64 (OMe), 2.29 (CH), 1.98-1.66 (CH₂).

3 Composite sample testing procedures

3.1 Preparation of composite samples

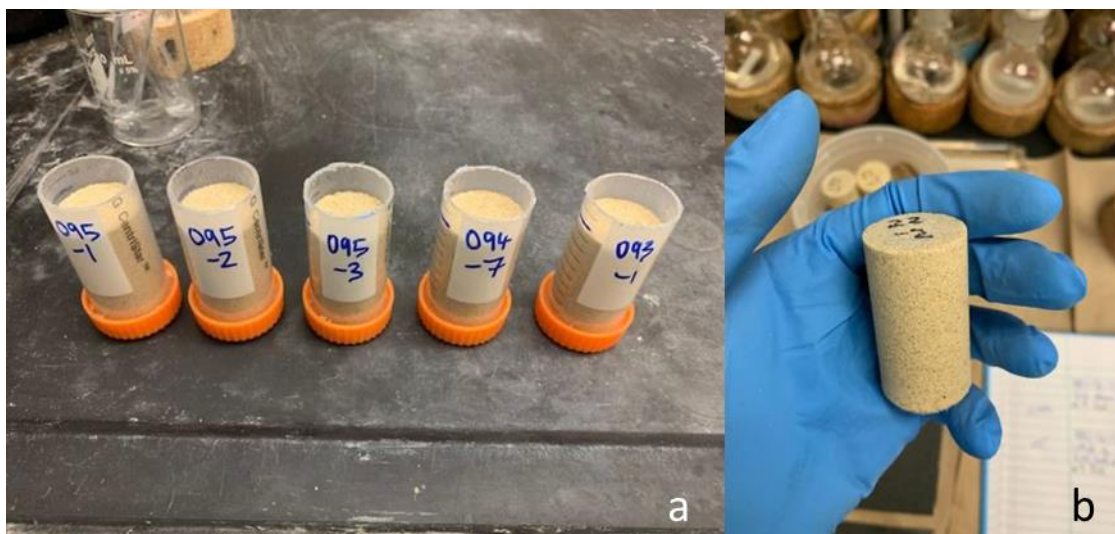


Figure 41: Composite samples a) Drying in the cylindrical moulds b) Sample removed from the mould before compression testing

To prepare the composite samples and uniformly evaluate their compressive strength and curing time, the amount of sand (g) and volume of PVPA-co-AA polymer solution (mL) were monitored and kept consistent. The PVPA-co-AA polymer solution was used without any purification steps directly after polymerization. The sand was premeasured in the moulds for a certain height and weight, the polymer solution was then added to the sand in a separate mixing glass and mixed manually. Proper care was taken to ensure that a homogenous mixture was achieved. Differences in viscosity between each ratio mix of PVPA-co-AA polymer solution caused some difficulty in mixing due to the stickiness of the polymer but generally the composite materials mixed well. Once thoroughly mixed, the mixture was scooped into cylindrical moulds. The sand polymer composites were then compacted so that each sample was of uniform height. The samples were then left to air dry in the fume hood for 4-7 days. When the samples were dry enough to be extracted from the mould without damaging them, they were removed using a Weber press as the samples stuck to the inside of the plastic moulds. Once the samples were extracted from the moulds, they were baked in an oven for 4 hours at 150 °C, this was done to ensure all the water had completely evaporated. The samples were then stored in a desiccator until they could be tested on the compression instrument, usually overnight.

3.2 Unconfined compression test

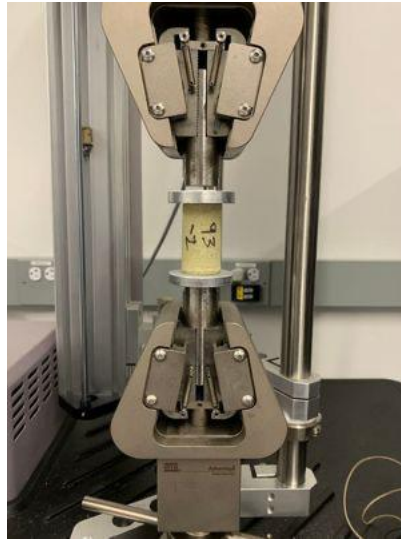


Figure 42: Compressive strength testing of composite samples

Unconfined compression tests were conducted using a universal mechanical testing system (MTS Model 43). The applied axial strain throughout the test was constant and maintained at a rate of 6 mm/min. The test was terminated when the stress exceeded the strength of the composite material. The unconfined compressive strength (UCS) of the samples were determined from the stress-strain graphs resulting from the test. NOTE: The rate of compression for the samples tested by the technical staff from the department of civil and environmental engineering was 0.6 mm/min.

3.3 Setting time measurements

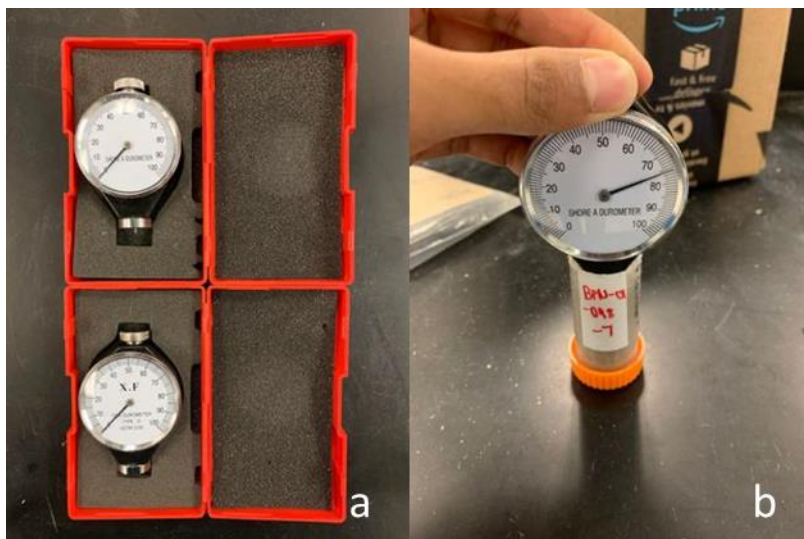
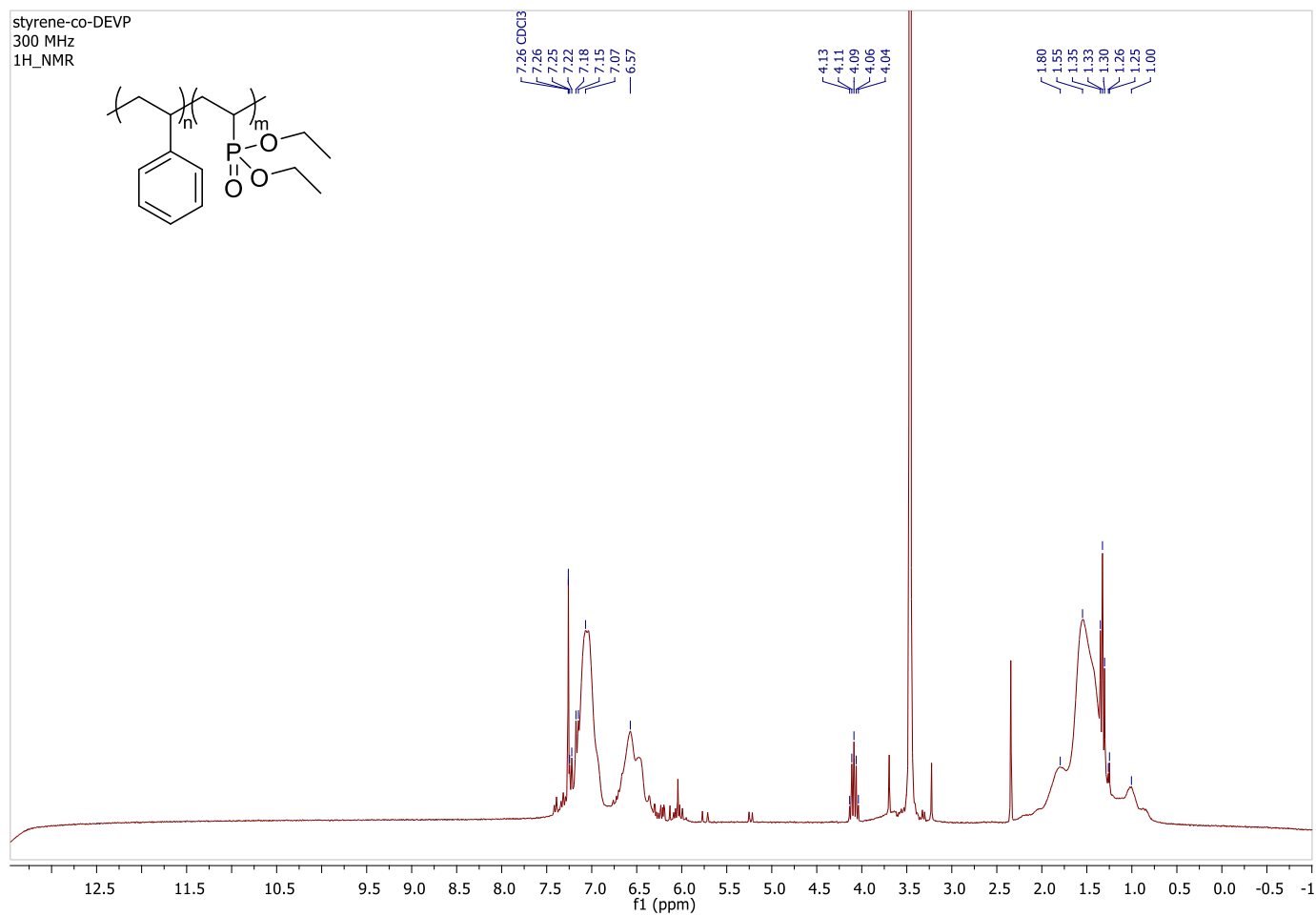


Figure 43: Setting time instrument a) Shore durometer Type A and B b) Demonstration of setting time measurement

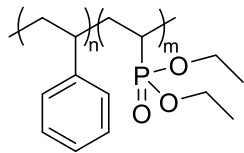
The setting time of each type of PVPA-co-AA polymer composite material was monitored using a Shore durometer. A Shore durometer is a device that is used to measure the hardness of a material, typically polymers and rubbers. The durometer measures the depth of an indentation that is allowed by the material given a standardized force by the durometer tip. Two types of durometers were used, a type A and type D. Type A and the type A scale is used for softer materials while type D and the type D scale is used for harder materials. The setting time was evaluated at consistent time intervals over the course of a few hours to measure the influence of certain variables on setting time. The measurements were terminated if the surface of the sample looked damaged after multiple rounds of testing.

4 Spectral data

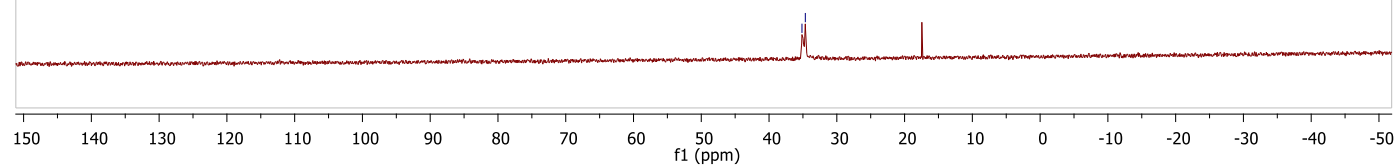
Styrene-co-DEVP



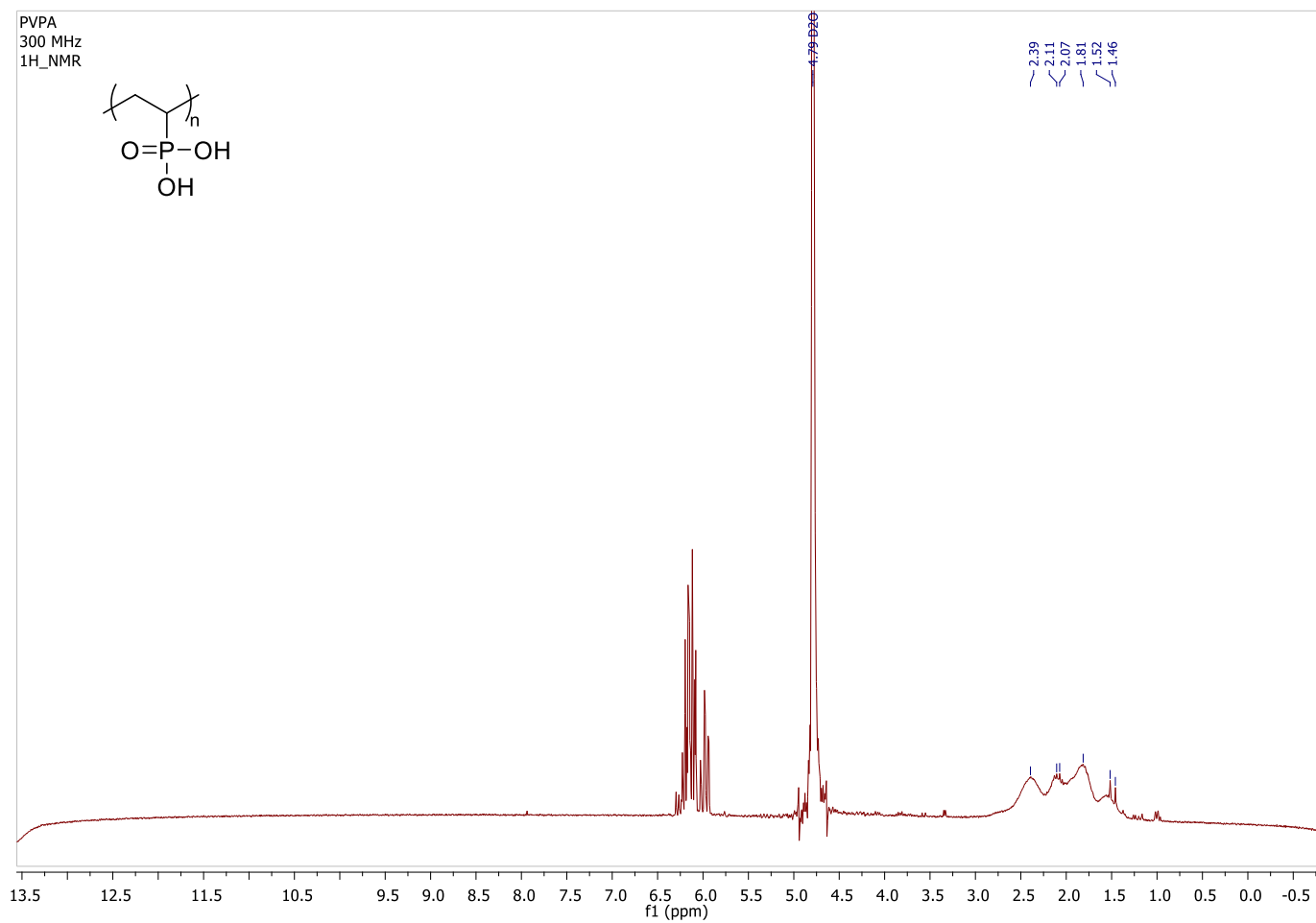
styrene-co-DEVP
121.4 MHz
31P_NMR

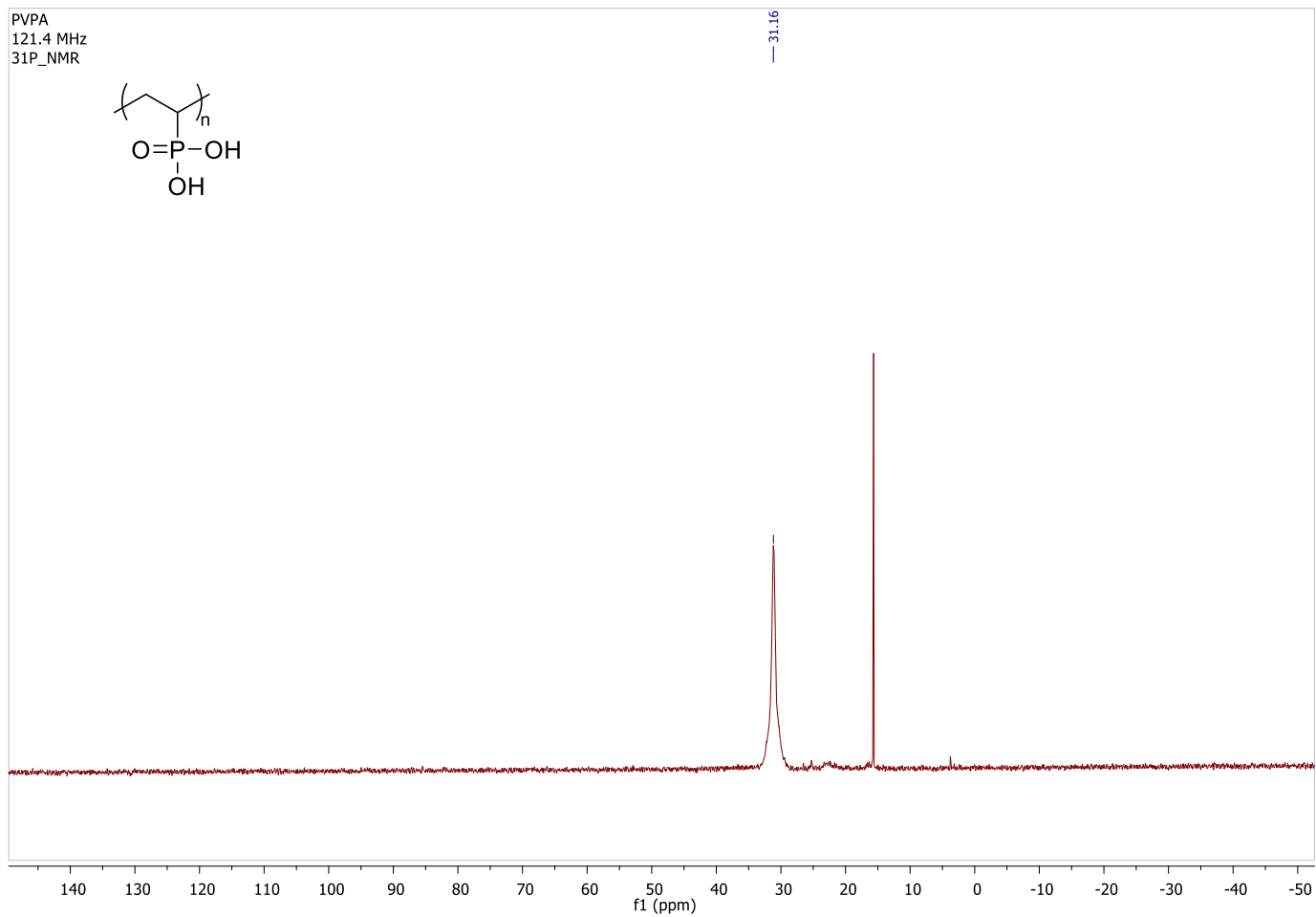


35.14
34.65

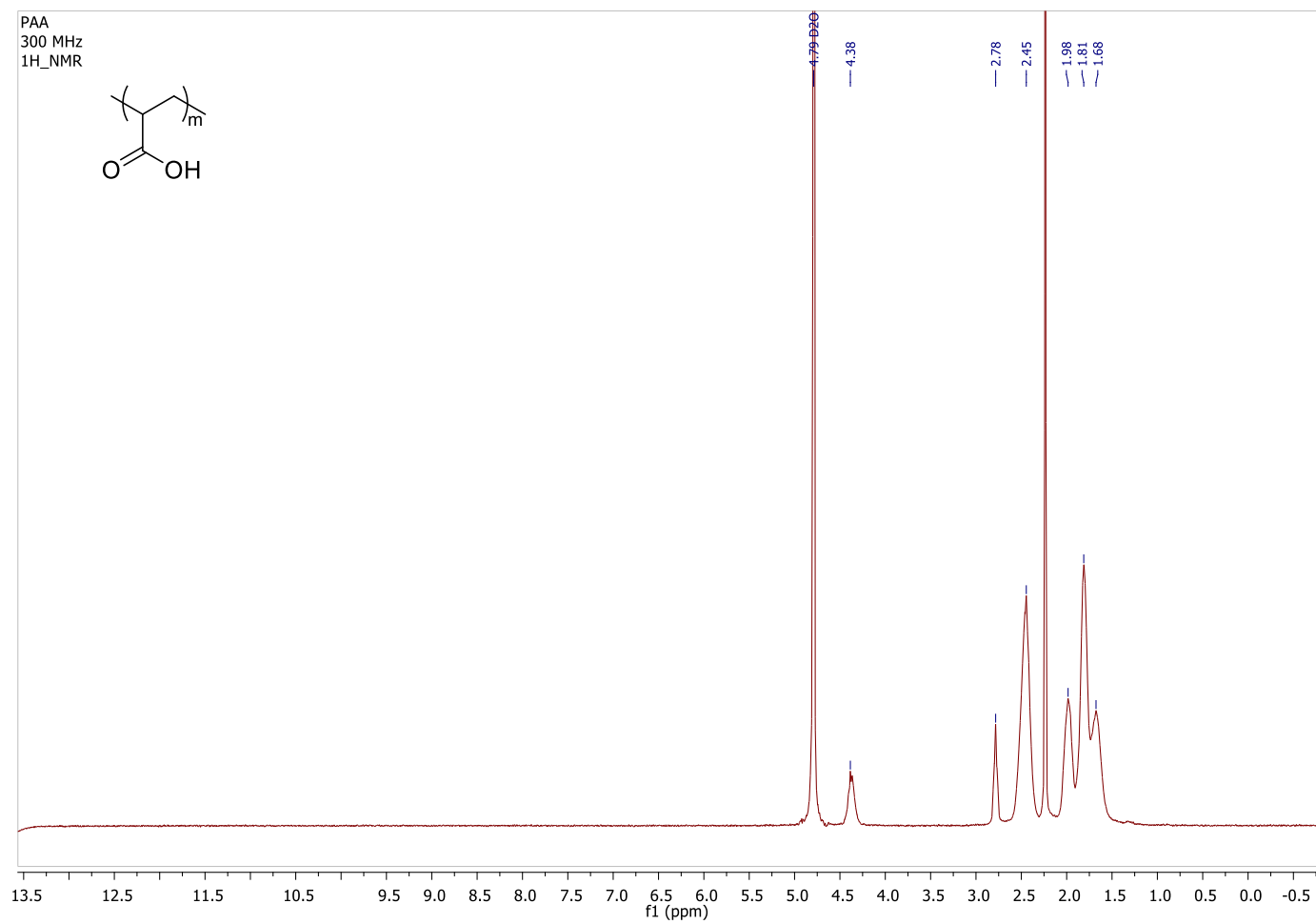


PVPA

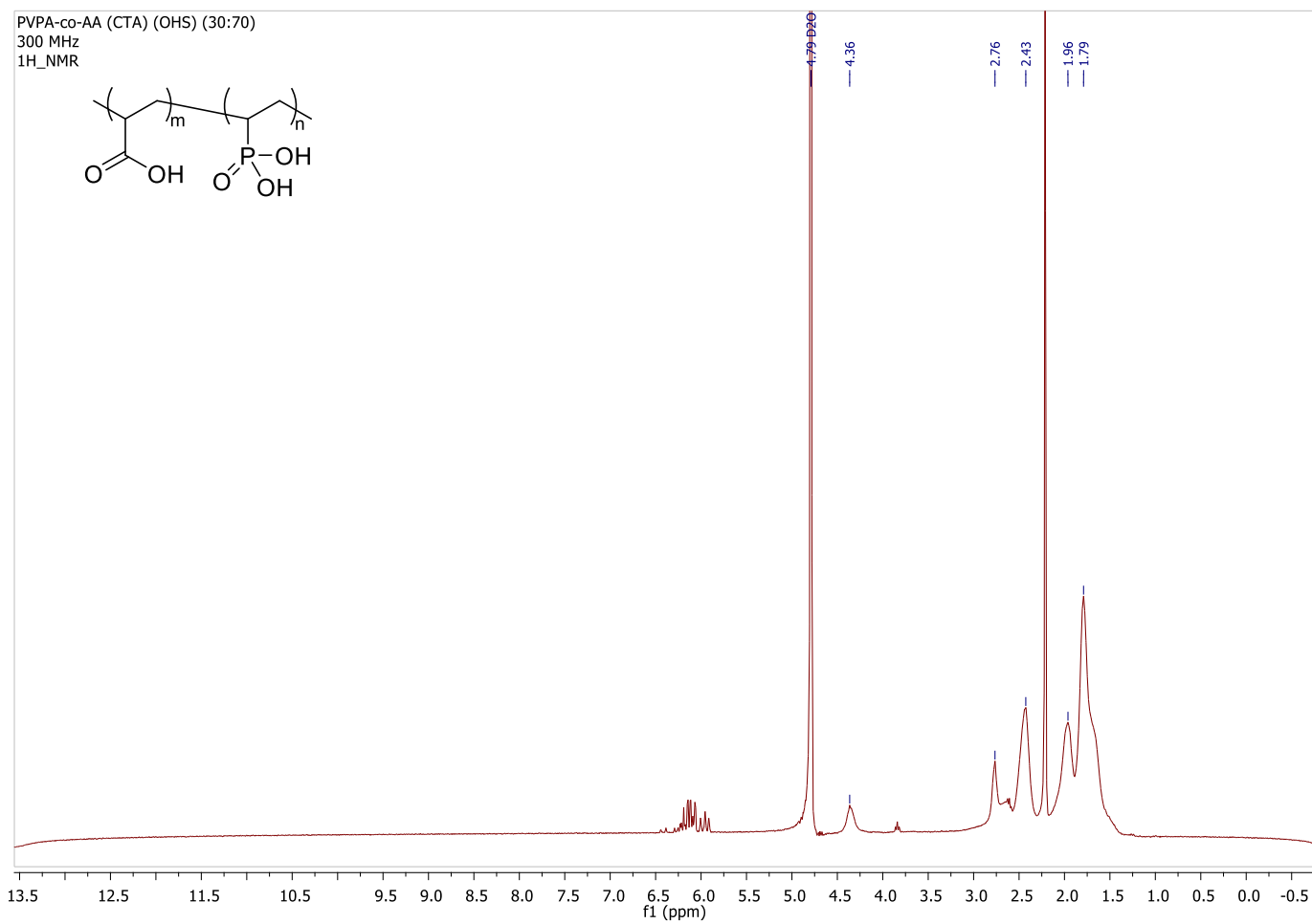




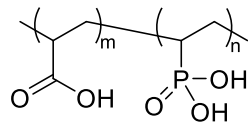
PAA



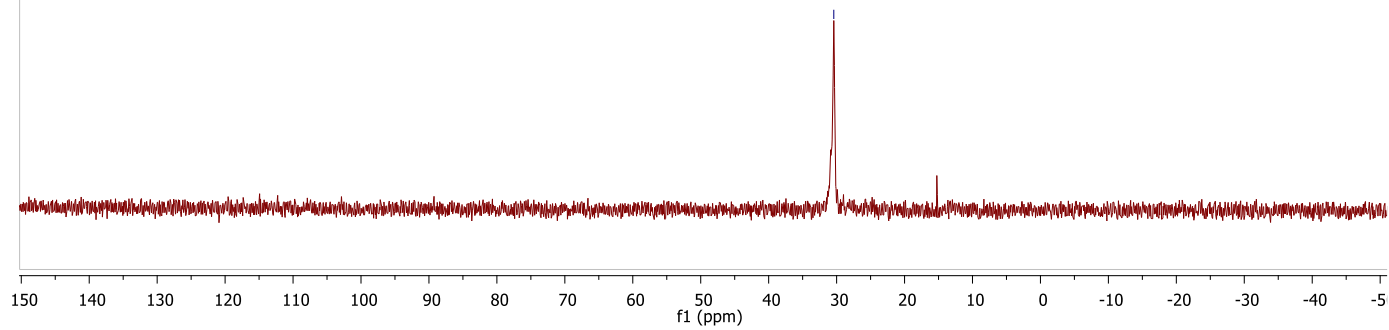
PVPA-co-AA (CTA) (OHS) (30:70)



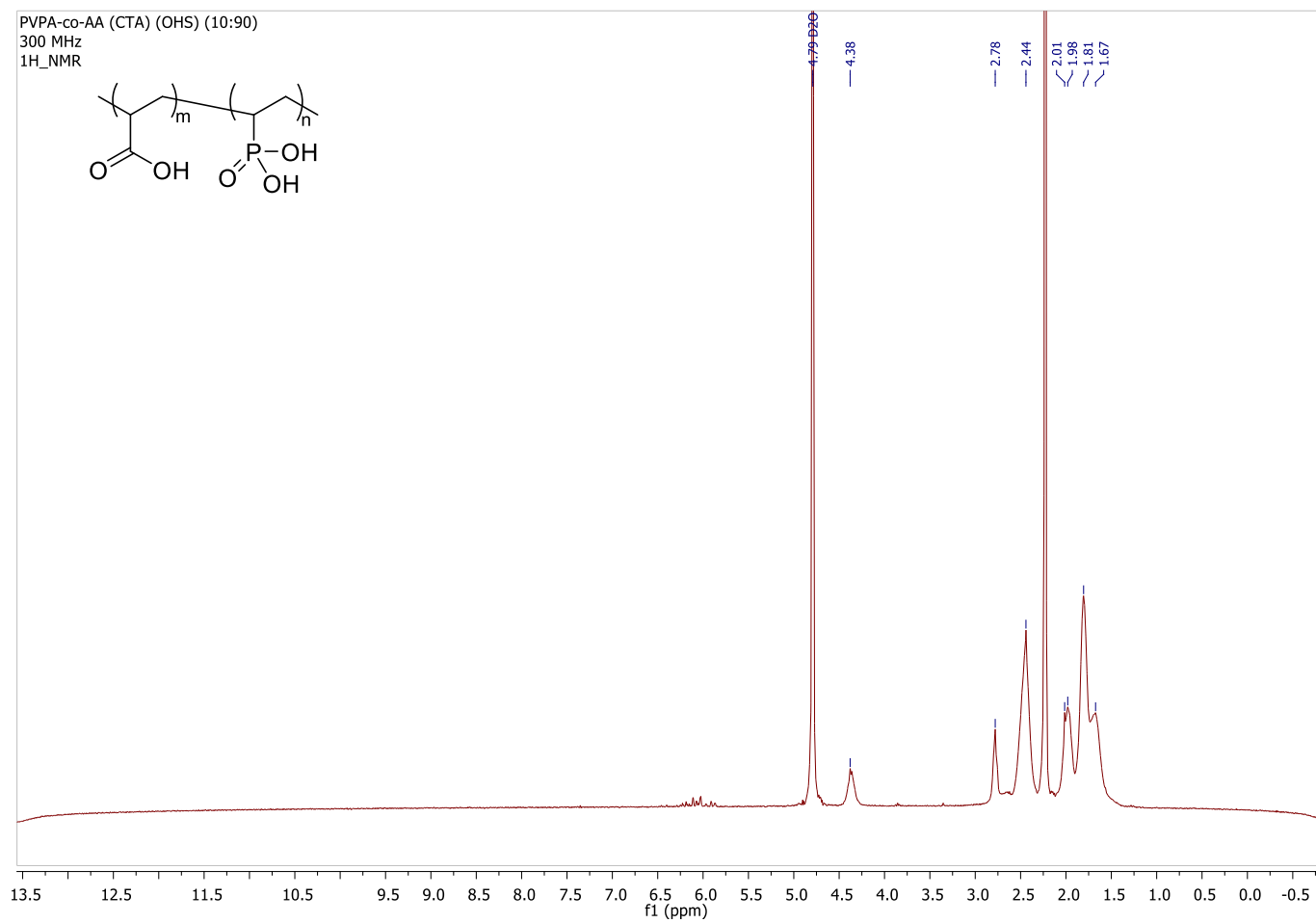
31P_NMR



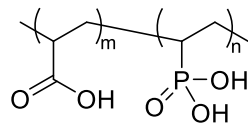
— 30.41



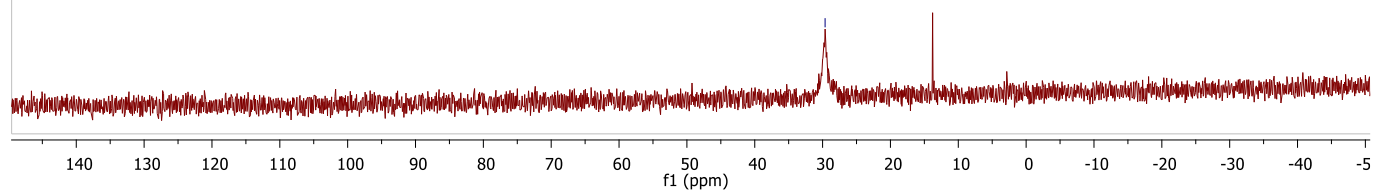
PVPA-co-AA (CTA) (OHS) (10:90)



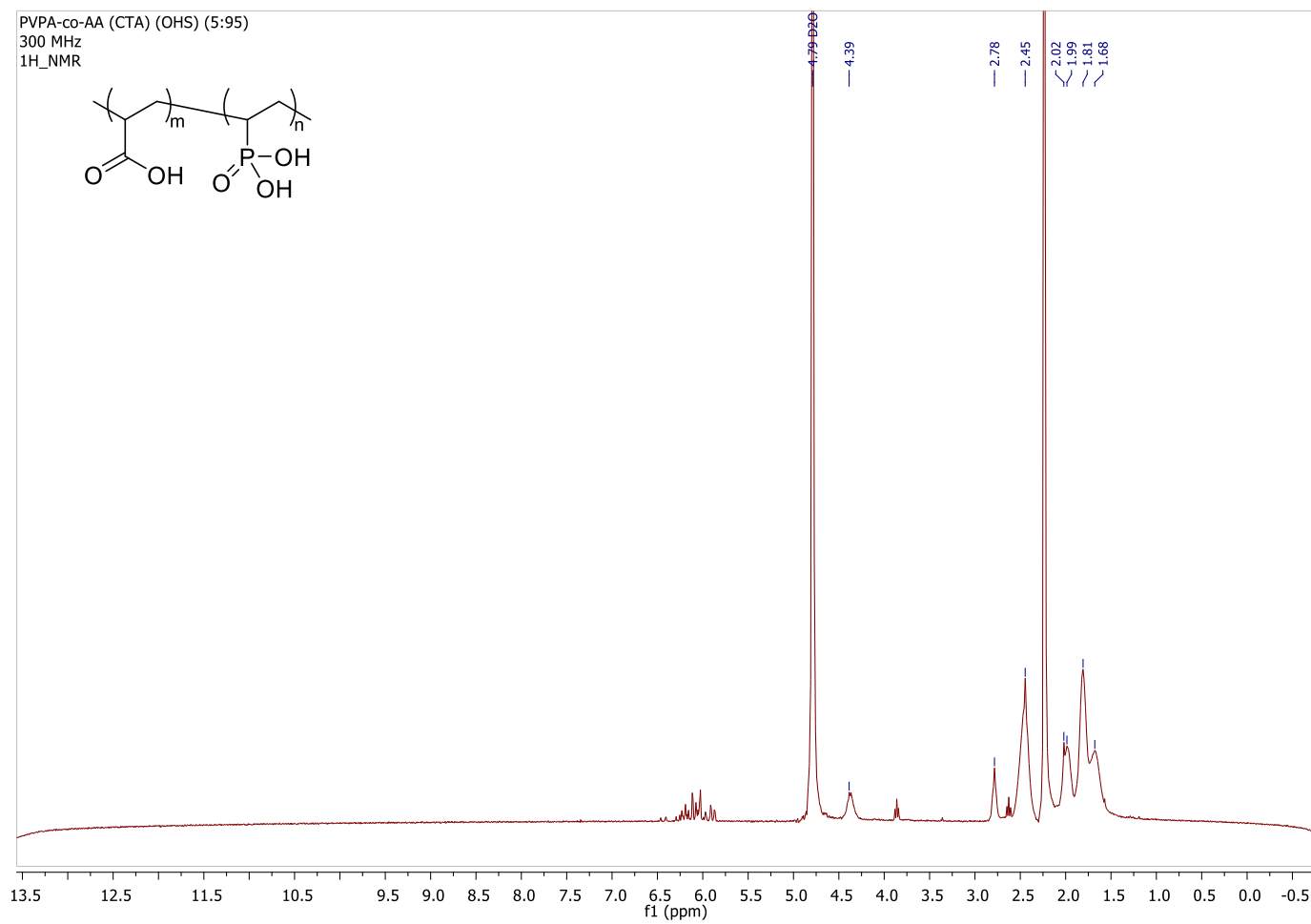
PVPA-co-AA (CTA) (OHS) (10:90)
121.4 MHz
31P_NMR



— 29.63



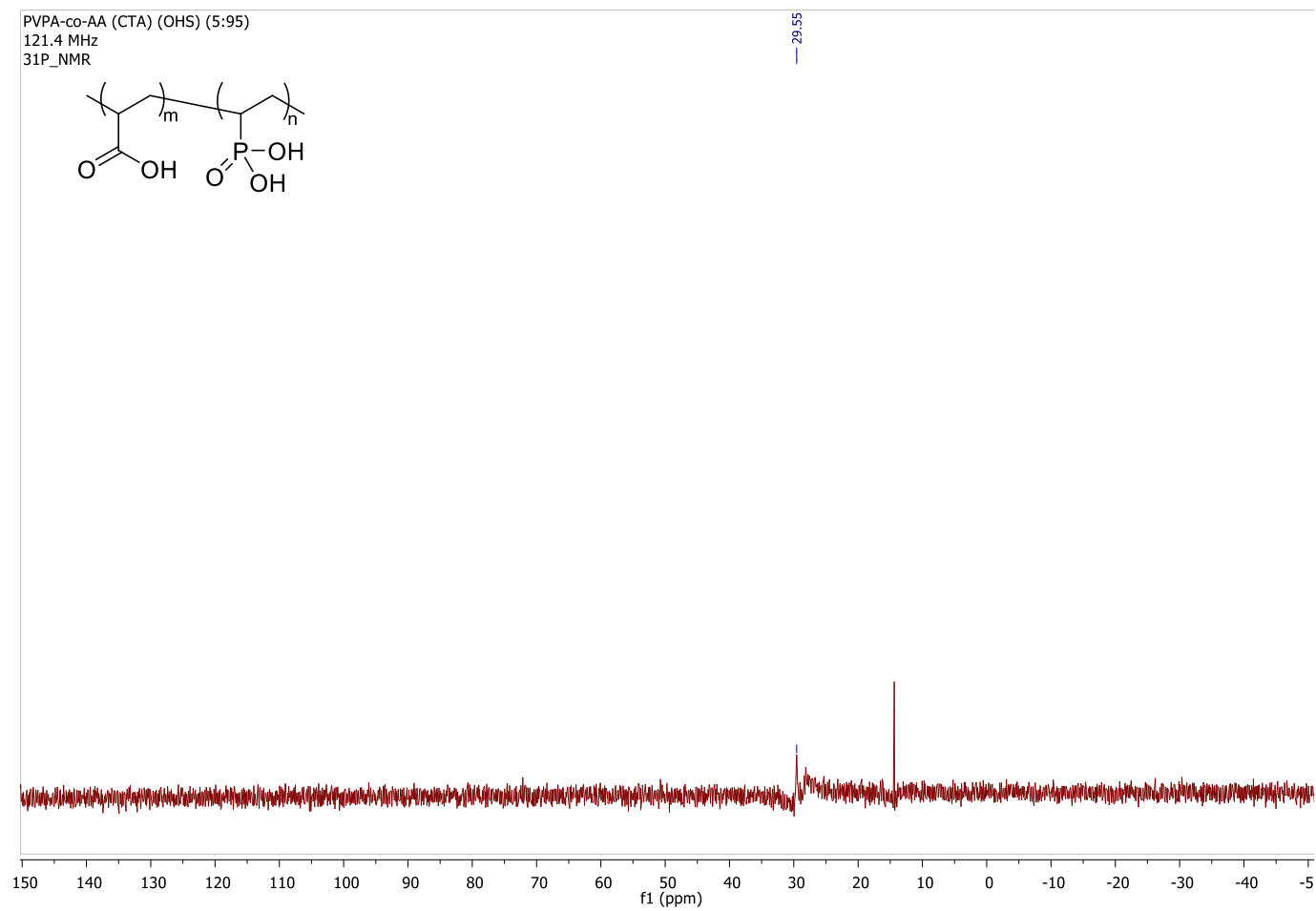
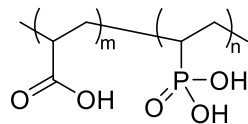
PVPA-co-AA (CTA) (OHS) (5:95)



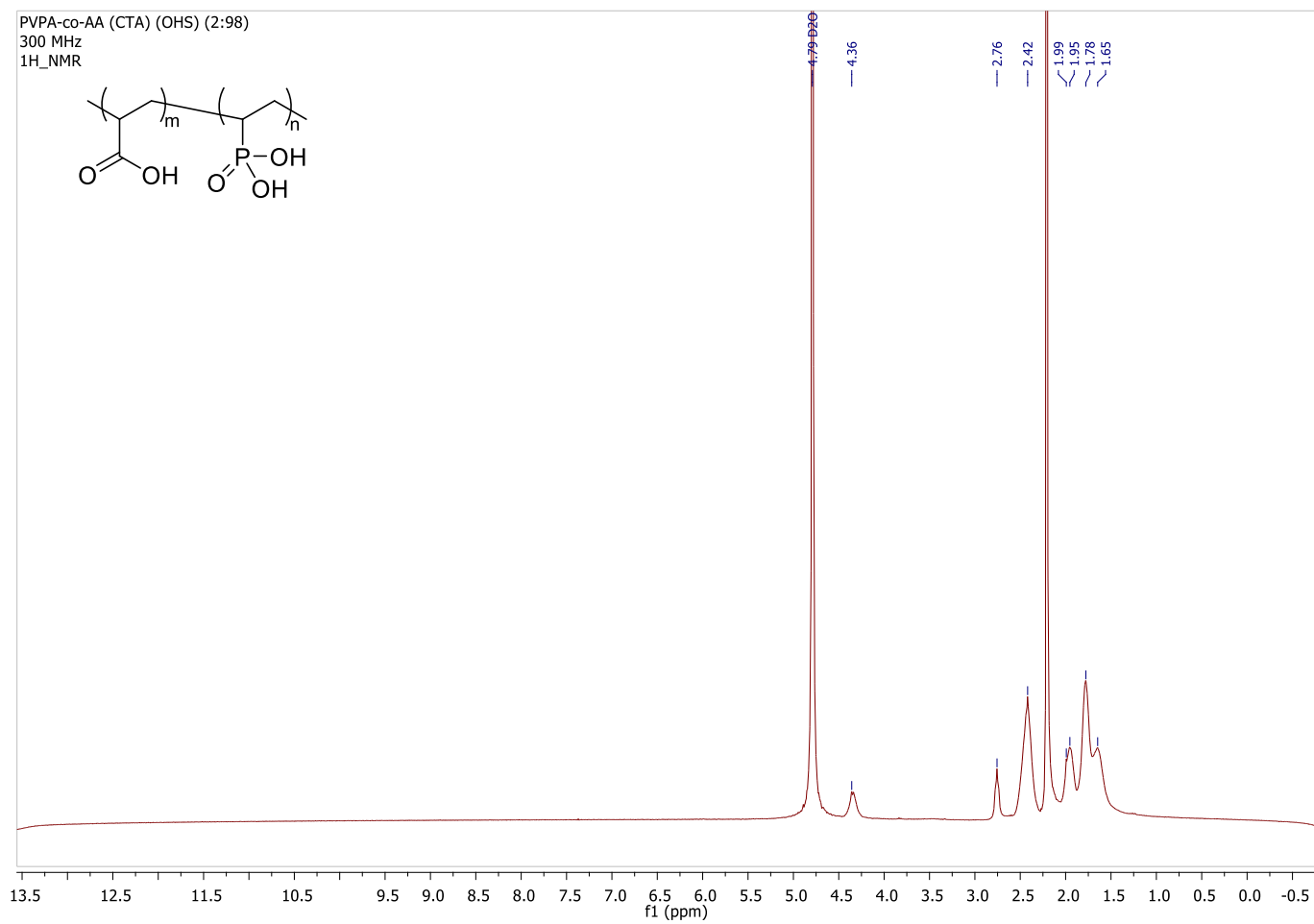
PVPA-co-AA (CTA) (OHS) (5:95)

121.4 MHz

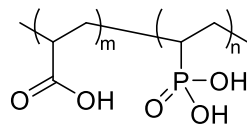
31P_NMR



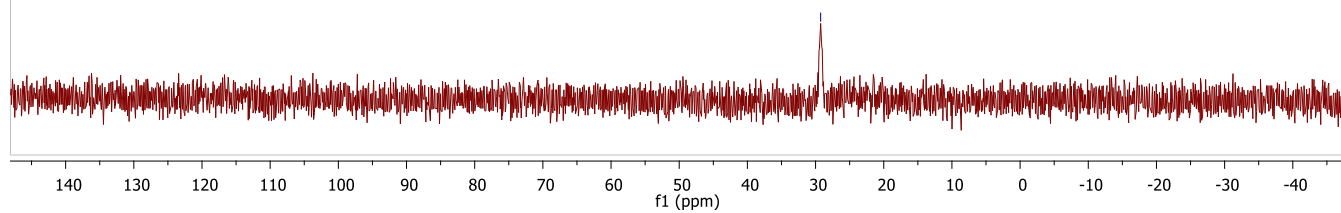
PVPA-co-AA (CTA) (OHS) (2:98)



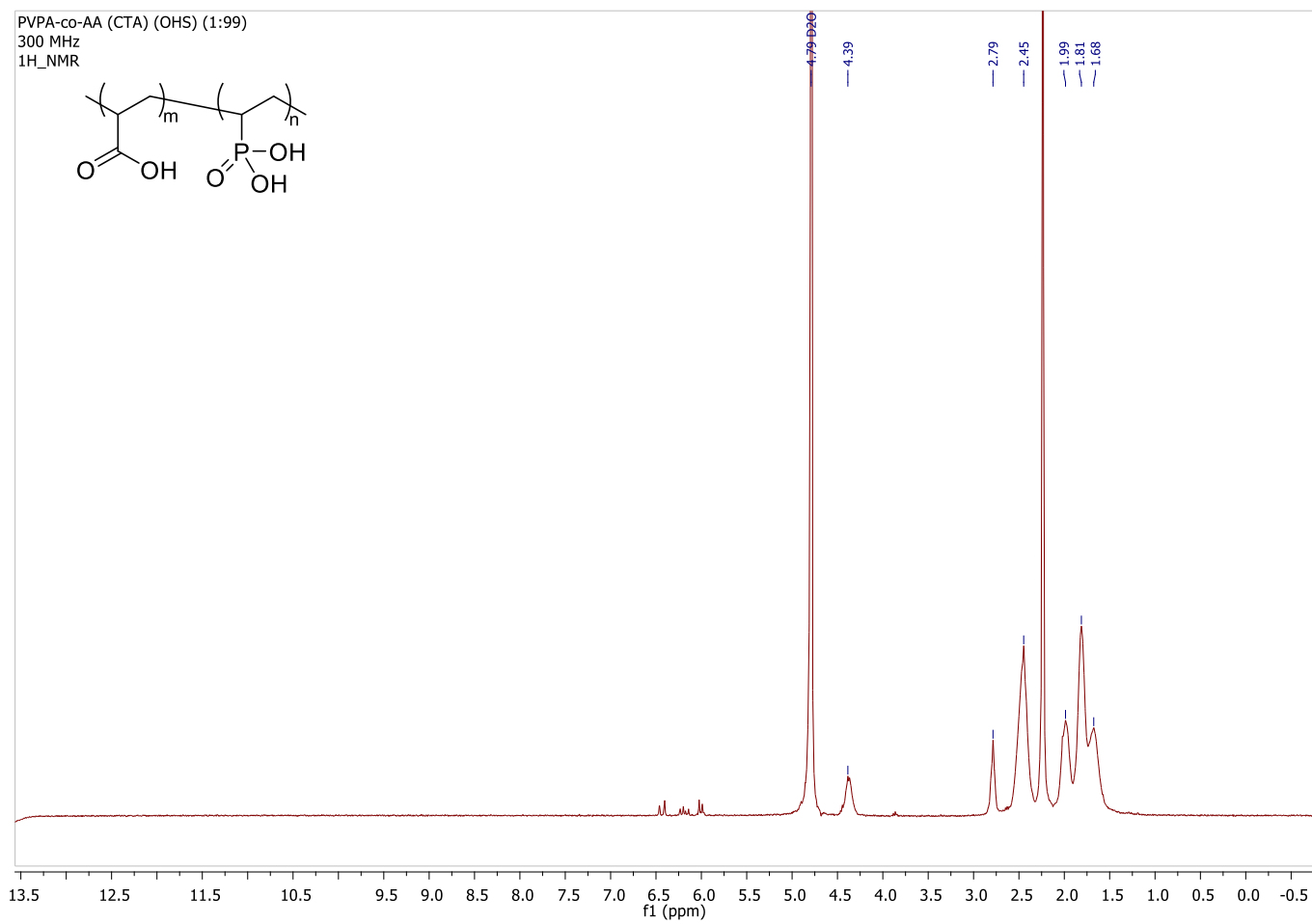
PVPA-co-AA (CTA) (OHS) (2:98)
121.4 MHz
31P_NMR



— 29.26



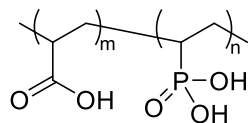
PVPA-co-AA (CTA) (OHS) (1:99)



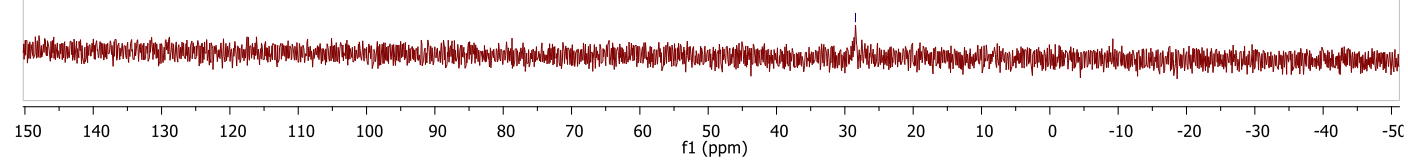
PVPA-co-AA (CTA) (OHS) (1:99)

121.4 MHz

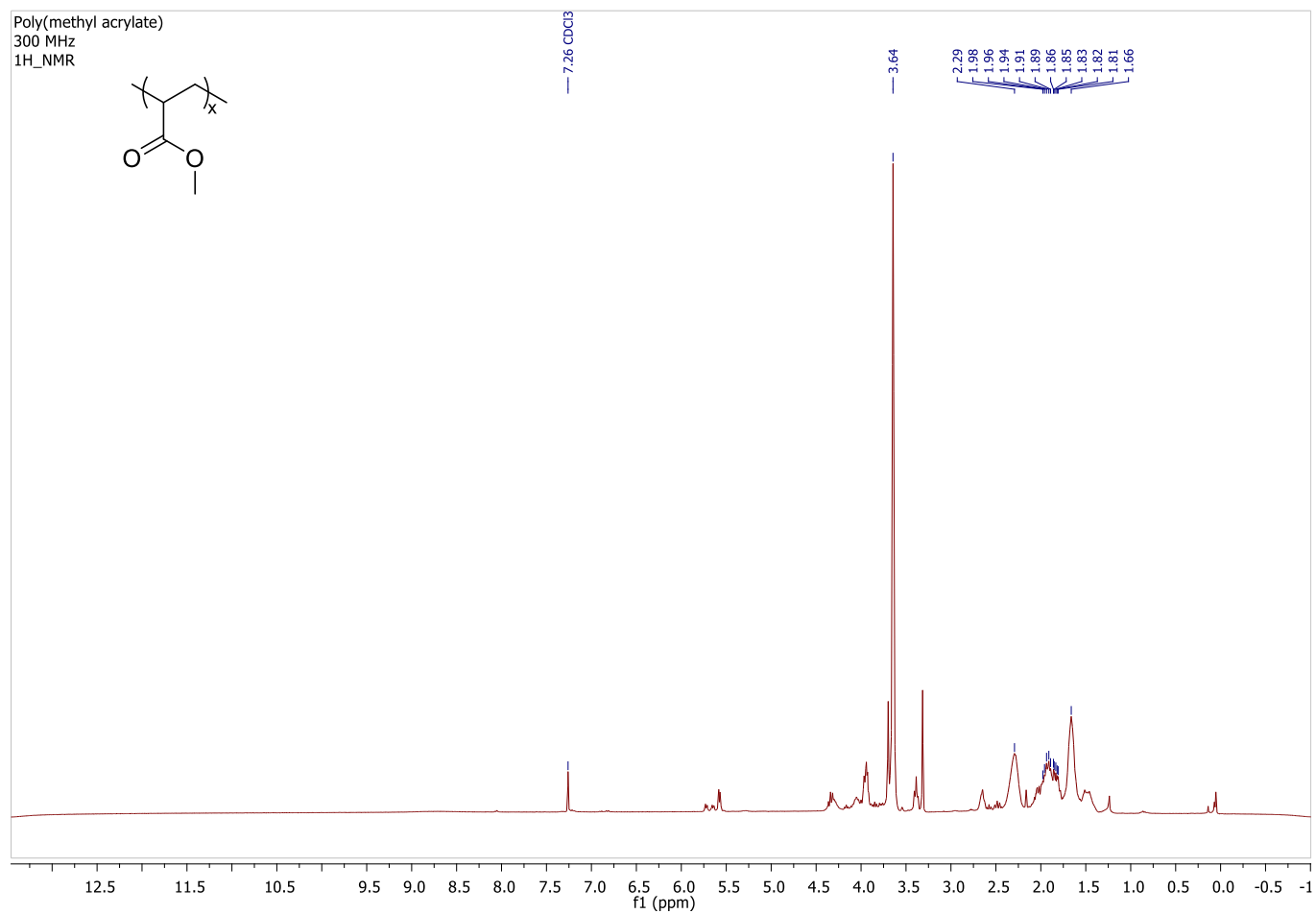
31P_NMR



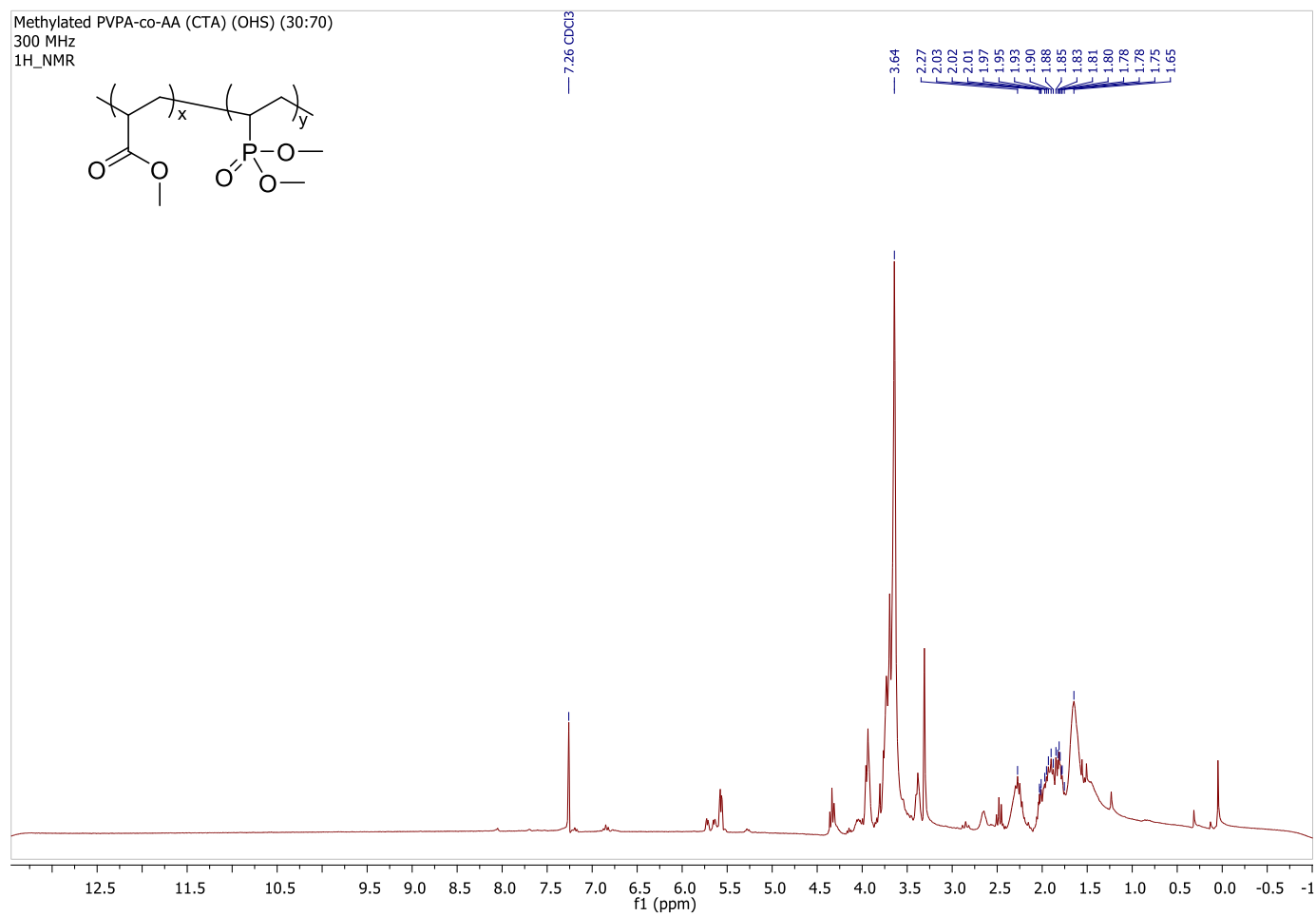
28.44



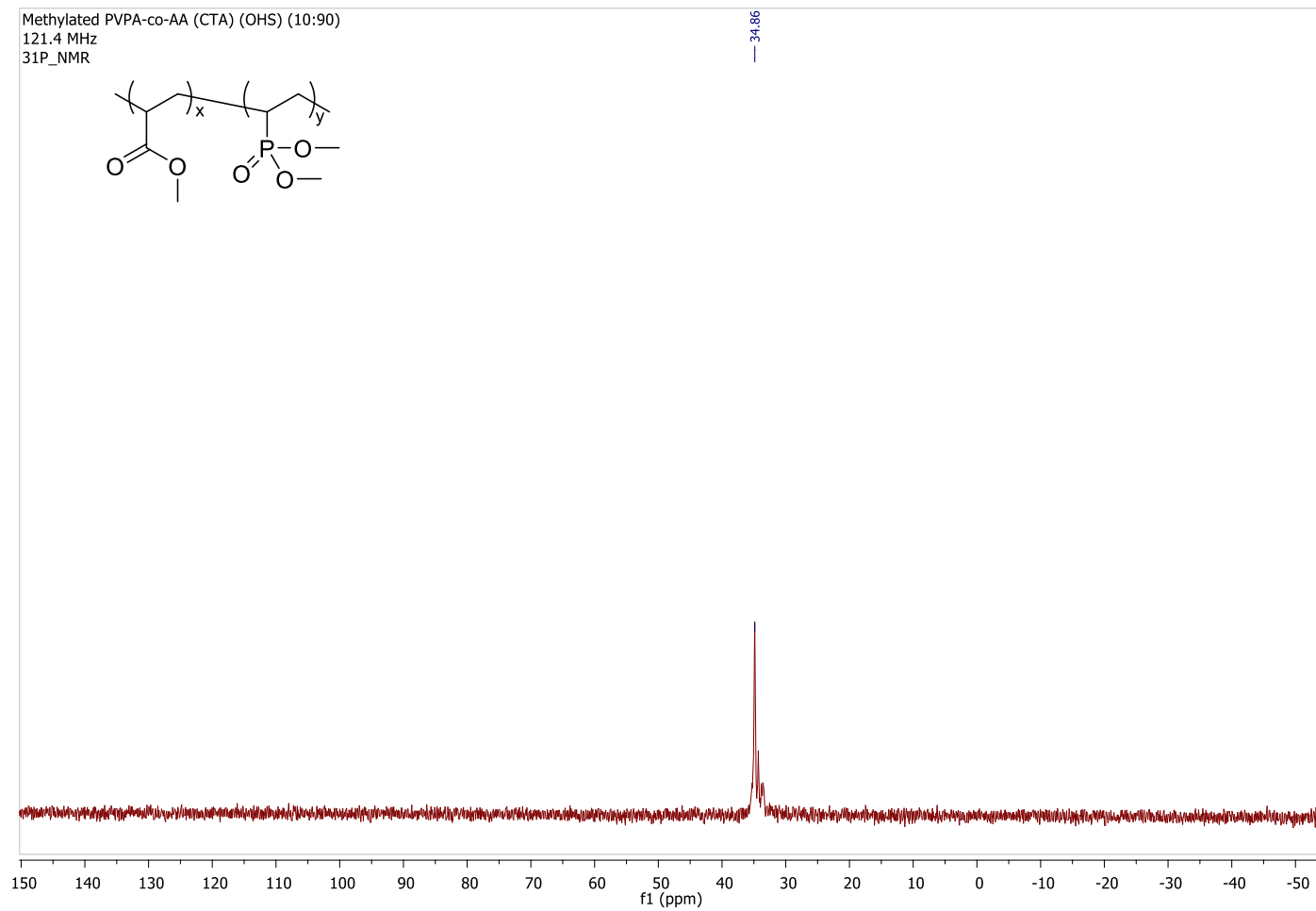
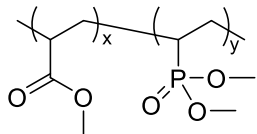
Poly(methyl acrylate)



Methylated PVPA-co-AA (CTA) (OHS) (30:70)

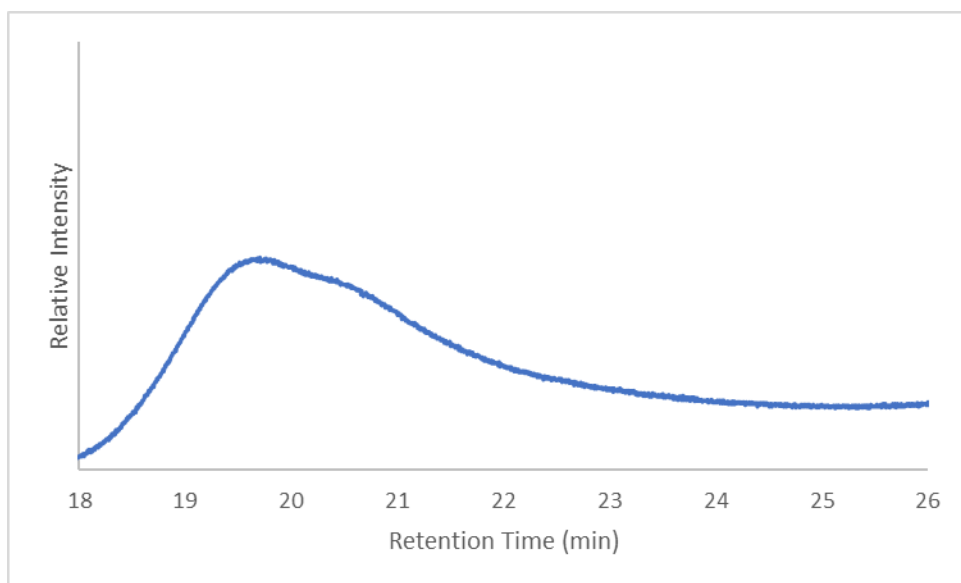


Methylated PVPA-co-AA (CTA) (OHS) (10:90)
121.4 MHz
31P_NMR

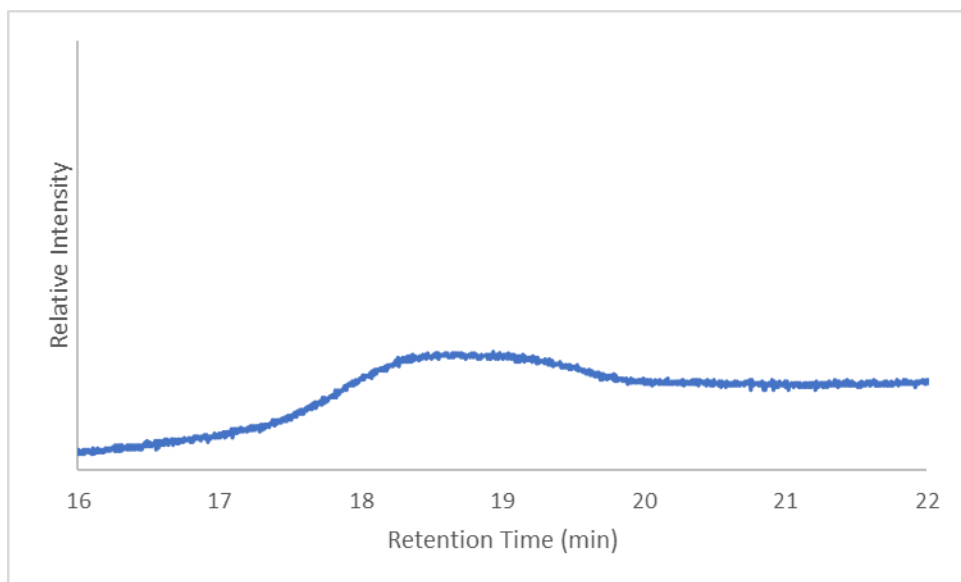


GPC Traces

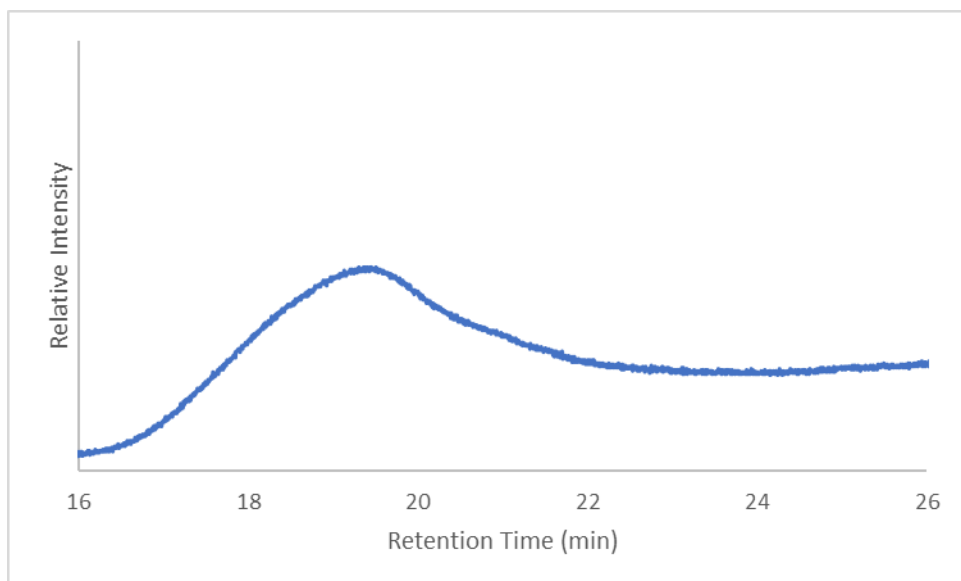
Methylated polyacrylic acid – Stir bar



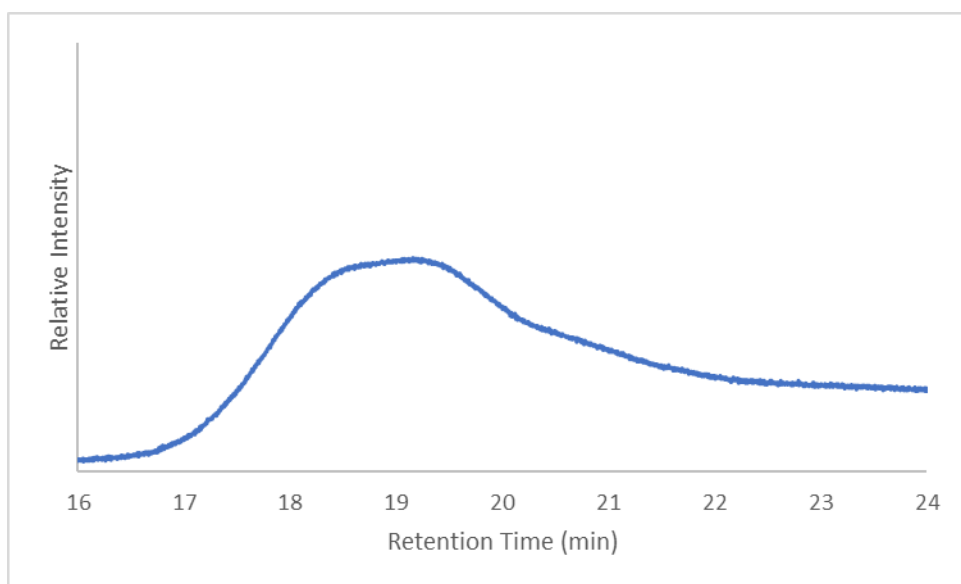
Methylated PVPA-co-AA (CTA) (30:70) – Stir bar



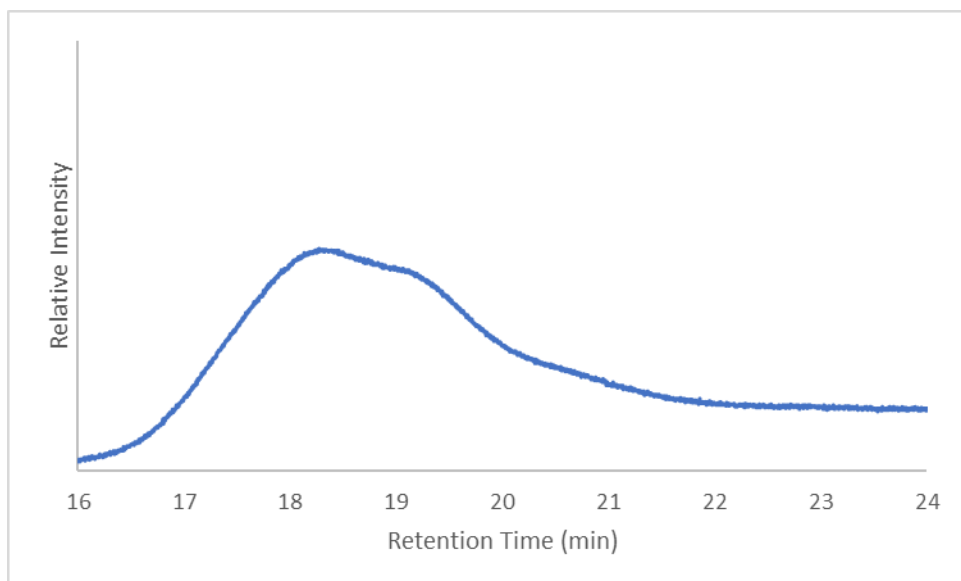
Methylated PVPA-co-AA (CTA) (10:90) – Stir bar



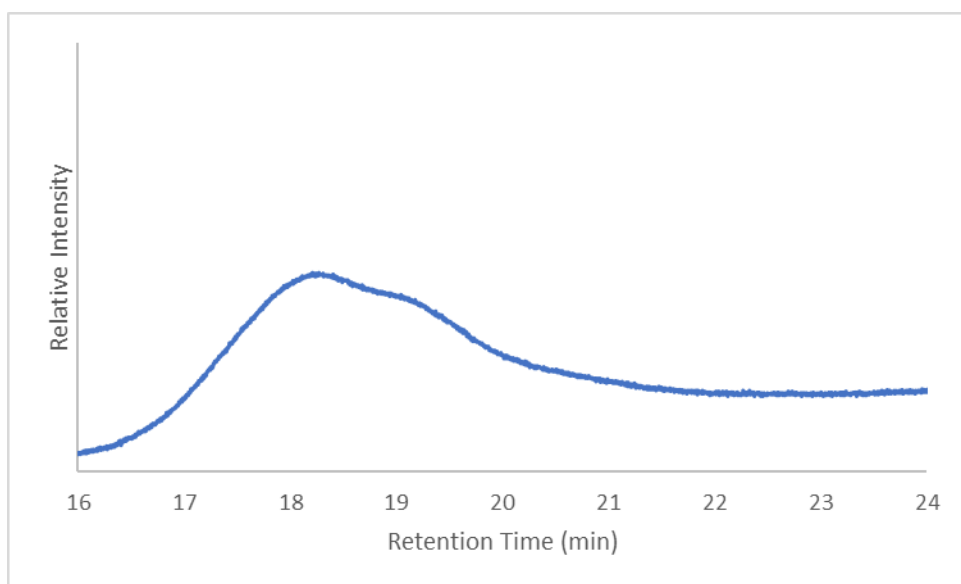
Methylated PVPA-co-AA (CTA) (5:95) – Stir bar



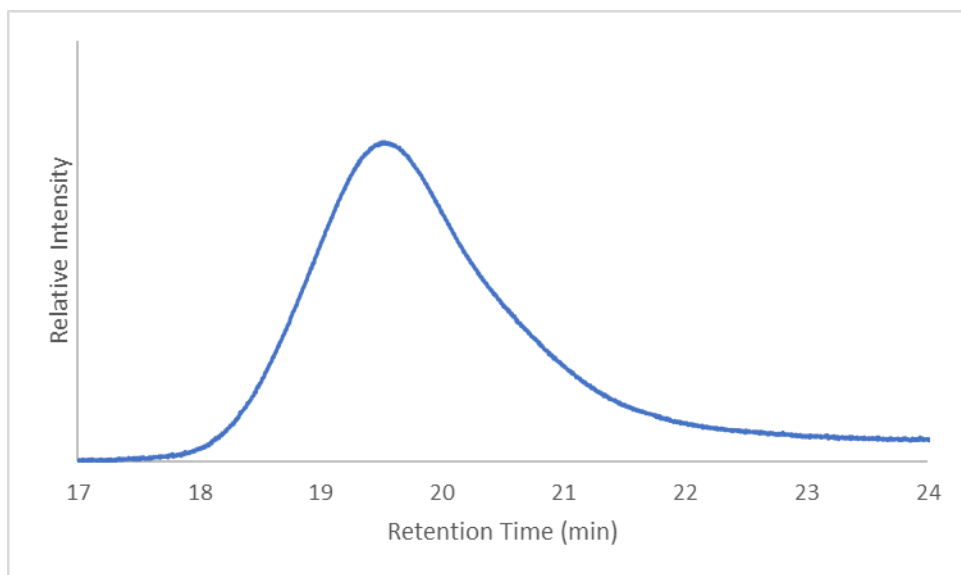
Methylated PVPA-co-AA (CTA) (2:98) – Stir bar



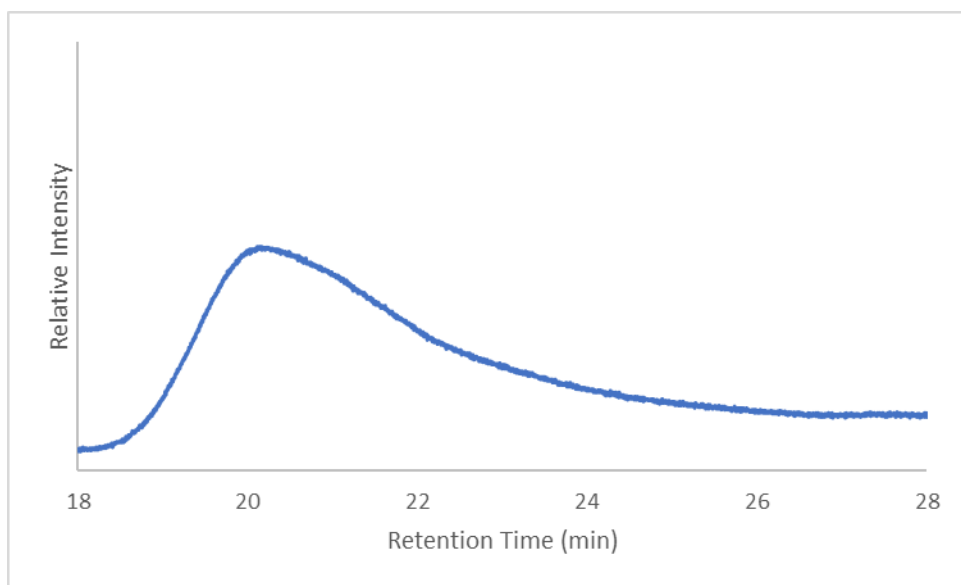
Methylated PVPA-co-AA (CTA) (1:99) – Stir bar



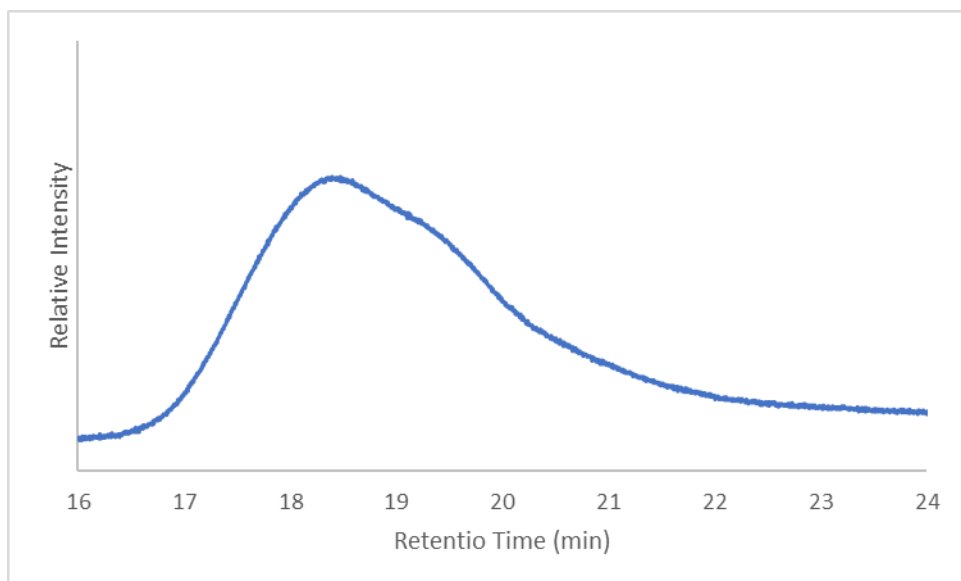
Methylated polyacrylic acid – OHS – Composite samples 39-42



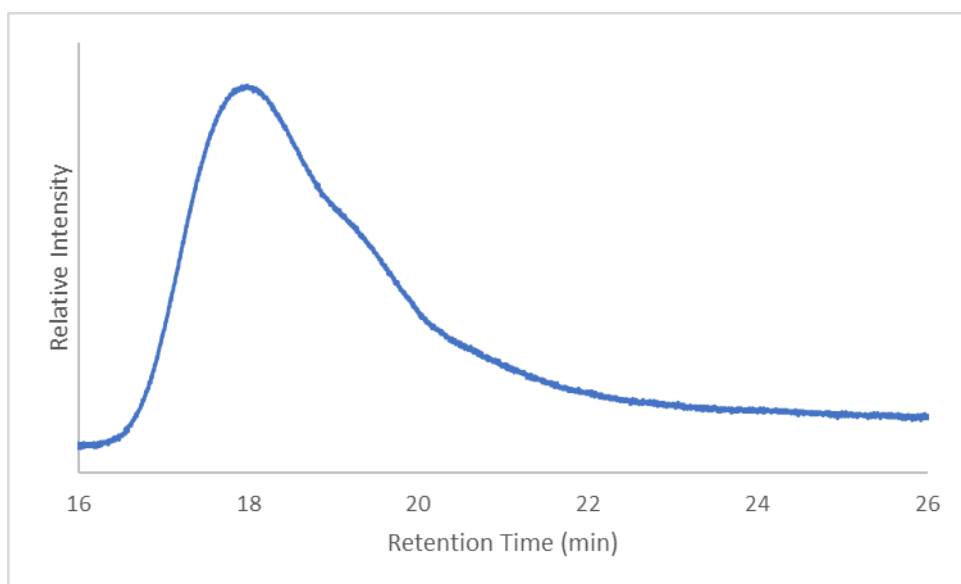
Methylated PVPA-co-AA (CTA) (30:70) – OHS – Composite samples 43-46



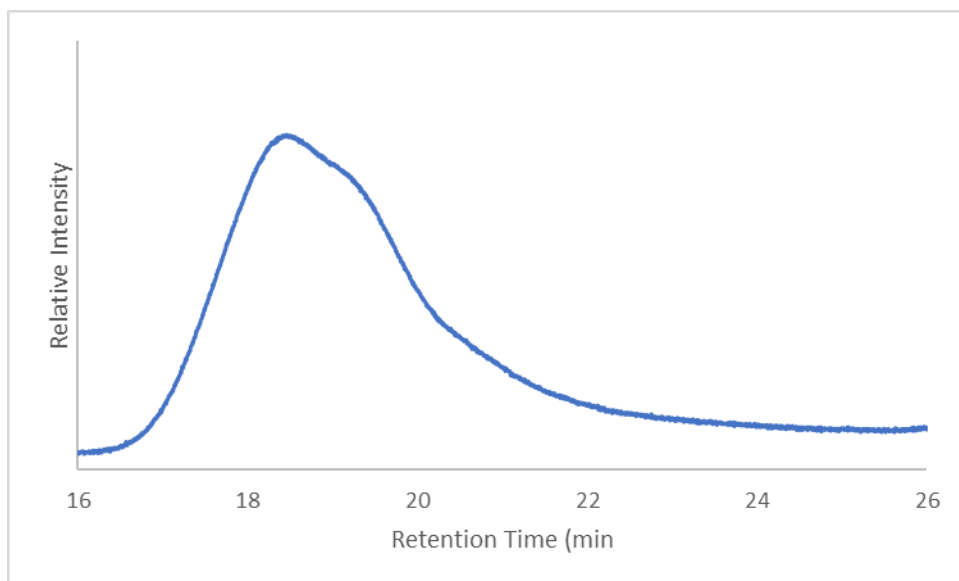
Methylated PVPA-co-AA (CTA) (10:90) – OHS – Composite samples 47-51



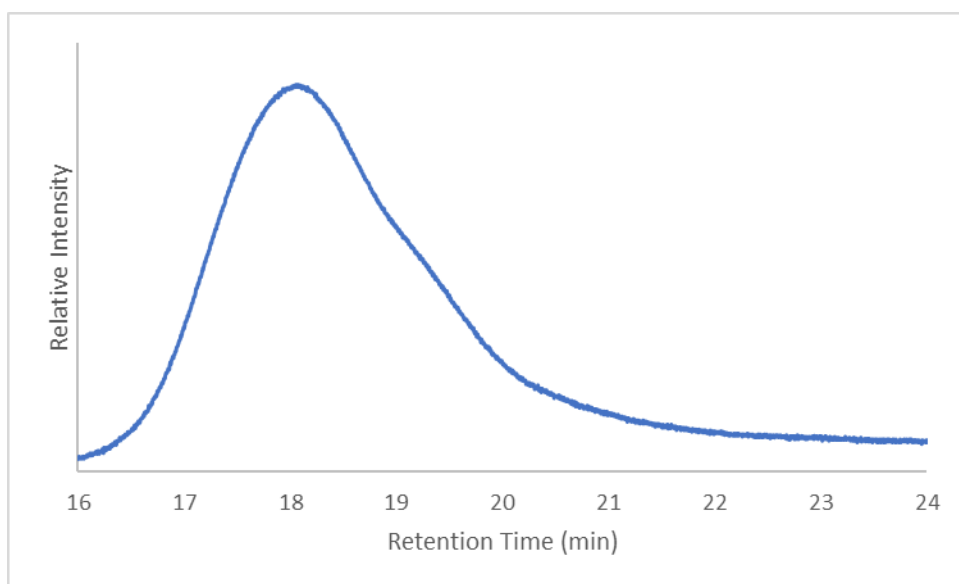
Methylated PVPA-co-AA (CTA) (5:95) – OHS – Composite samples 52-55



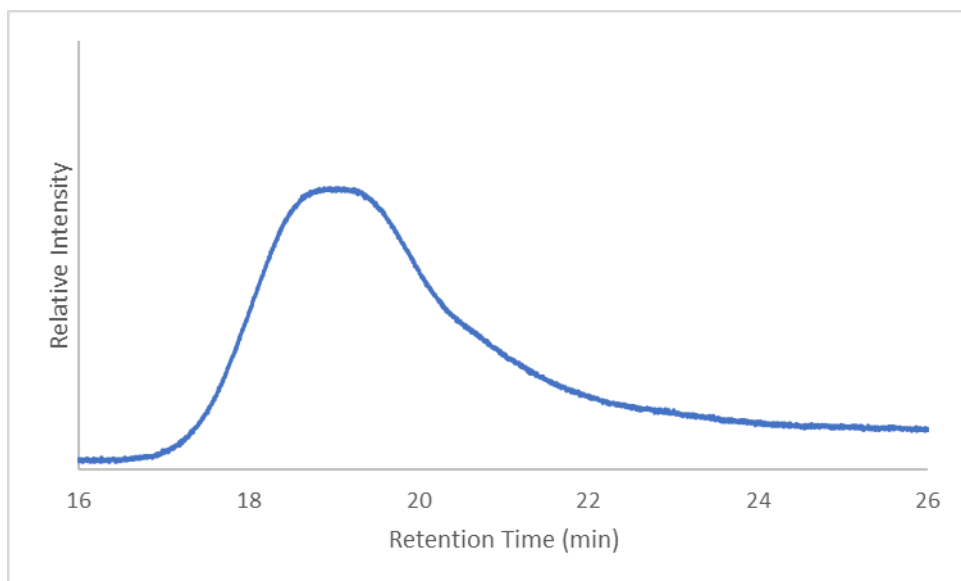
Methylated PVPA-co-AA (CTA) (2:98) – OHS – Composite samples 56-59



Methylated PVPA-co-AA (CTA) (1:99) – OHS – Composite samples 60-63



Methylated PVPA-co-AA (CTA) (10:90) – OHS – Composite samples 64-66



5 Composite samples produced

Sample Number	Polymer	Metal Oxide	Pour over/ Mixed	Polymer Amount	Polymer Weight (grams)*	Water Amount	Metal Oxide Amount (grams)	Polymer*/Sand (%)	VPA weight (grams)*	VPA*/Sand (%)	Overnight dry	Vacuum Oven	Oven (150°C)	Diameter (m)	Max stress (MPa)	Tested by:
1	PVPA (3 hr)	Sand S25-3	Pour over	0.6 ml	0.3960	10 ml	46.255	0.86	0.396	0.86	Yes	4 hrs	2 hrs	0.0260	0.695	Tech Staff
2	PVPA-co-AA (CTA) (30.70)	Sand S25-3	Pour over	0.6 ml	0.2225	9 ml	40.8577	0.54	0.0868	0.21	Yes	6 hrs	2 hrs	0.0266	0.698	Tech Staff
3	PVPA-co-AA (CTA) (30.70)	Sand S25-3	Mixed	0.6 ml	0.2225	9 ml	41.6408	0.53	0.0868	0.21	Yes	6 hrs	2 hrs	0.0266	0.939	Tech Staff
4	PVPA-co-AA (CTA) (10.90)	Sand S25-3	Mixed	1 ml	0.3498	8 ml	43.2891	0.81	0.05	0.12	Yes (6 days)	-	22 hrs	0.0272	1.825	Tech Staff
5	PVPA-co-AA (CTA) (10.90)	Sand S25-3	Mixed	1 ml	0.3498	-	43.0694	0.81	0.05	0.12	Yes (6 days)	-	22 hrs	0.0267	5.370	Tech Staff
6	PVPA-co-AA (CTA) (30.70)	Sand S25-3	Mixed	1 ml	0.3708	-	42.9120	0.86	0.1447	0.34	Yes (6 days)	-	4 hours	0.0267	3.431	Tech Staff
7	PVPA-co-AA (CTA) (30.70)	Sand S25-3	Mixed	2 ml	0.7416	-	43.1606	1.72	0.2894	0.67	Yes (6 days)	-	4 hours	0.0266	11.501	Tech Staff
8	PVPA-co-AA (CTA) (30.70)	Sand S25-3	Mixed	3 ml	1.1124	-	43.3664	2.57	0.4340	1	Yes (6 days)	-	4 hours	0.0267	22.149	Tech Staff
9	Polyacrylic acid (CTA)	Sand S25-3	Mixed	1 ml	0.3498	-	43.0143	0.81	-	-	Yes (8 days)	-	4 hrs	0.0266	5.295	Tech Staff
10	Polyacrylic acid (CTA)	Sand S25-3	Mixed	2 ml	0.6996	-	43.1304	1.62	-	-	Yes (8 days)	-	4 hrs	0.0272	11.102	Tech Staff
11	Polyacrylic acid (CTA)	Sand S25-3	Mixed	3 ml	1.0494	-	43.0091	2.44	-	-	Yes (8 days)	-	4 hrs	0.0273	16.206	Tech Staff
12	PVPA-co-AA (30.70)	Sand S25-3	Mixed	1 ml	0.3708	-	43.8144	0.85	0.1447	0.33	Yes (11 days)	-	4 hours	0.0267	4.504	Tech Staff
13	PVPA-co-AA (30.70)	Sand S25-3	Mixed	2 ml	0.7416	-	43.2350	1.72	0.2894	0.67	Yes (11 days)	-	4 hours	0.0266	12.709	Tech Staff
14	PVPA-co-AA (30.70)	Sand S25-3	Mixed	3 ml	1.1124	-	43.1233	2.58	0.4341	1.01	Yes (11 days)	-	4 hours	0.0267	18.744	Tech Staff
15	PVPA-co-AA (10.90)	Sand S25-3	Mixed	1 ml	0.3498	-	43.2380	0.81	0.0500	0.12	Yes (4 days)	-	4 hours	0.0267	4.341	Tech Staff
16	PVPA-co-AA (10.90)	Sand S25-3	Mixed	2 ml	0.6996	-	43.8522	1.60	0.0999	0.23	Yes (4 days)	-	4 hours	0.0268	11.607	Tech Staff
17	PVPA-co-AA (10.90)	Sand S25-3	Mixed	3 ml	1.0494	-	43.5743	2.41	0.1499	0.34	Yes (4 days)	-	4 hours	0.0267	15.622	Tech Staff
18	PVPA-co-AA (CTA) (10.90)	Sand S25-3	Mixed	1 ml	0.3498	-	43.0675	0.81	0.0500	0.12	Yes (6 days)	-	4 hours	0.0267	6.709	Tech Staff
19	PVPA-co-AA (CTA) (10.90)	Sand S25-3	Mixed	2 ml	0.6996	-	43.2955	1.62	0.0999	0.23	Yes (6 days)	-	4 hours	0.0267	18.702	Tech Staff
20	PVPA-co-AA (CTA) (10.90)	Sand S25-3	Mixed	3 ml	1.0494	-	43.0563	2.44	0.1499	0.35	Yes (6 days)	-	4 hours	0.0268	19.503	Tech Staff

Sample Number	Polymer	Metal Oxide	Pour over/ Mixed	Polymer Amount	Polymer Weight (grams)*	Water Amount	Metal Oxide Amount (grams)	Polymer*/Sand (%)	VPA weight (grams)*	VPA*/Sand (%)	Overnight dry	Vacuum Oven	Oven (150°C)	Diameter (m)	Max stress (MPa)	Tested by:
21	PVPA-co-AA (CTA) (30.70)	Sand S25-3	Mixed	1 ml	0.3708	0	43.2834	0.86	0.1447	0.33	Yes (6 days)	-	4 hours	0.0267	3.312	Tech Staff
22	PVPA-co-AA (CTA) (30.70)	Sand S25-3	Mixed	0.3708 g	0.3708	1.5 ml	43.2867	0.86	0.1440	0.33	Yes (6 days)	-	4 hours	0.0267	4.731	Tech Staff
23	PVPA-co-AA (CTA) (2.98)	Sand S25-3	Mixed	3 ml	1.0233	-	42.3787	2.41	0.0306	0.07	Yes (5 days)	-	4 hours	0.0266	18.527	Boris
24	PVPA-co-AA (CTA) (2.98)	Sand S25-3	Mixed	3 ml	1.0233	3 ml	43.1579	2.37	0.0306	0.07	Yes (5 days)	-	4 hours	0.0267	20.493	Boris
25	PVPA-co-AA (CTA) (2.98)	Sand S25-3	Mixed	1.5 ml	0.5117	1.5 ml	42.3051	1.21	0.0153	0.04	Yes (5 days)	-	4 hours	0.0267	11.853	Boris
26	PVPA-co-AA (CTA) (1.99)	Sand S25-3	Mixed	3 ml	1.0200	-	42.7251	2.39	0.0152	0.04	Yes (5 days)	-	4 hours	0.0267	19.227	Boris
27	PVPA-co-AA (CTA) (1.99)	Sand S25-3	Mixed	3 ml	1.0200	3 ml	42.2849	2.41	0.0152	0.04	Yes (5 days)	-	4 hours	0.0266	22.182	Boris
28	PVPA-co-AA (CTA) (1.99)	Sand S25-3	Mixed	1.5 ml	0.5100	1.5 ml	42.4175	1.2	0.0076	0.02	Yes (5 days)	-	4 hours	0.0269	11.868	Boris
29	Mw ~ 450,000 PAA powder	Sand S25-3	Polymer powder was mixed with sand. Water was then added and mixed together	-	1.0487	3 ml	43.2791	2.42	-	-	Yes (13 days)	-	4 hours	0.0266	11.494	Boris
30	Mw ~ 1,000,000 PAA powder	Sand S25-3		-	1.0455	3 ml	42.7338	2.45	-	-	Yes (13 days)	-	4 hours	0.0265	9.003	Boris
31	Mw ~ 4,000,000 PAA powder	Sand S25-3		-	1.0402	3 ml	43.2196	2.41	-	-	Yes (13 days)	-	4 hours	0.0265	7.151	Boris
32	Mw ~ 450,000 PAA powder	Sand S25-3	Polymer dissolved in water then mixed with sand	-	1.0458	3 ml	43.1281	2.42	-	-	Yes (14 days)	-	4 hours	0.0265	12.613	Boris
33	Mw ~ 1,000,000 PAA powder	Sand S25-3		-	1.0450	3 ml	43.1486	2.42	-	-	Yes (14 days)	-	4 hours	0.0266	1.289	Boris
34	Mw ~ 4,000,000 PAA powder	Sand S25-3		-	1.0460	3 ml	43.1975	2.42	-	-	Yes (14 days)	-	4 hours	0.0267	1.615	Boris
35	PVPA-co-AA (CTA) (5.95)	Sand S25-3	Mixed	1	0.3444	0	43.3732	0.79	0.0252	0.06	Yes (37 days)	-	4 hours	0.0267	5.684	Boris
36	PVPA-co-AA (CTA) (5.95)	Sand S25-3	Mixed	2	0.6888	0	43.4664	1.58	0.0504	0.12	Yes (37 days)	-	4 hours	0.0266	11.276	Boris
37	PVPA-co-AA (CTA) (5.95)	Sand S25-3	Mixed	3	1.0332	0	43.3725	2.38	0.0756	0.17	Yes (37 days)	-	4 hours	0.0267	22.511	Boris
38	PVPA-co-AA (CTA) (10.90)	Sand S25-3	Mixed	3	1.0494	0	43.2376	2.43	0.1499	0.35	Yes (8 days)	-	4 hours	0.0266	22.793	Tech Staff

Sample Number	Polymer	Metal Oxide	Pour over/ Mixed	Polymer Amount	Polymer Weight (grams)*	Water Amount	Metal Oxide Amount (grams)	Polymer*/Sand (%)	VPA weight (grams)*	VPA*/Sand (%)	Overnight dry	Vacuum Oven	Oven (150°C)	Diameter (m)	Max stress (MPa)	Tested by:
39	Poly Acrylic acid (CTA) (OHS)	Sand S25-3	Mixed	1	0.3486	0	43.0948	0.81	0	0	Yes (7 days)	-	4 hours	0.0266	5.614	Boris
40	Poly Acrylic acid (CTA) (OHS)	Sand S25-3	Mixed	2	0.6972	0	43.0941	1.62	0	0	Yes (7 days)	-	4 hours	0.0265	11.299	Boris
41	Poly Acrylic acid (CTA) (OHS)	Sand S25-3	Mixed	3	1.0458	0	42.9379	2.44	0	0	Yes (7 days)	-	4 hours	0.0267	20.083	Boris
42	Poly Acrylic acid (CTA) (OHS)	Sand S25-3/ 5% EDTA-Na	Mixed	3	1.0458	0	43.0426	2.43	0	0	Yes (7 days)	-	4 hours	0.0266	13.611	Boris
43	PVPA-co-AA (CTA) (OHS) (30.70)	Sand S25-3	Mixed	1	0.3708	0	43.0479	0.86	0.1451	0.34	Yes (7 days)	-	4 hours	0.0265	7.013	Boris
44	PVPA-co-AA (CTA) (OHS) (30.70)	Sand S25-3	Mixed	2	0.7416	0	43.1198	1.72	0.2902	0.67	Yes (7 days)	-	4 hours	0.0267	11.239	Boris
45	PVPA-co-AA (CTA) (OHS) (30.70)	Sand S25-3	Mixed	3	1.1124	0	43.316	2.57	0.4353	1	Yes (7 days)	-	4 hours	0.0268	22.738	Boris
46	PVPA-co-AA (CTA) (OHS) (30.70)	Sand S25-3/ 5% EDTA-Na	Mixed	3	1.1124	0	43.0086	2.59	0.4353	1.01	Yes (7 days)	-	4 hours	0.0267	13.065	Boris
47	PVPA-co-AA (CTA) (OHS) (10.90)	Sand S25-3	Mixed	1	0.3498	0	43.1772	0.81	0.05	0.12	Yes (7 days)	-	4 hours	0.0268	3.095	Boris
48	PVPA-co-AA (CTA) (OHS) (10.90)	Sand S25-3	Mixed	2	0.6996	0	43.0418	1.63	0.0999	0.23	Yes (7 days)	-	4 hours	0.0268	15.544	Boris
49	PVPA-co-AA (CTA) (OHS) (10.90)	Sand S25-3	Mixed	3	1.0494	0	43.0711	2.44	0.1499	0.35	Yes (7 days)	-	4 hours	0.0266	23.556	Boris
50	PVPA-co-AA (CTA) (OHS) (10.90)	Sand S25-3/ 5% EDTA-Na	Mixed	3	1.0494	0	43.1311	2.43	0.1499	0.35	Yes (7 days)	-	4 hours	0.0268	15.590	Boris
51	PVPA-co-AA (CTA) (OHS) (10.90)	Sand S25-3	Mixed	4	1.3992	0	43.2212	3.24	0.1998	0.46	Yes (7 days)	-	4 hours	0.0272	29.892	Boris
52	PVPA-co-AA (CTA) (OHS) (5.95)	Sand S25-3	Mixed	1	0.3444	0	43.0067	0.8	0.0252	0.06	Yes (6 days)	-	4 hours	0.0267	6.594	Boris
53	PVPA-co-AA (CTA) (OHS) (5.95)	Sand S25-3	Mixed	2	0.6888	0	43.0717	1.6	0.0504	0.12	Yes (7 days)	-	4 hours	0.0267	7.900	Boris
54	PVPA-co-AA (CTA) (OHS) (5.95)	Sand S25-3	Mixed	3	1.0332	0	43.0589	2.4	0.0756	0.18	Yes (7 days)	-	4 hours	0.0266	10.241	Boris
55	PVPA-co-AA (CTA) (OHS) (5.95)	Sand S25-3/ 5% EDTA-Na	Mixed	3	1.0332	0	43.1294	2.4	0.0756	0.18	Yes (6 days)	-	4 hours	0.0267	12.130	Boris

Sample Number	Polymer	Metal Oxide	Pour over/ Mixed	Polymer Amount	Polymer Weight (grams)*	Water Amount	Metal Oxide Amount (grams)	Polymer*/Sand (%)	VPA weight (grams)*	VPA*/Sand (%)	Overnight dry	Vacuum Oven	Oven (150°C)	Diameter (m)	Max stress (MPa)	Tested by:
56	PVPA-co-AA (CTA) (OHS) (2.98)	Sand S25-3	Mixed	1	0.3411	0	43.2795	0.79	0.0101	0.02	Yes (7 days)	-	4 hours	0.0266	0.548	Boris
57	PVPA-co-AA (CTA) (OHS) (2.98)	Sand S25-3	Mixed	2	0.6822	0	43.2486	1.58	0.0203	0.05	Yes (7 days)	-	4 hours	0.0268	10.781	Boris
58	PVPA-co-AA (CTA) (OHS) (2.98)	Sand S25-3	Mixed	3	1.0233	0	43.1512	2.37	0.0304	0.07	Yes (7 days)	-	4 hours	0.0269	27.117	Boris
59	PVPA-co-AA (CTA) (OHS) (2.98)	Sand S25-3/ 5% EDTA-Na	Mixed	3	1.0233	0	43.1226	2.37	0.0304	0.07	Yes (7 days)	-	4 hours	0.0268	10.440	Boris
60	PVPA-co-AA (CTA) (OHS) (1.99)	Sand S25-3	Mixed	1	0.34	0	43.0236	0.79	0.0051	0.01	Yes (7 days)	-	4 hours	0.0266	2.046	Boris
61	PVPA-co-AA (CTA) (OHS) (1.99)	Sand S25-3	Mixed	2	0.68	0	43.1919	1.57	0.0101	0.02	Yes (7 days)	-	4 hours	0.0267	9.149	Boris
62	PVPA-co-AA (CTA) (OHS) (1.99)	Sand S25-3	Mixed	3	1.02	0	43.0781	2.37	0.0152	0.04	Yes (7 days)	-	4 hours	0.0266	11.215	Boris
63	PVPA-co-AA (CTA) (OHS) (1.99)	Sand S25-3/ 5% EDTA-Na	Mixed	3	1.02	0	43.1323	2.36	0.0152	0.04	Yes (7 days)	-	4 hours	0.0266	11.549	Boris
64	PVPA-co-AA (CTA) (OHS) (10.90)	Sand S25-3	Mixed	4	1.3992	0	43.3184	3.23	0.1998	0.46	Yes (7 days)	-	4 hours	0.0266	19.868	Boris
65	PVPA-co-AA (CTA) (OHS) (10.90)	Sand S25-3	Mixed	5	1.7490	0	43.0523	4.06	0.2498	0.58	Yes (7 days)	-	4 hours	0.0267	39.910	Boris
66	PVPA-co-AA (CTA) (OHS) (10.90)	Sand S25-3	Mixed	6	2.0988	0	43.5709	4.82	0.2997	0.70	Yes (7 days)	-	4 hours	0.0266	33.817	Boris
67	PVPA-co-AA (CTA) (10.90)	Sand S25-3	Mixed	3	1.0494	0	42.3098	2.48	0.1499	0.35	Yes (9 days)	-	4 hours	0.0267	23.174	Boris
68	PVPA-co-AA (CTA) (10.90) NaOH	Sand S25-3	Mixed	3	1.0494	0	42.2543	2.48	0.1499	0.35	Yes (9 days)	-	4 hours	0.0266	9.304	Boris
69	PVPA-co-AA (CTA) (10.90) KOH	Sand S25-3	Mixed	3	1.0494	0	42.5574	2.47	0.1499	0.35	Yes (9 days)	-	4 hours	0.0266	18.101	Boris
70	PVPA-co-AA (CTA) (10.90)	Sand S25-3	Mixed	3	1.0494	0	42.2275	2.49	0.1499	0.35	Yes (6 days)	-	4 hours	0.0267	16.390	Boris
71	PVPA-co-AA (CTA) (10.90)	Sand S25-3/ 10% Tartaric acid	Mixed	3	1.0494	0	42.2858	2.48	0.1499	0.35	Yes (6 days)	-	4 hours	0.0266	16.892	Boris

Sample Number	Polymer	Metal Oxide	Pour over/ Mixed	Polymer Amount	Polymer Weight (grams)*	Water Amount	Metal Oxide Amount (grams)	Polymer/Sand (%)	VPA weight (grams)*	VPA/Sand (%)	Overnight dry	Vacuum Oven	Oven (150°C)	Diameter (m)	Max stress (MPa)	Tested by:
72	PVPA-co-AA (CTA) (30.70)	~50 mesh masonry sand	Mixed	3	1.1124	0	44.3693	2.51	0.1499	0.34	Yes (40 days)	-	20.5 hours	0.0267	0.298	Boris
-	PVPA-co-AA (CTA) (5.95)	~50 mesh masonry sand	Mixed	3	1.0332	0	44.223	2.34	0.0756	0.17	Yes (40 days)	-	-	-	-	-
-	PVPA-co-AA (CTA) (5.95)	~50 mesh masonry sand	Mixed	3	1.0332	0	43.4892	2.38	0.0756	0.17	Yes (40 days)	-	-	-	-	-
73	PVPA-co-AA (CTA) (10.90)	Recycled glass 50/100 grit	Mixed	3	1.0494	0	35.7278	2.94	0.1499	0.42	Yes (39 days)	-	4 hours	0.0267	12.12	Boris
74	PVPA-co-AA (CTA) (30.70)	Recycled glass 50/100 grit	Mixed	3	1.1124	0	35.2562	3.16	0.434	1.23	Yes (39 days)	-	4 hours	0.0266	9.202	Boris
-	PVPA-co-AA (CTA) (10.90)	Canoe Cove PEI	Mixed	2	0.6996	0	44.612	1.57	0.0999	0.22	Yes (18 days)	-	-	-	-	-
75	PVPA-co-AA (CTA) (10.90)	Greenwich PEI (Beach)	Mixed	3	1.0494	0	43.4904	2.41	0.1499	0.34	Yes (18 days)	-	20.5 hours	0.0267	24.371	Boris

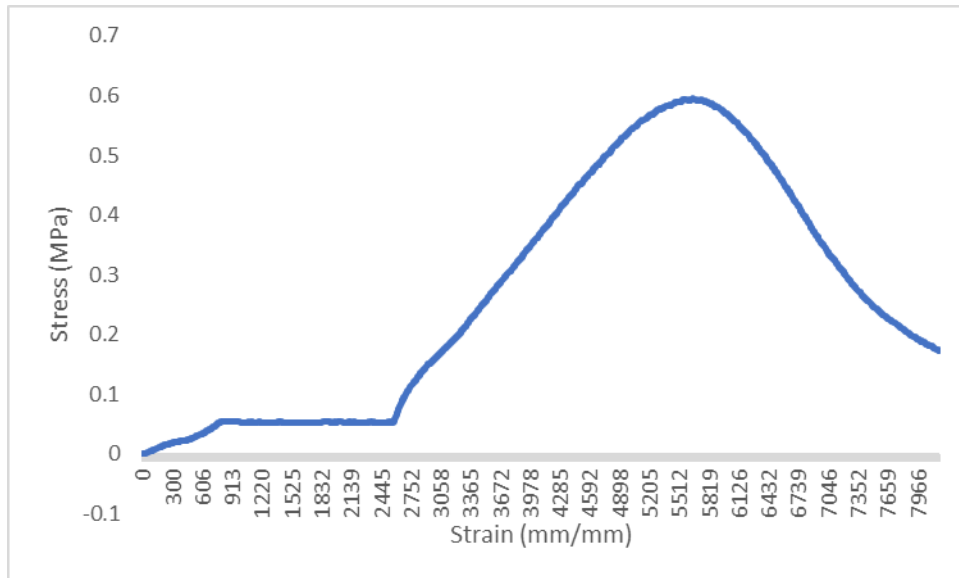
*Note: These values were calculated assuming complete polymerization

*Note: **Sample 20** was too strong and exceeded the capacity of the frame it was being assessed with, the sample is likely stronger

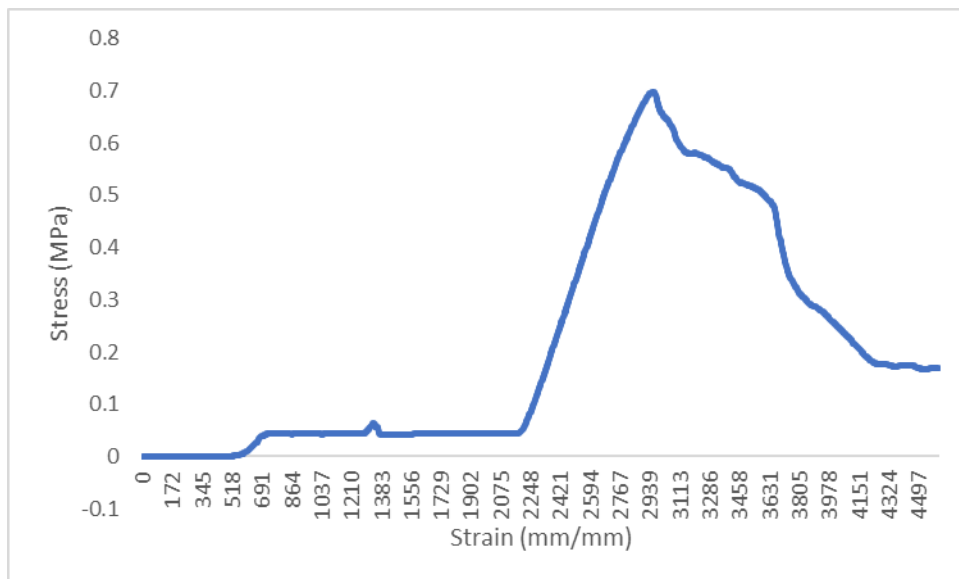
*Note: **Sample 65** the mechanical testing system stopped mid-run; this sample may be stronger

6 Stress-strain curves

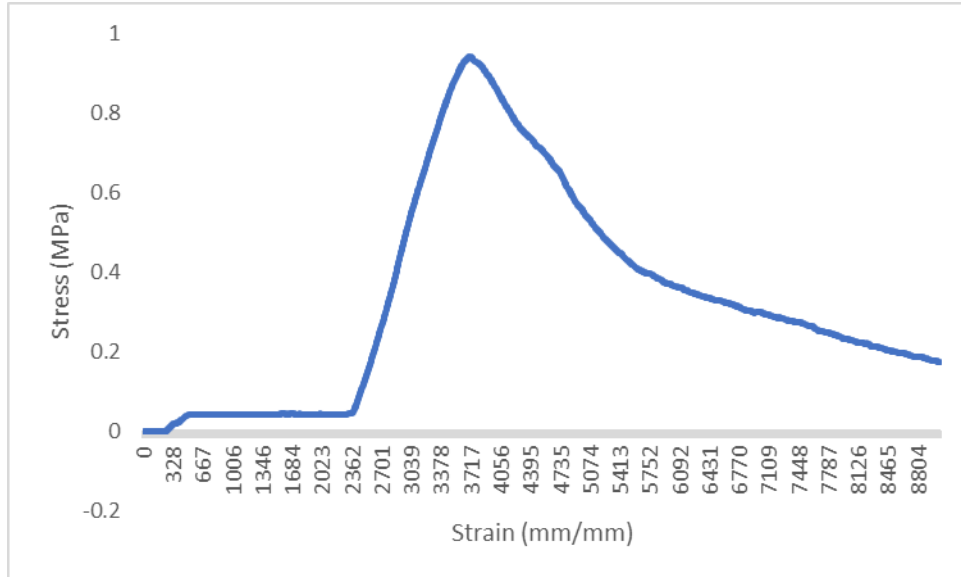
Sample 1



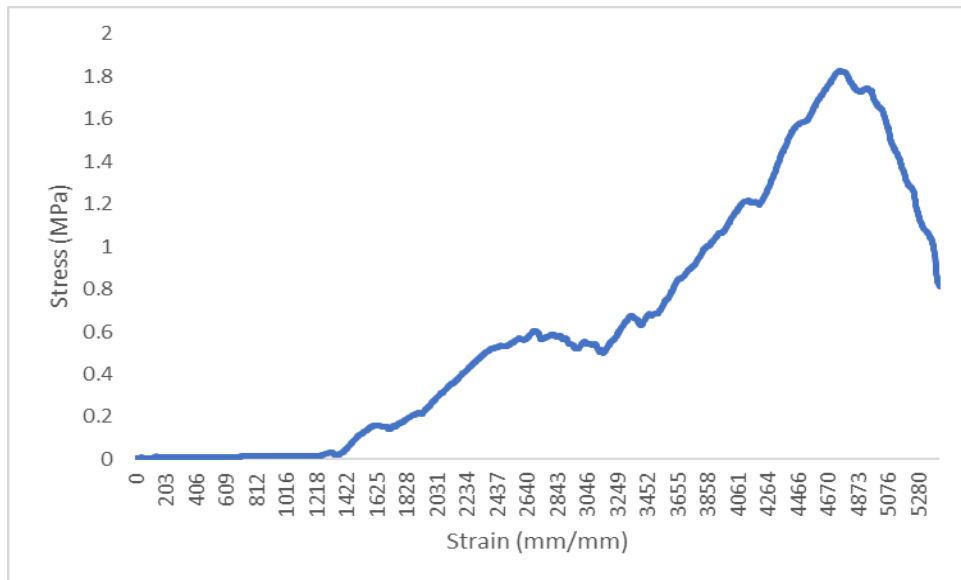
Sample 2



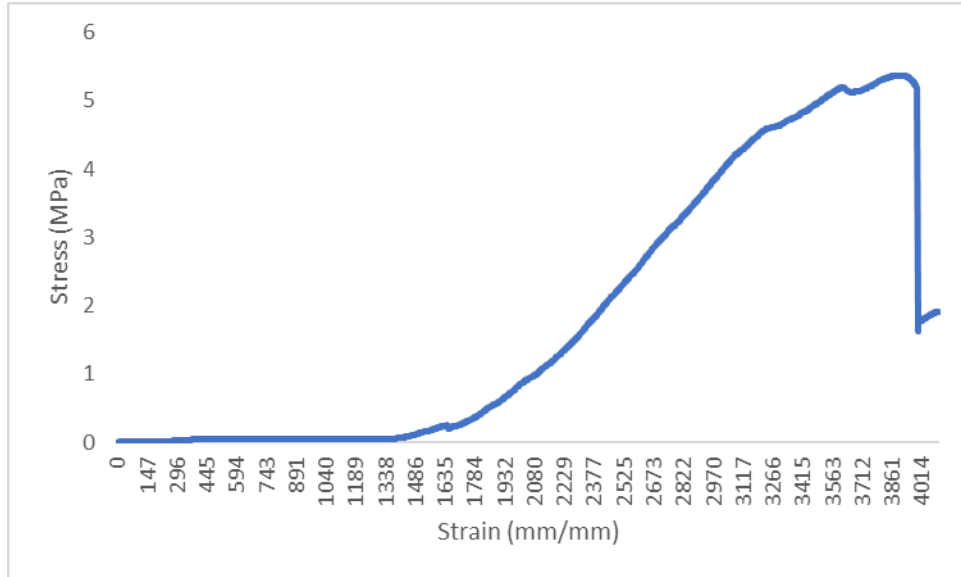
Sample 3



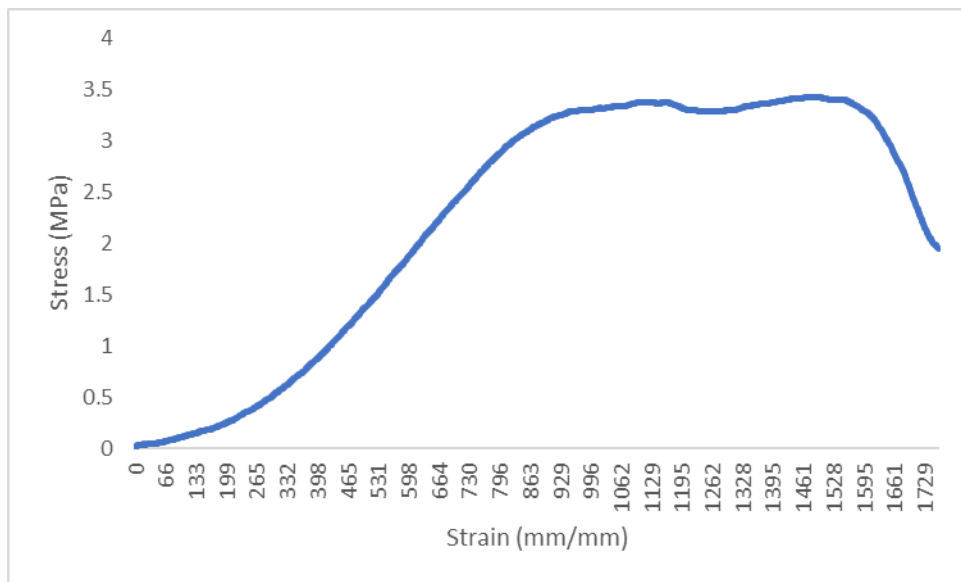
Sample 4



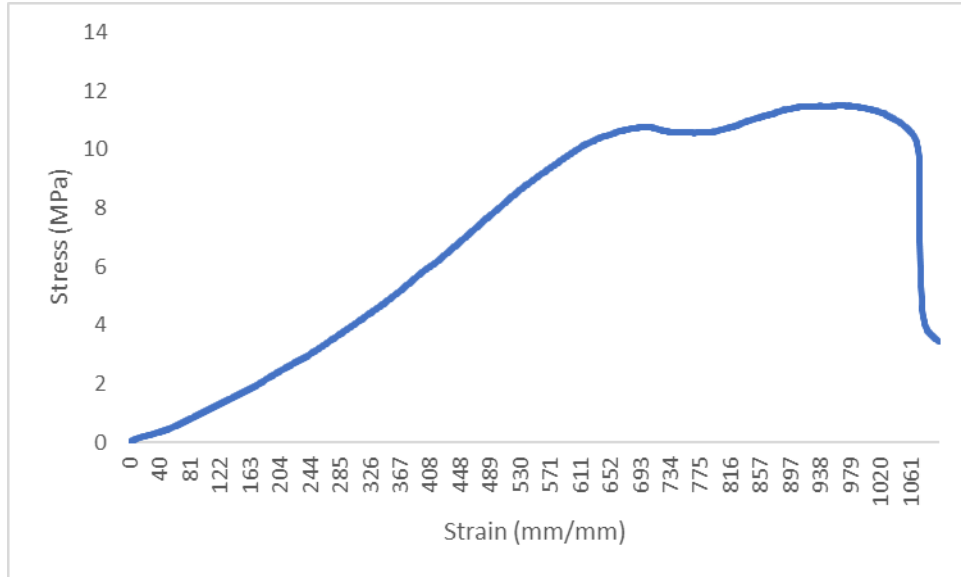
Sample 5



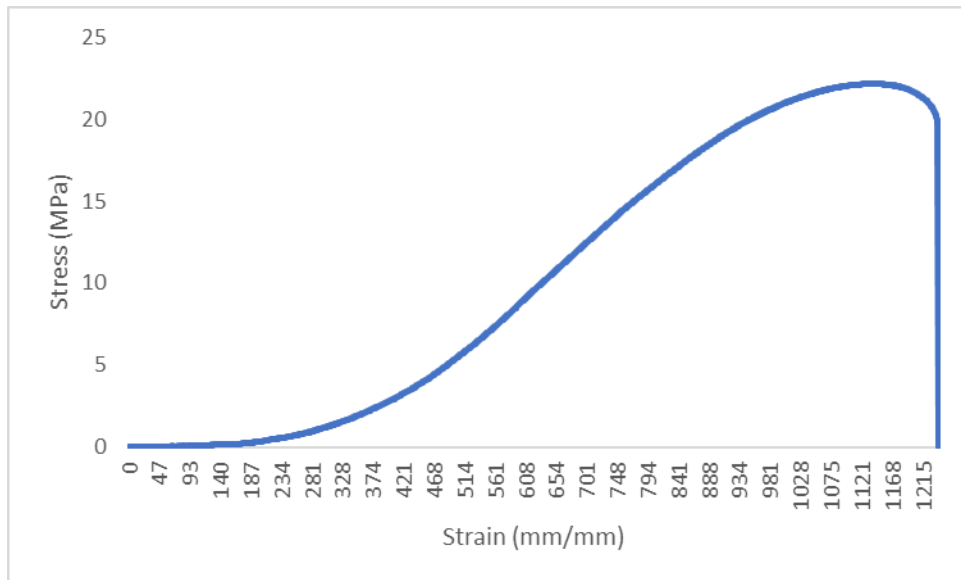
Sample 6



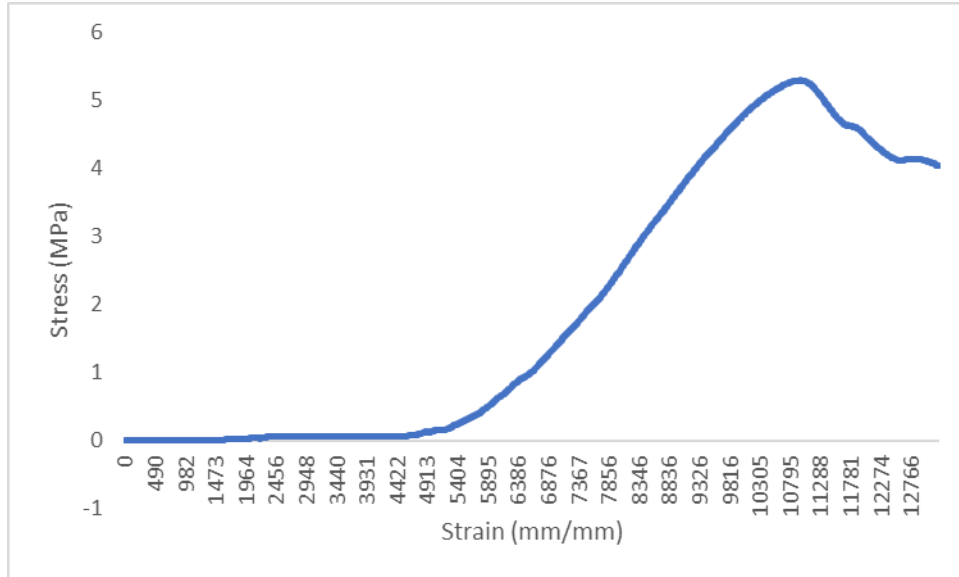
Sample 7



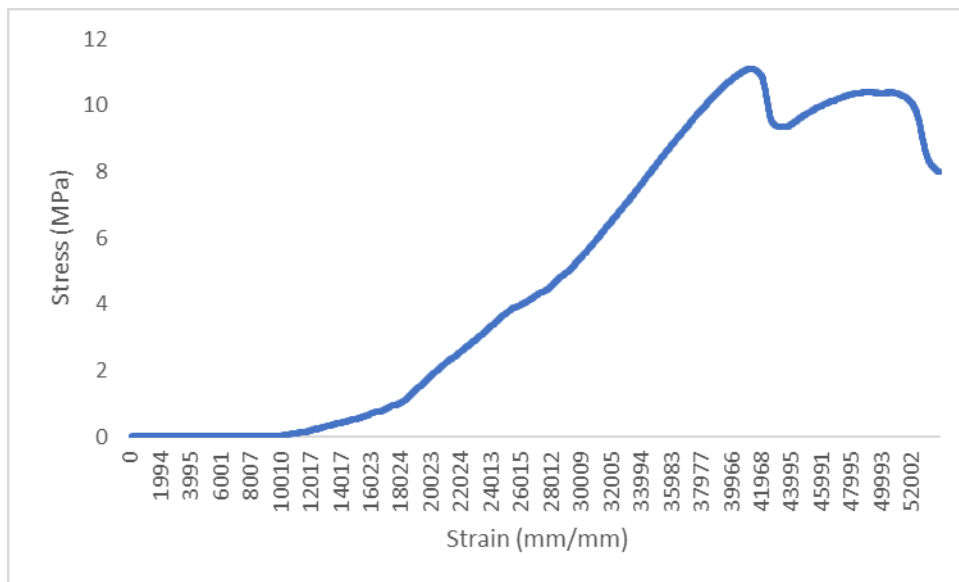
Sample 8



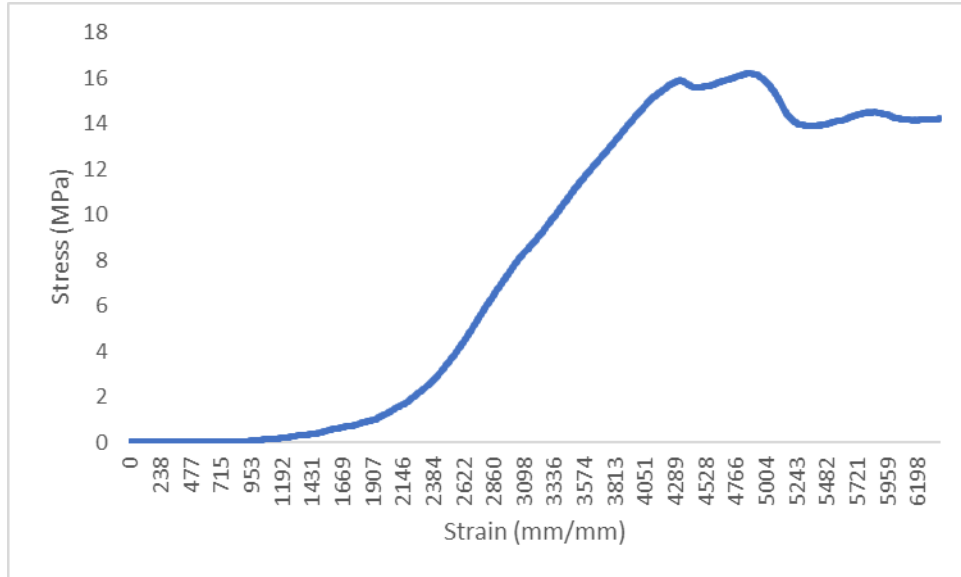
Sample 9



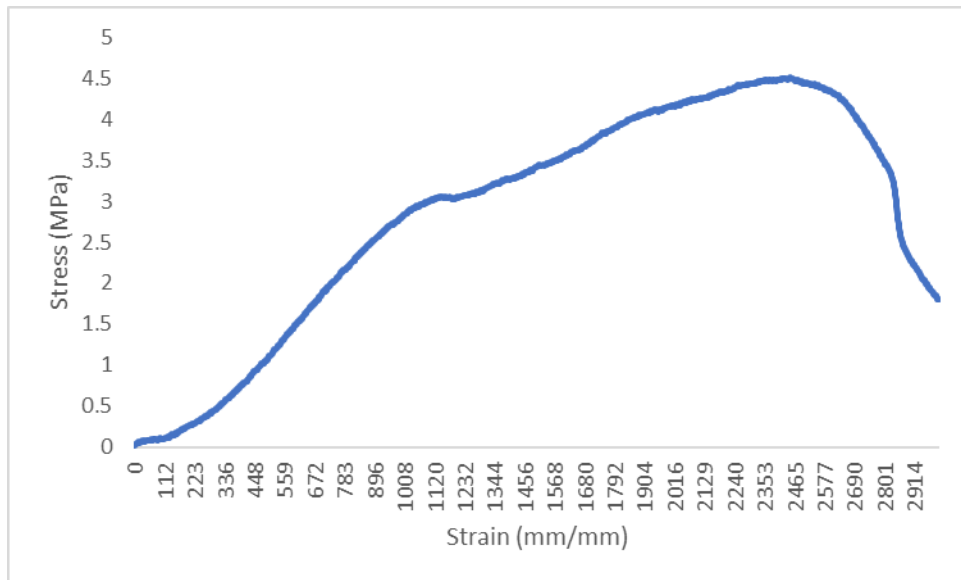
Sample 10



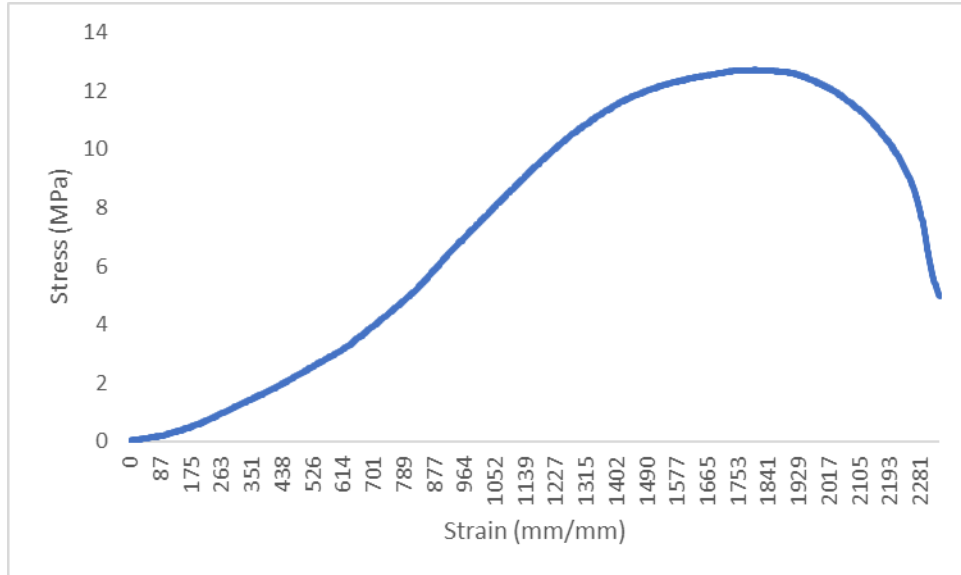
Sample 11



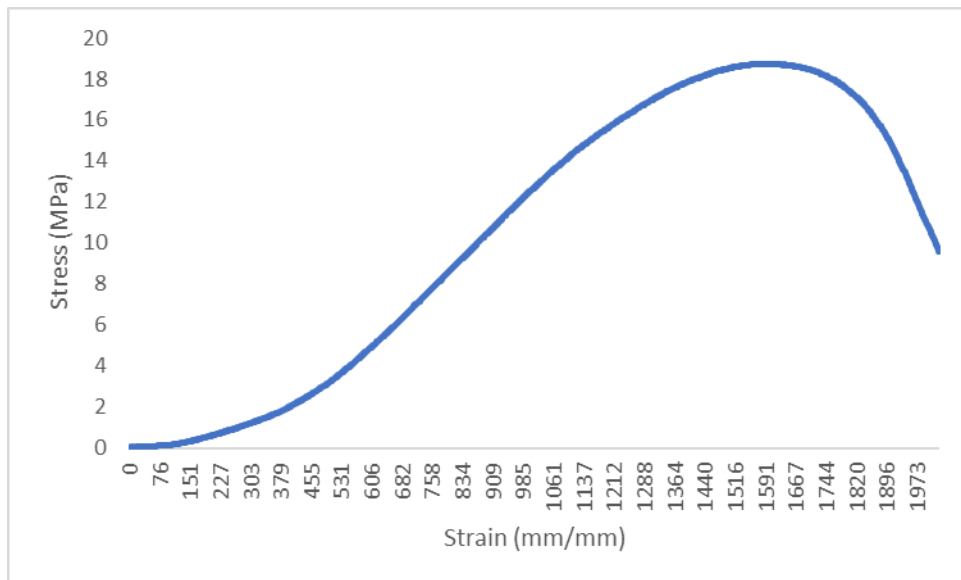
Sample 12



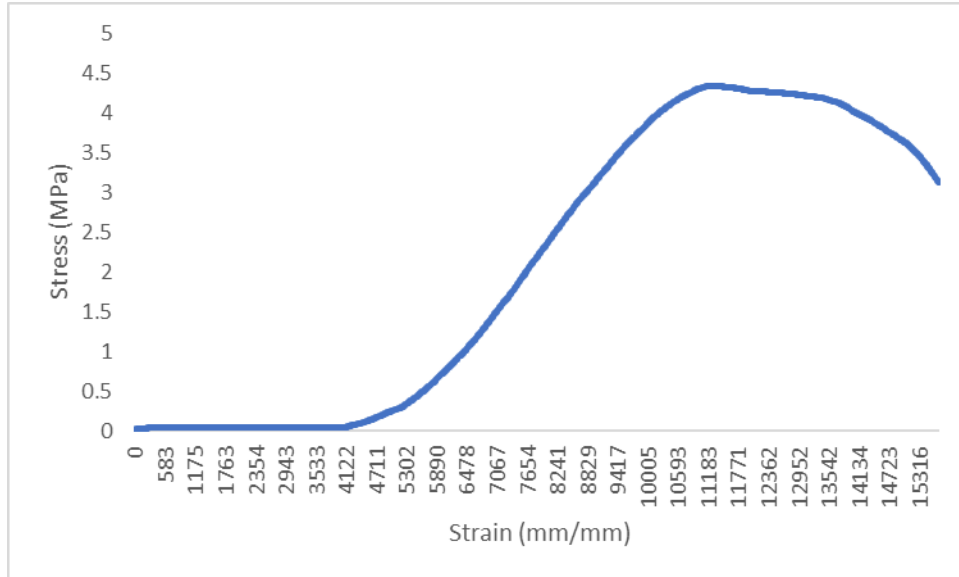
Sample 13



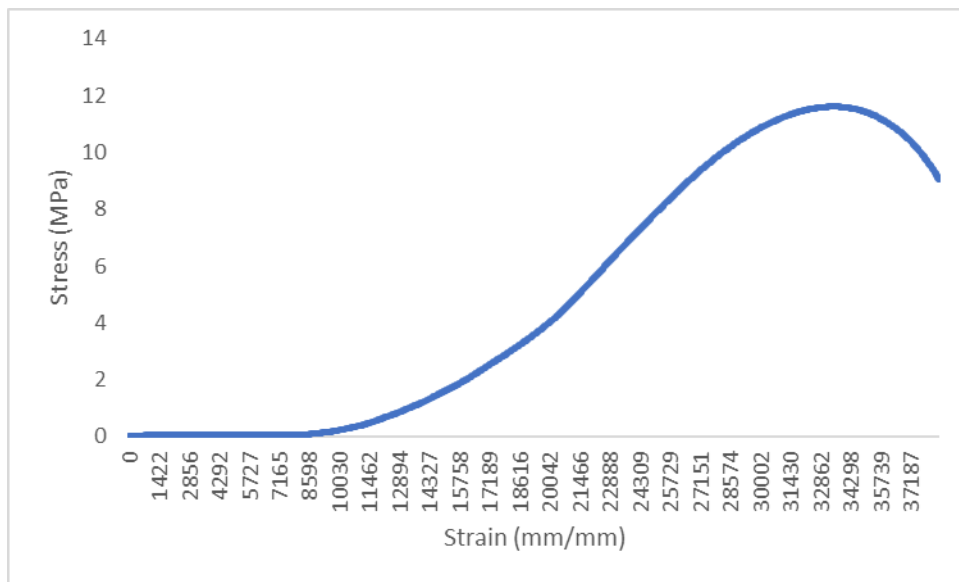
Sample 14



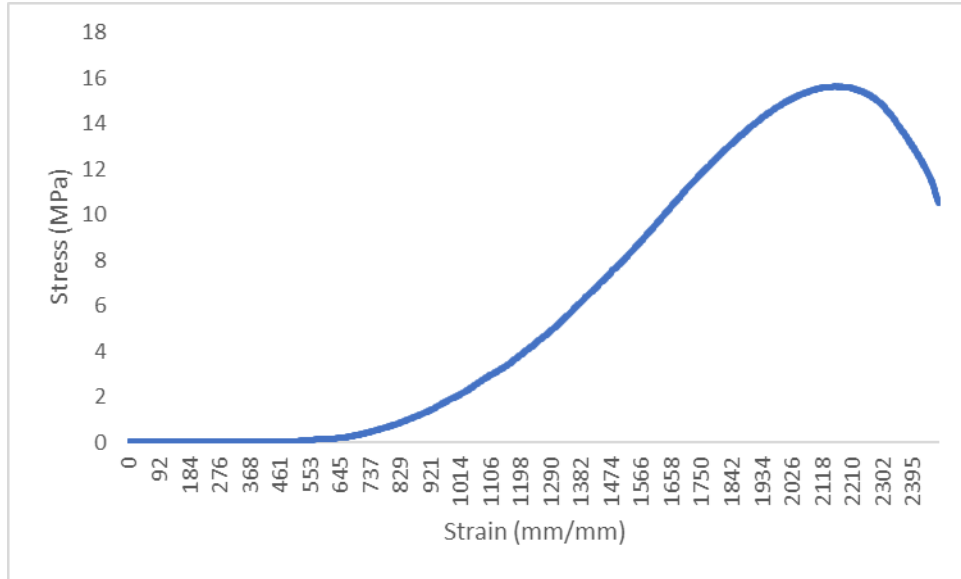
Sample 15



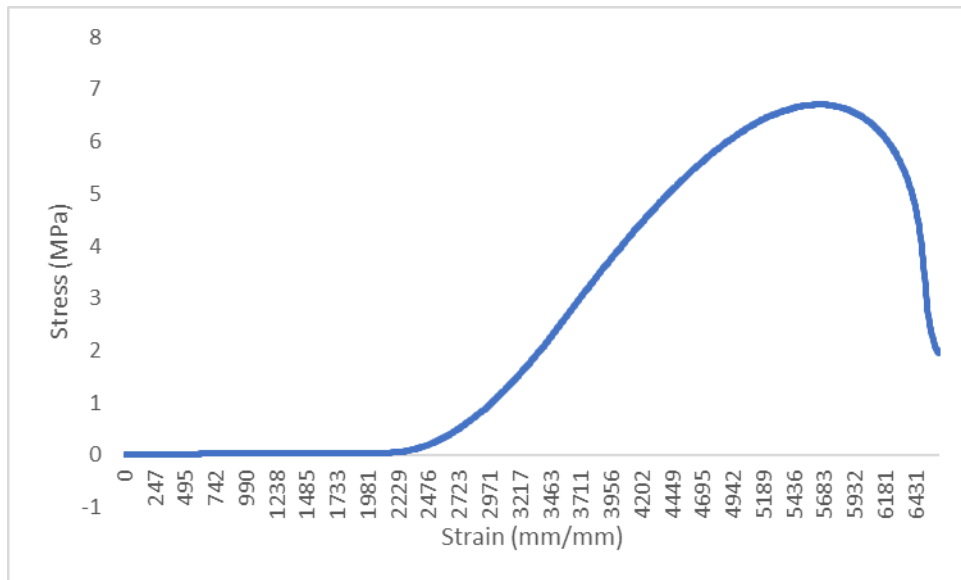
Sample 16



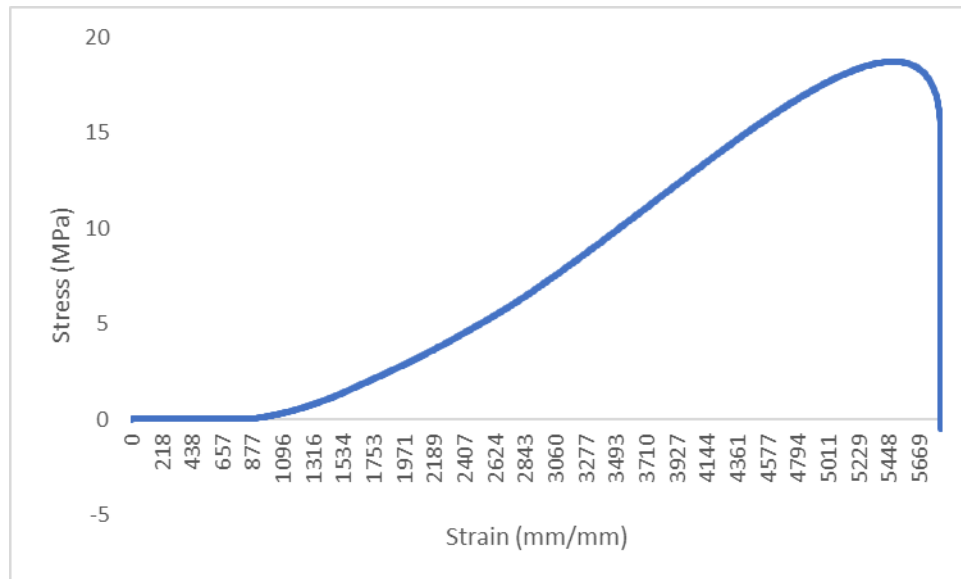
Sample 17



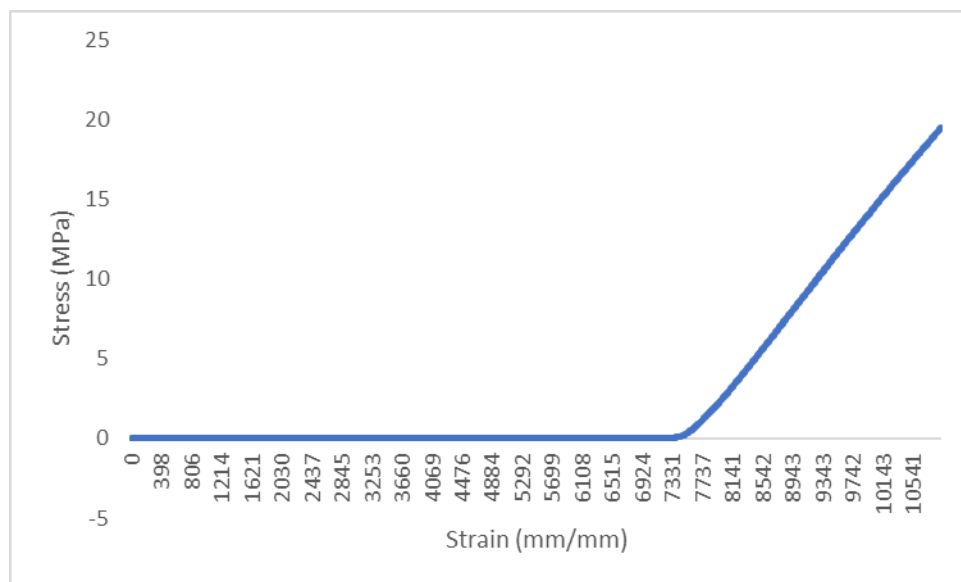
Sample 18



Sample 19

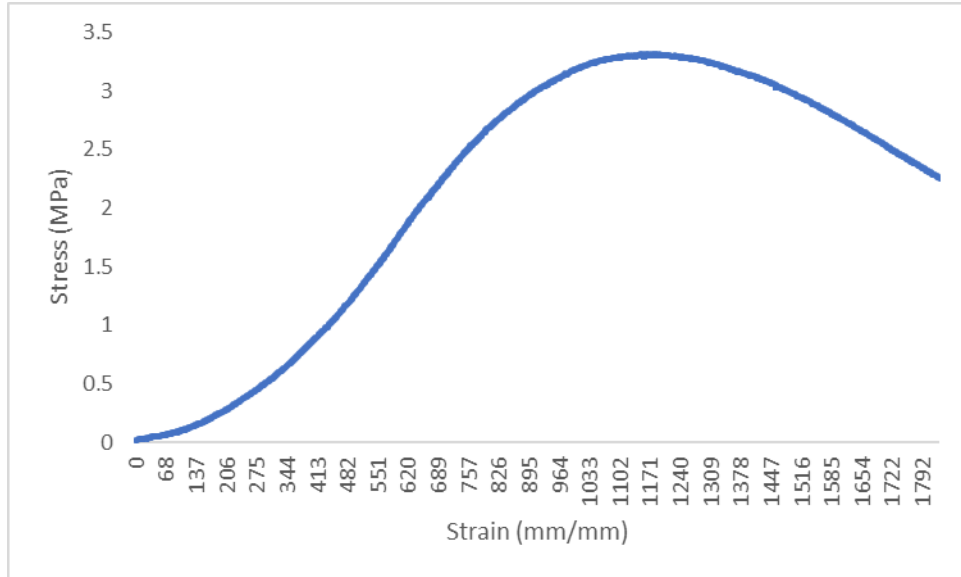


Sample 20*

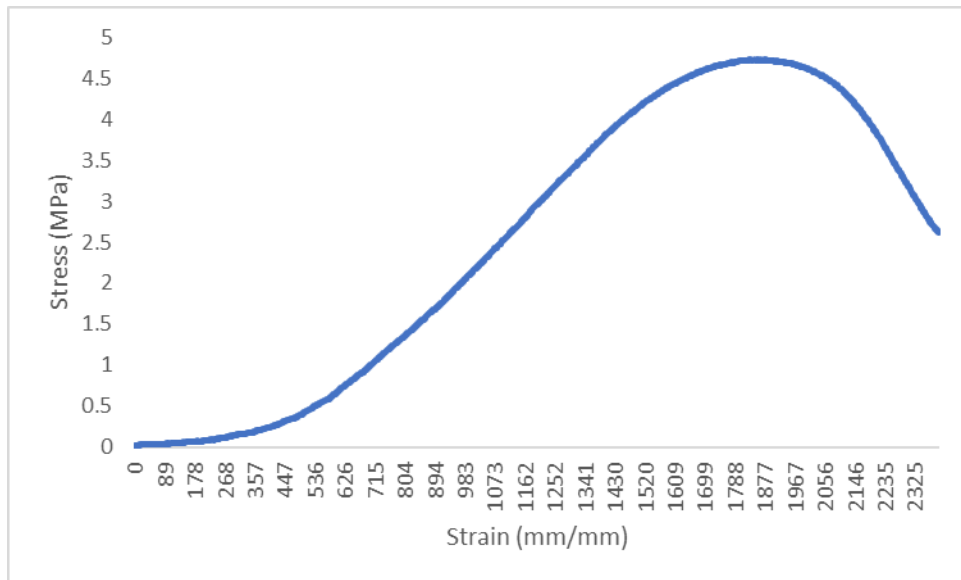


*Note: This sample was too strong and exceeded the capacity of the frame it was being assessed with, the sample is likely stronger

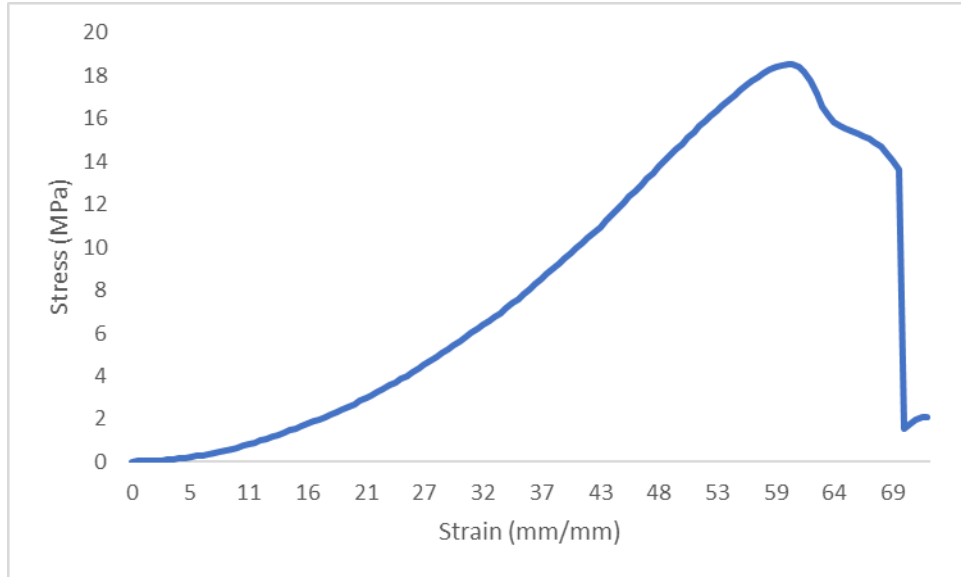
Sample 21



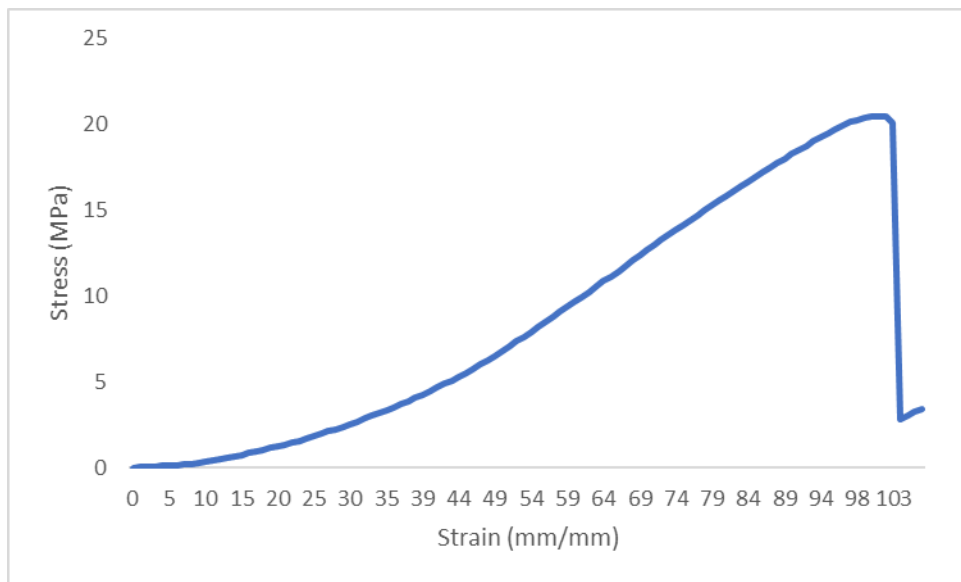
Sample 22



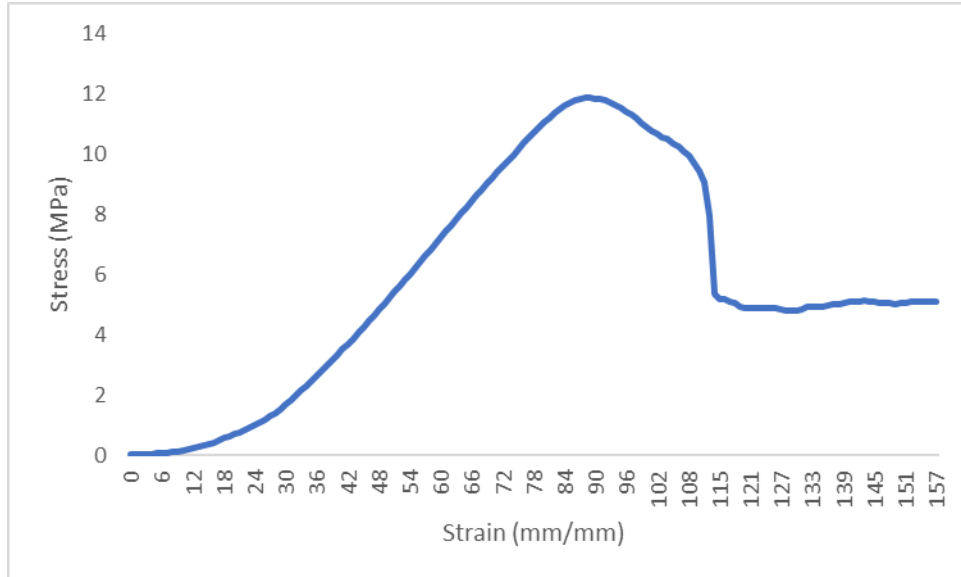
Sample 23



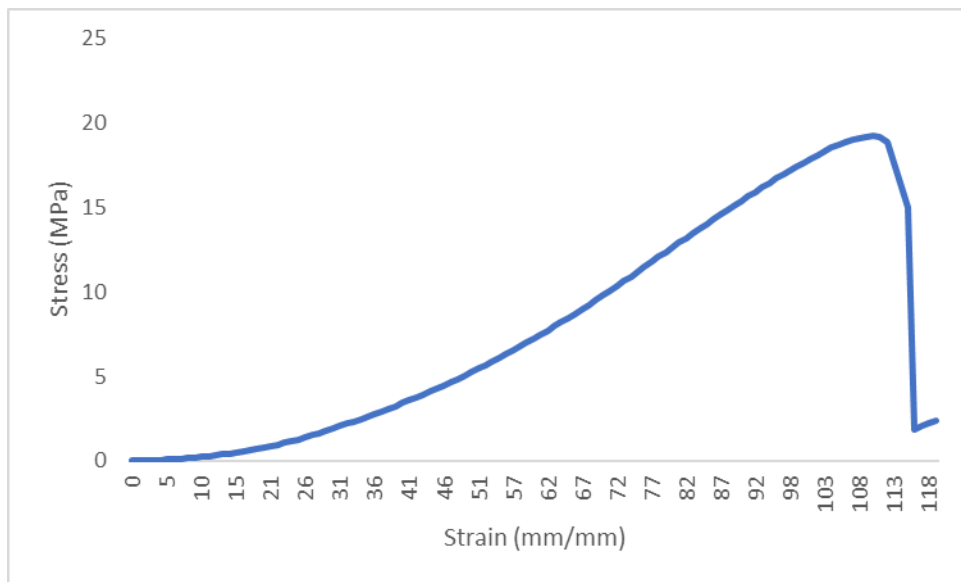
Sample 24



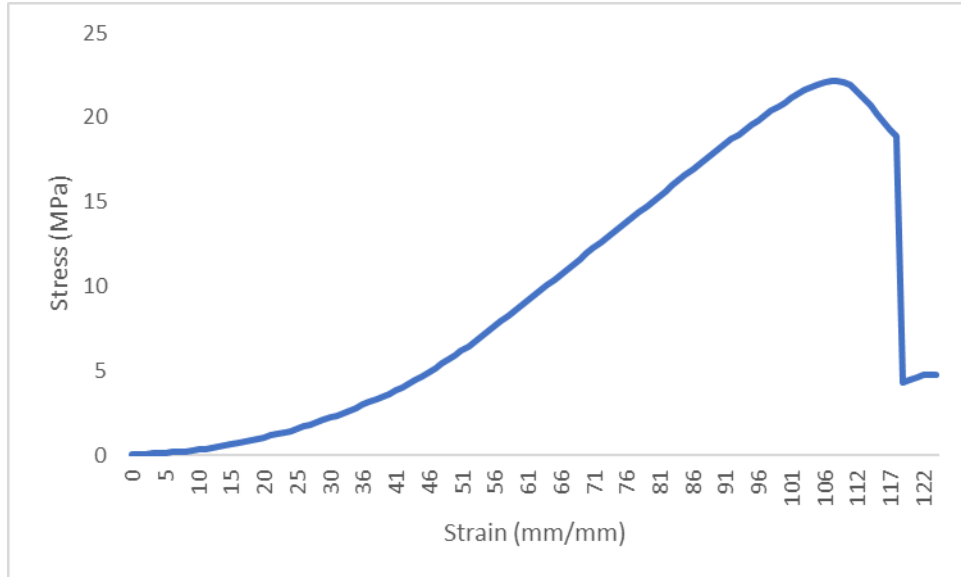
Sample 25



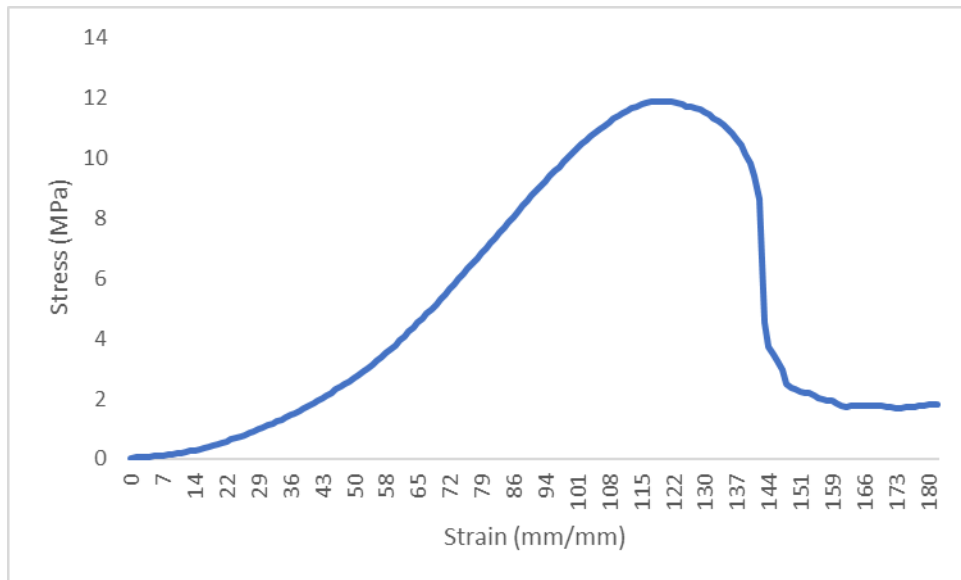
Sample 26



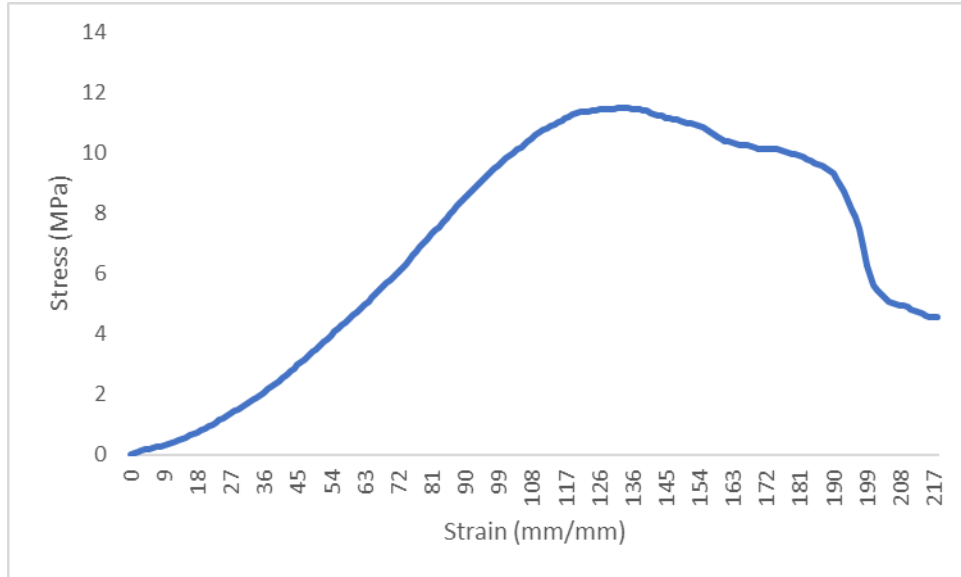
Sample 27



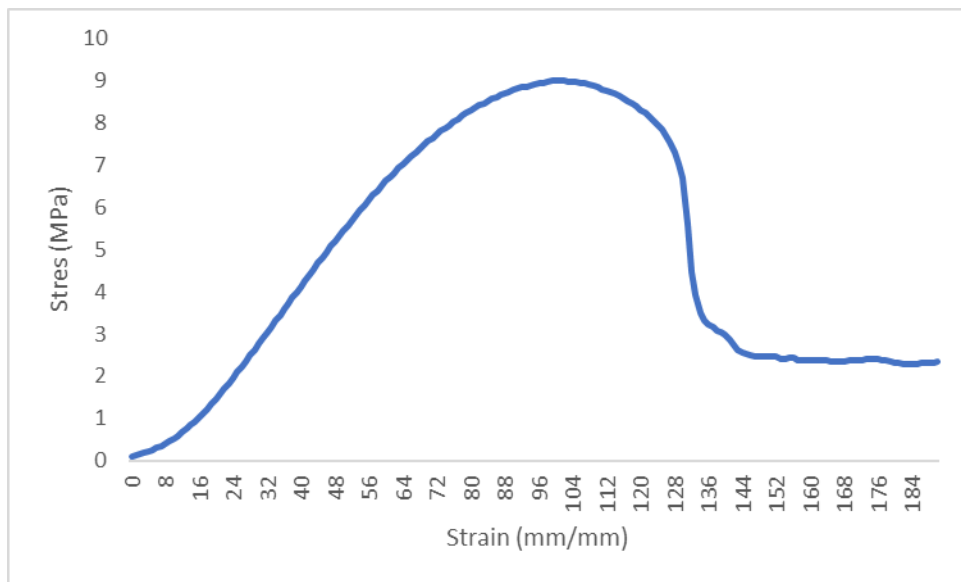
Sample 28



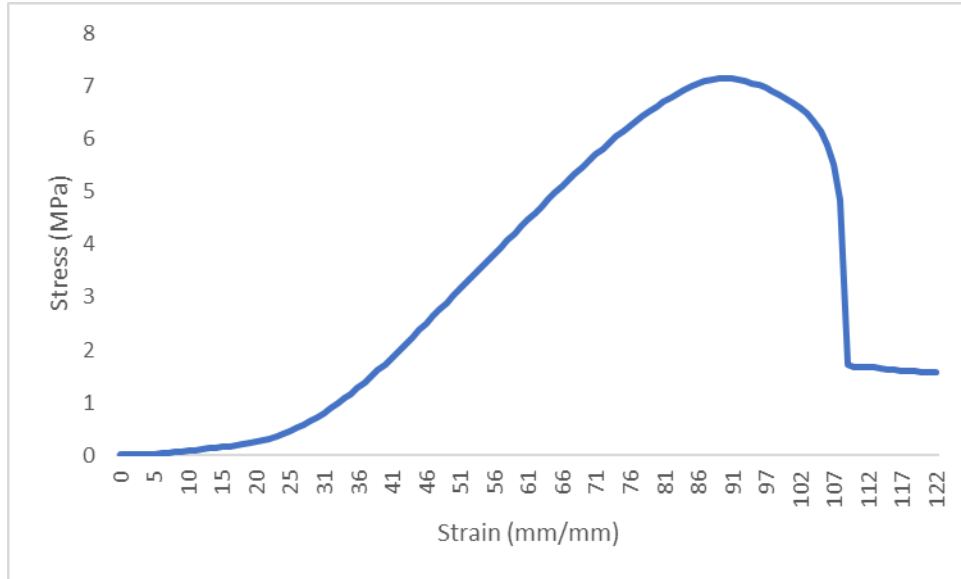
Sample 29



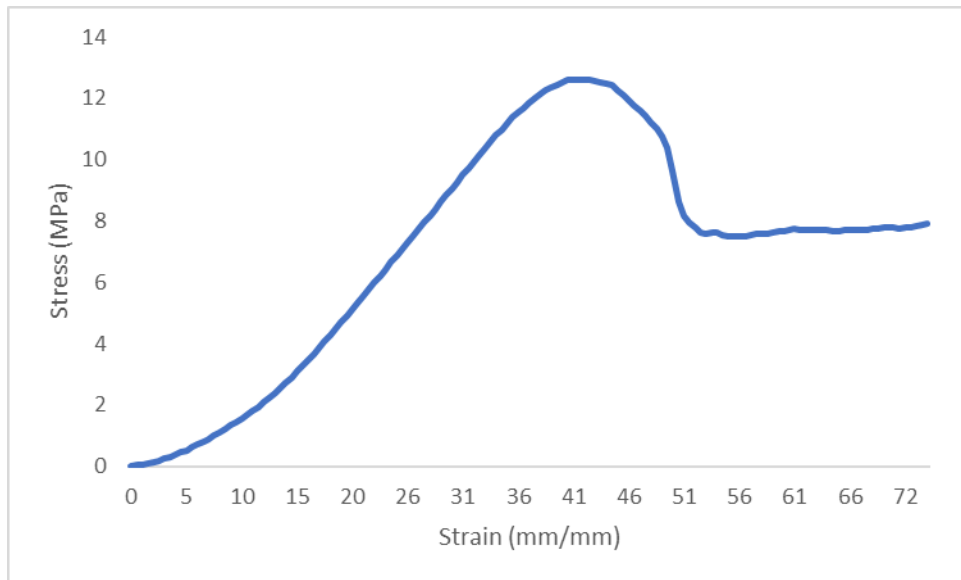
Sample 30



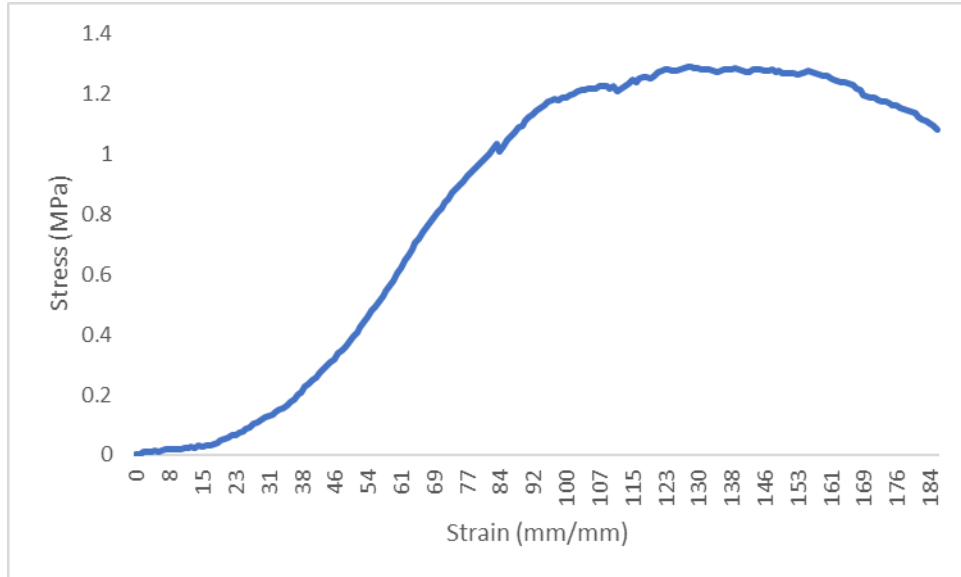
Sample 31



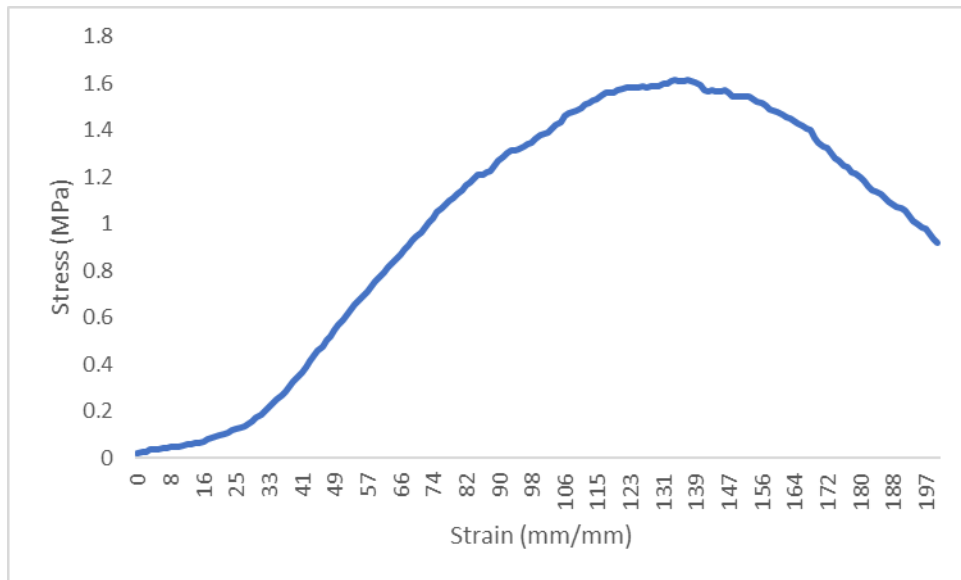
Sample 32



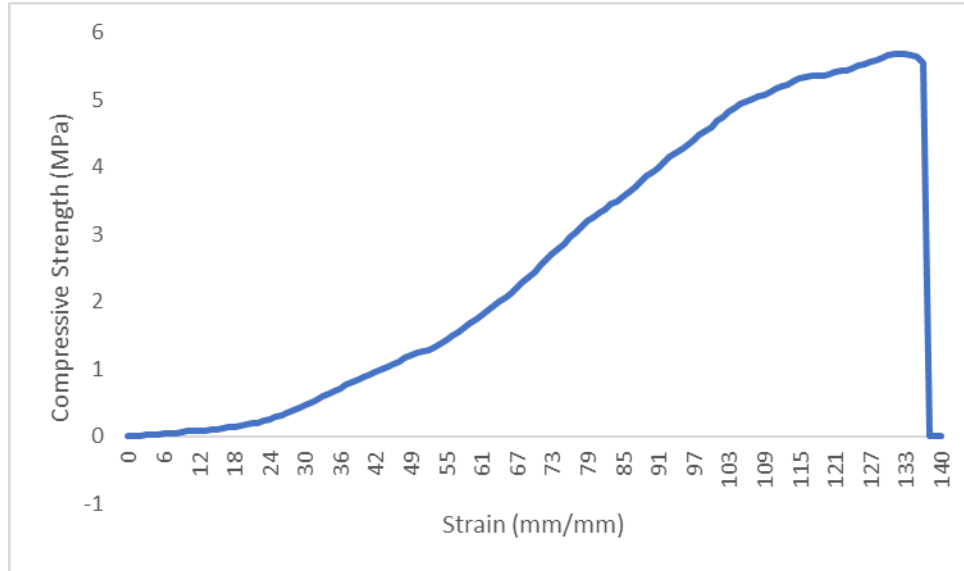
Sample 33



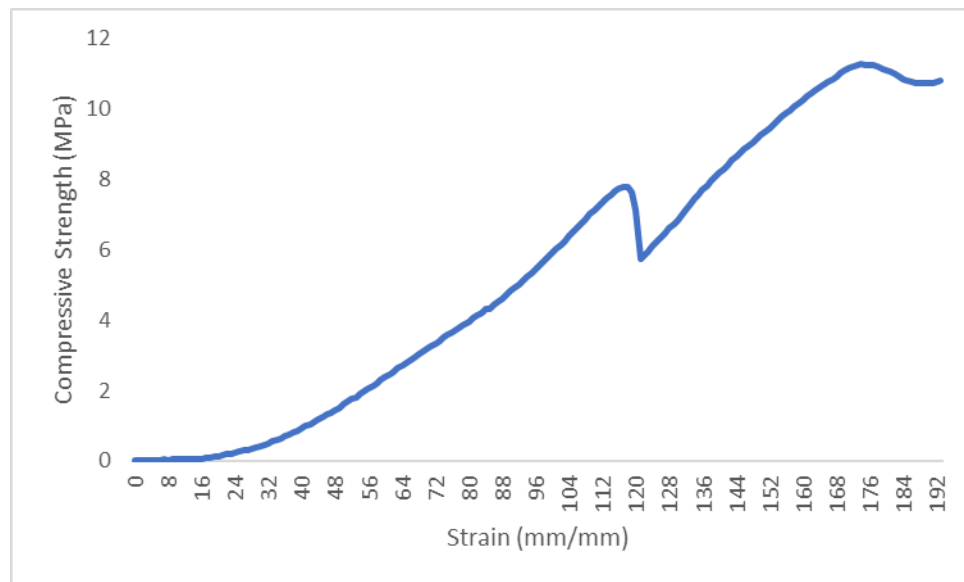
Sample 34



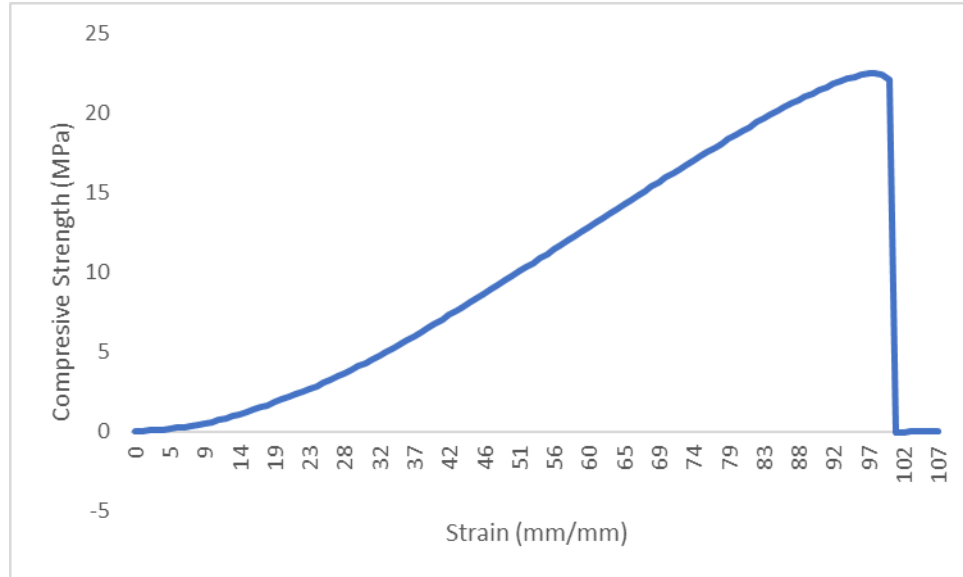
Sample 35



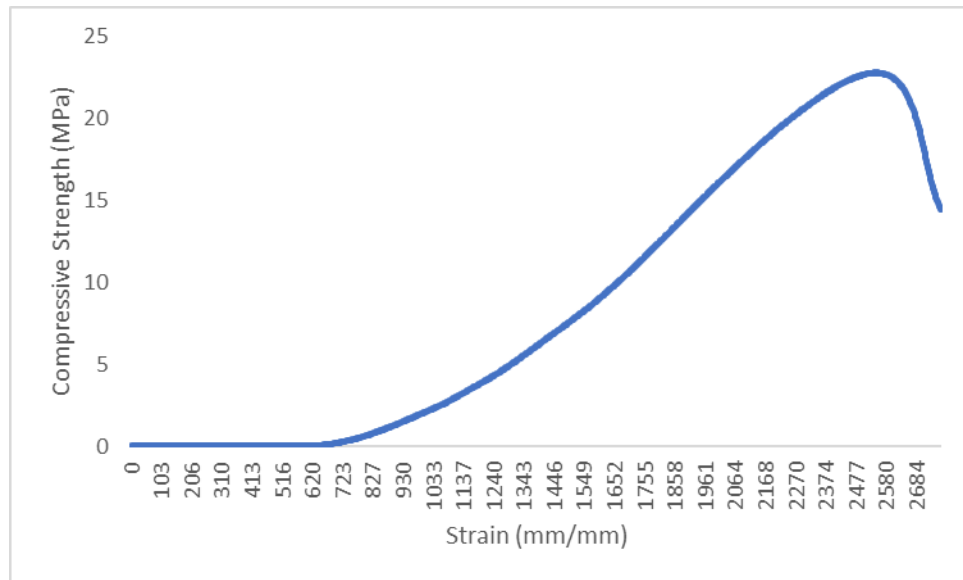
Sample 36



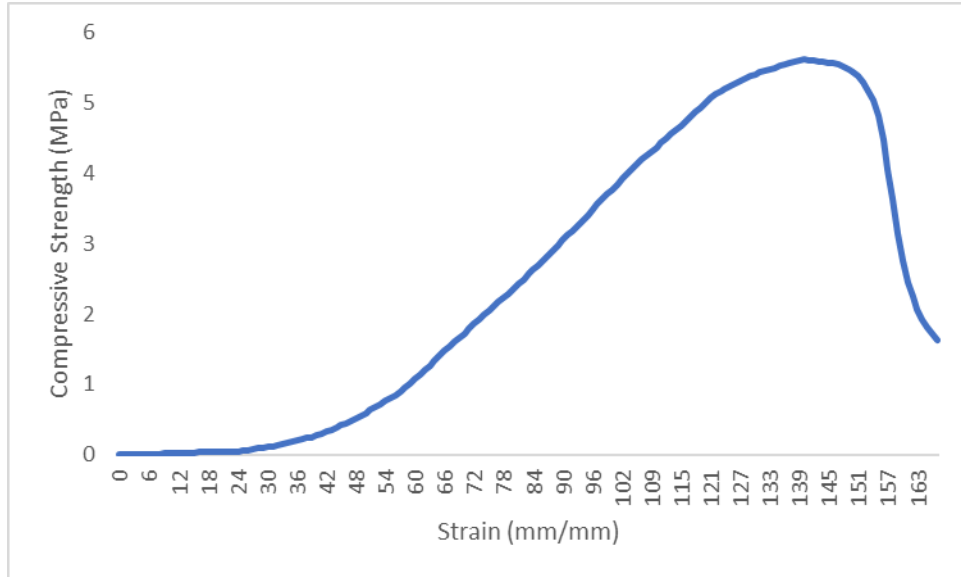
Sample 37



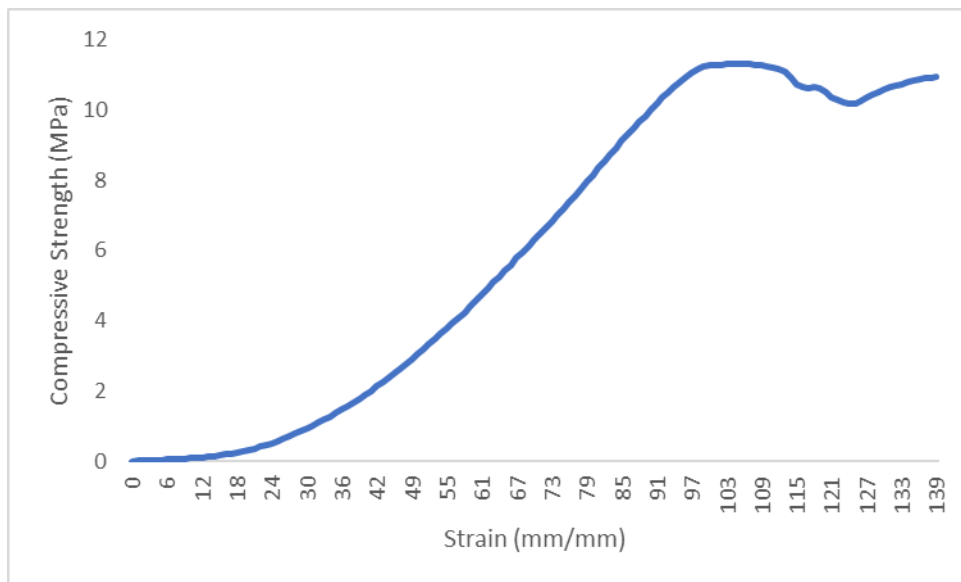
Sample 38



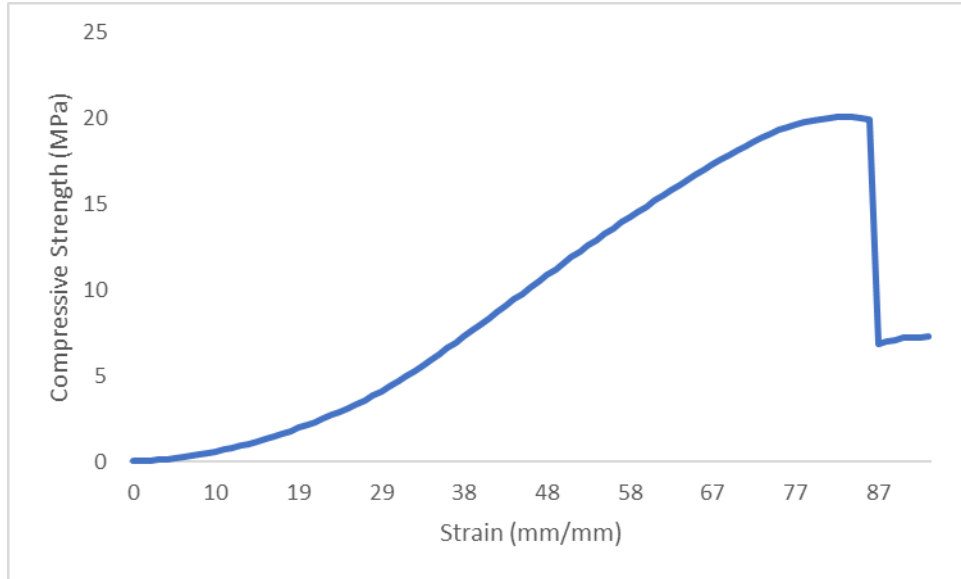
Sample 39



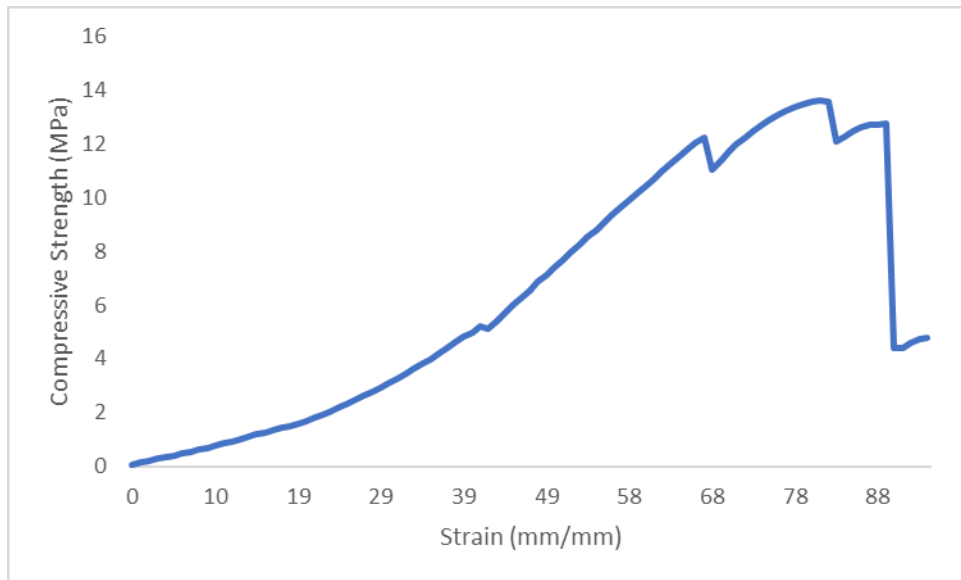
Sample 40



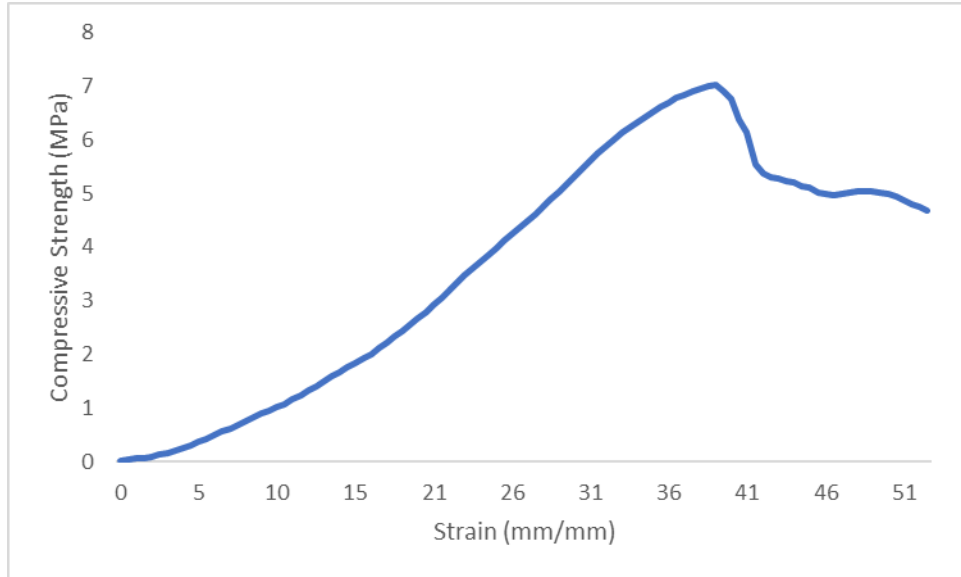
Sample 41



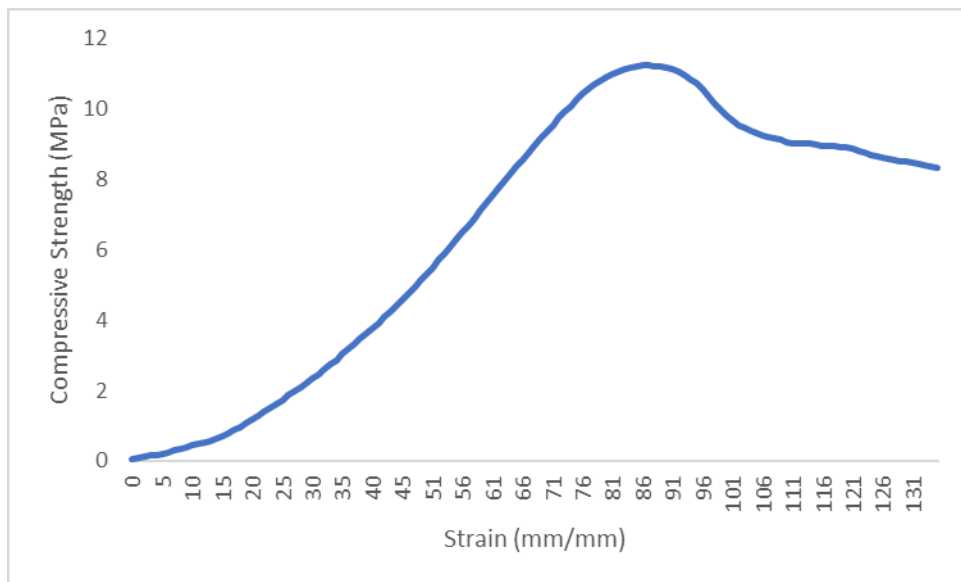
Sample 42



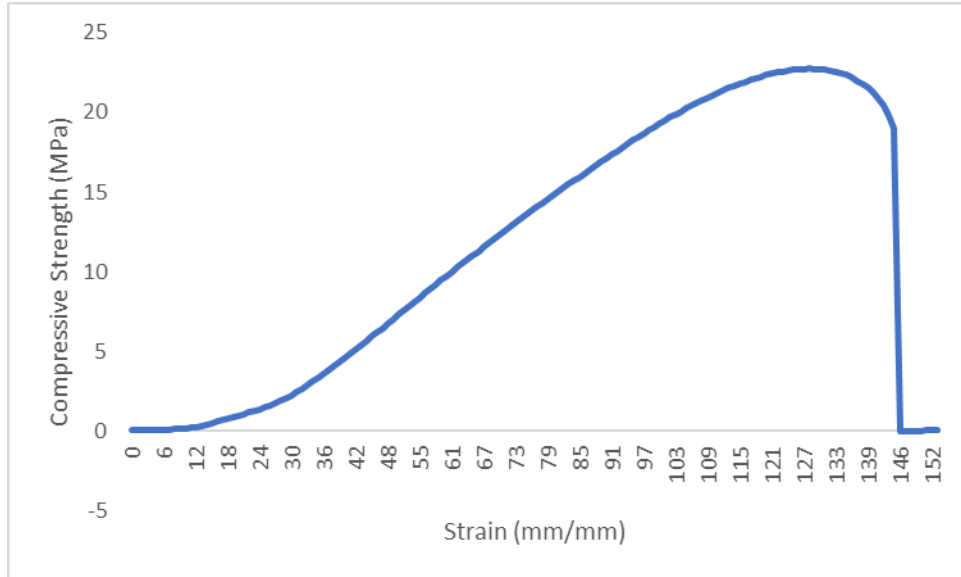
Sample 43



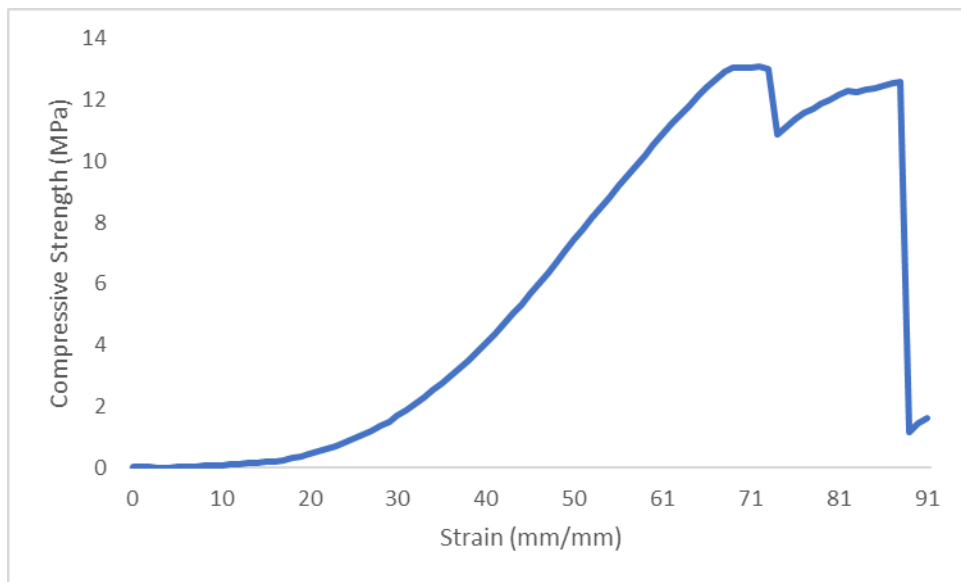
Sample 44



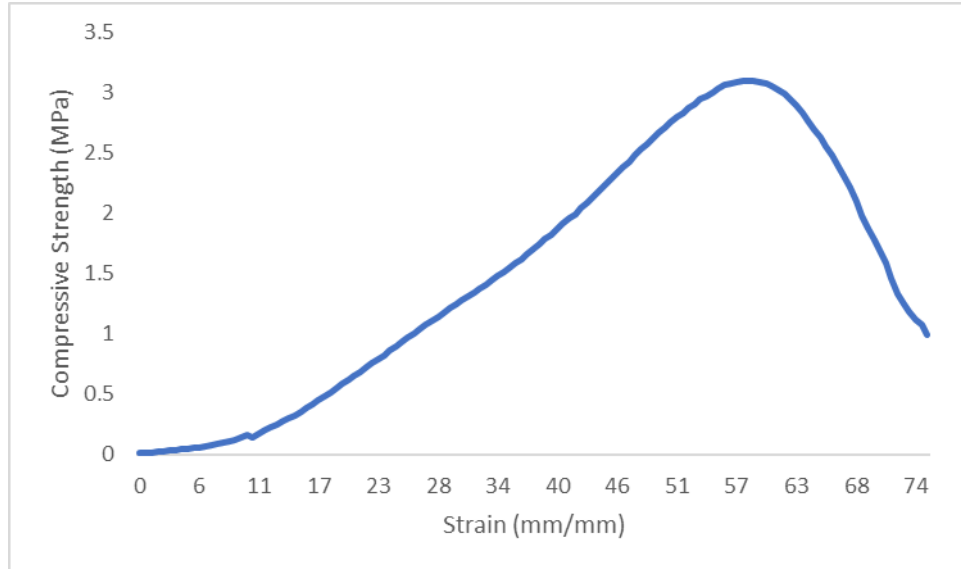
Sample 45



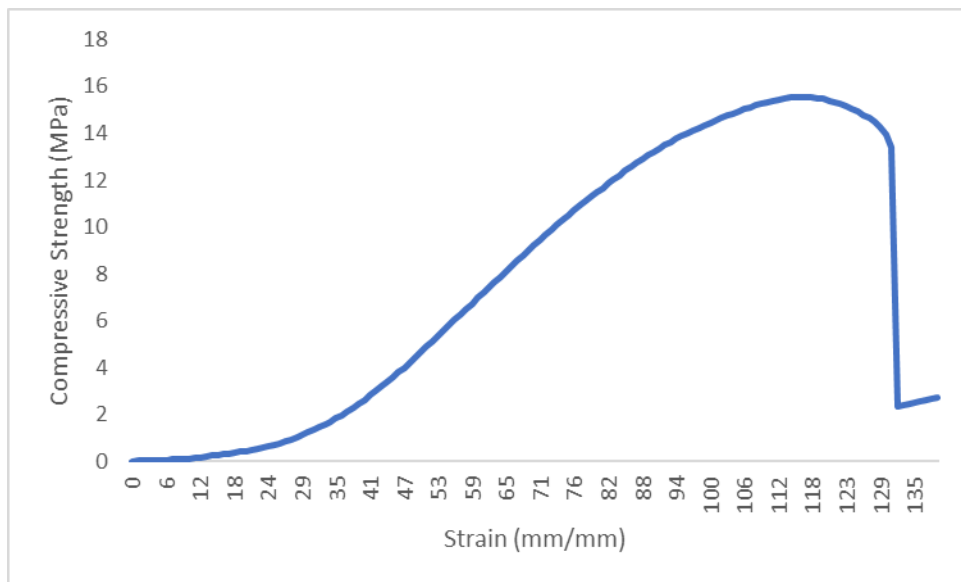
Sample 46



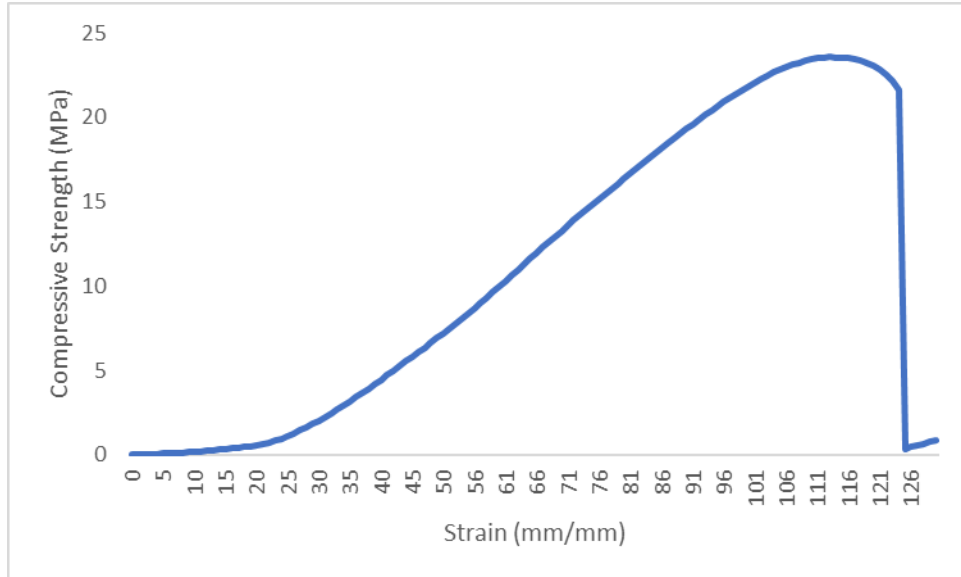
Sample 47



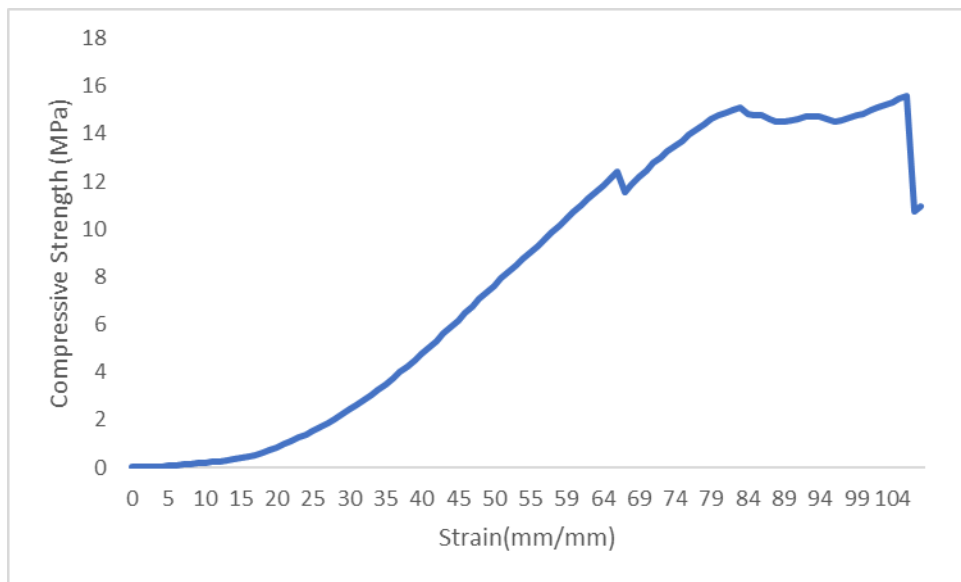
Sample 48



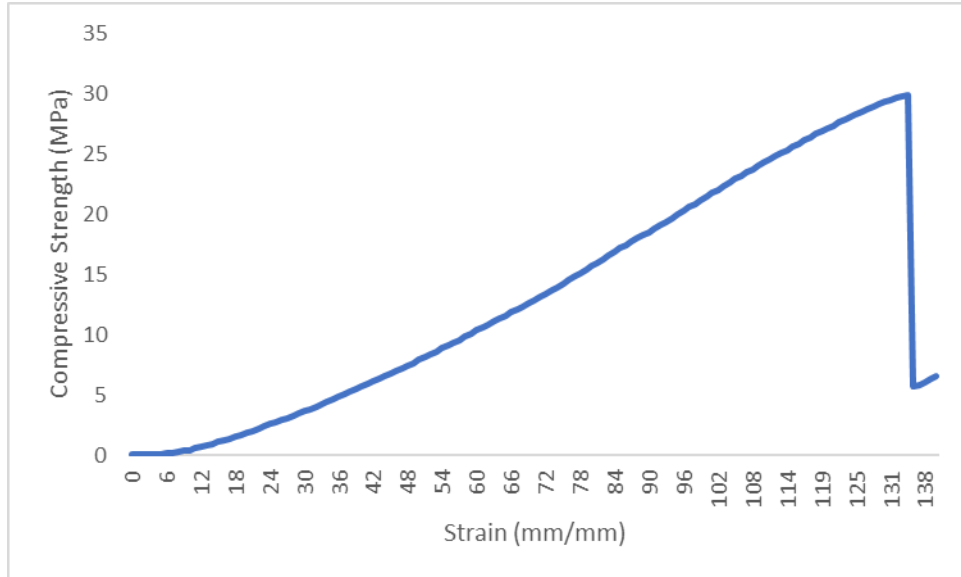
Sample 49



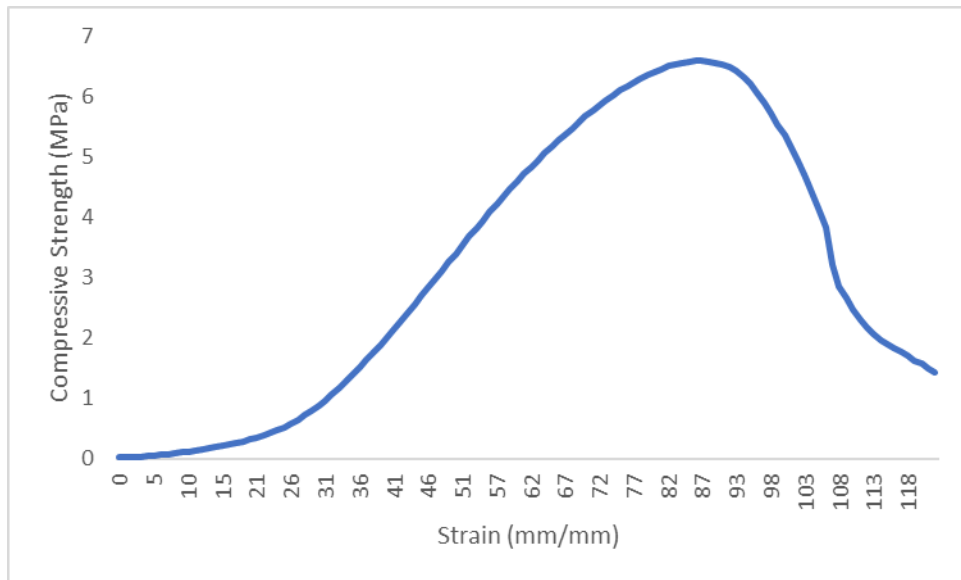
Sample 50



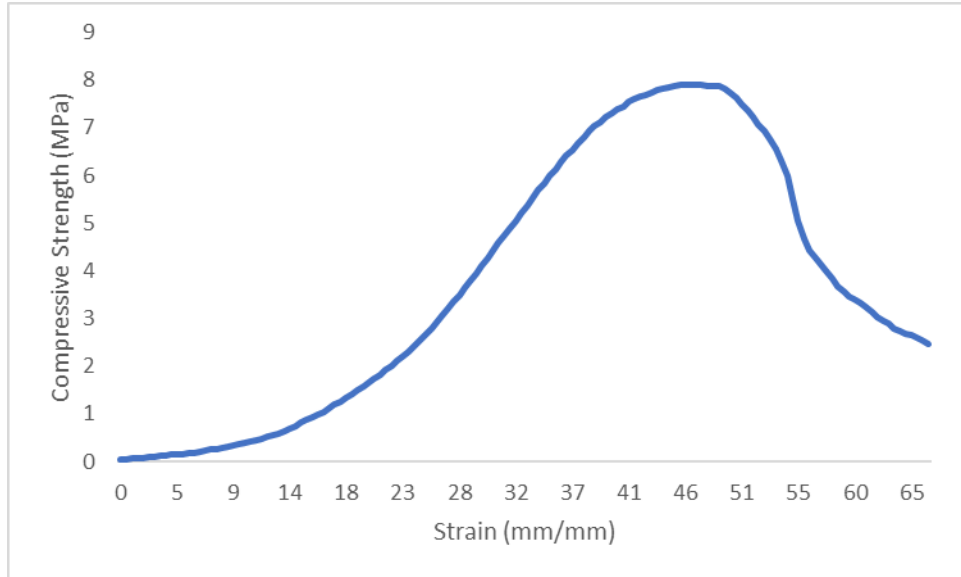
Sample 51



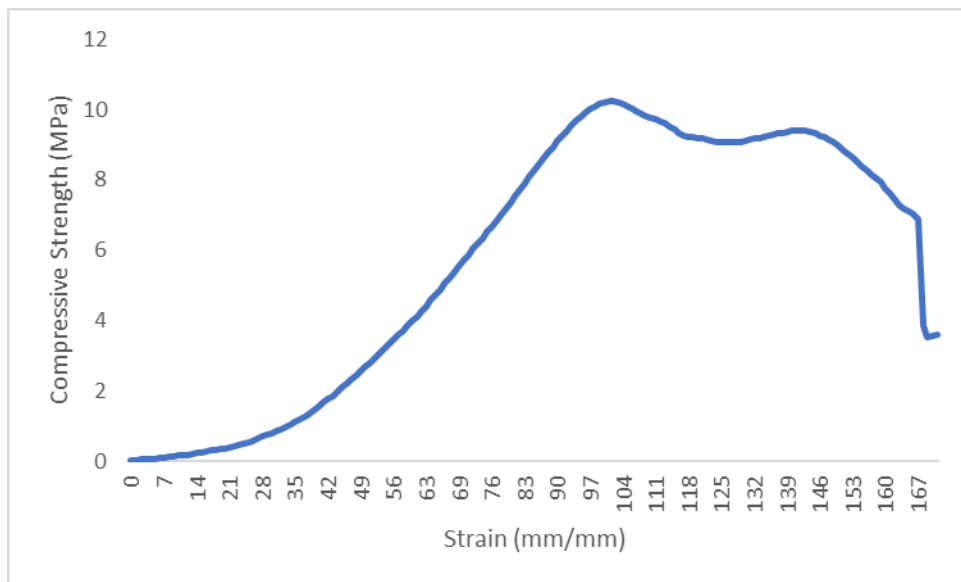
Sample 52



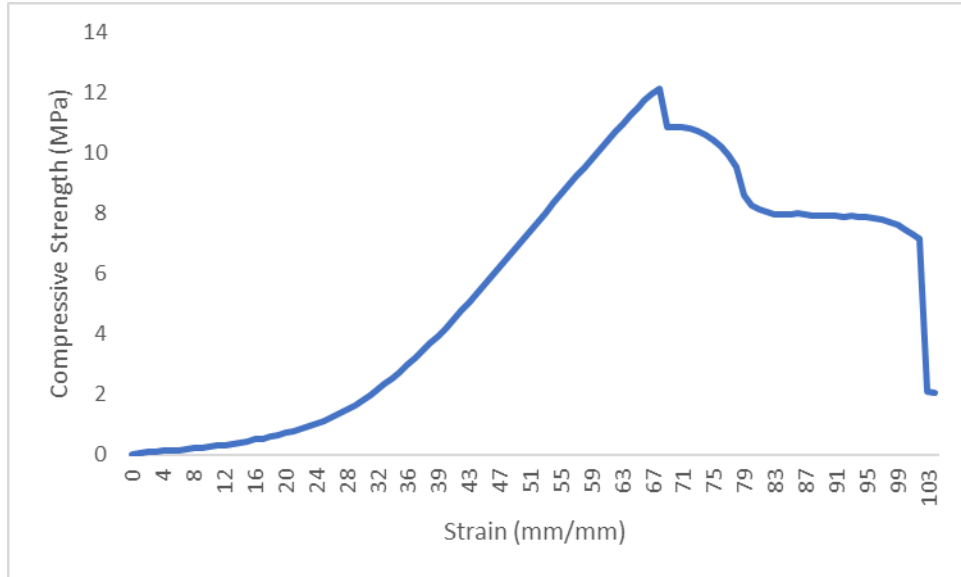
Sample 53



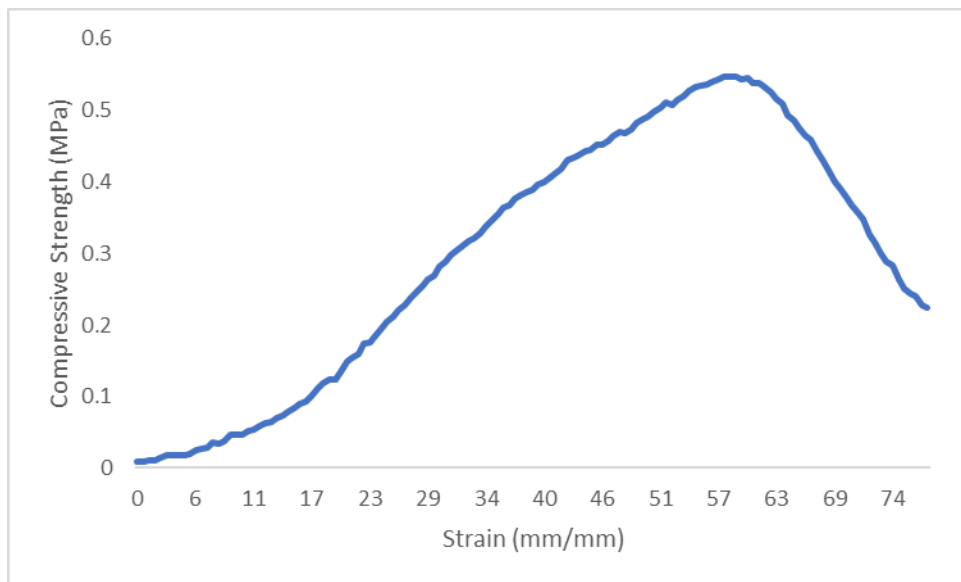
Sample 54



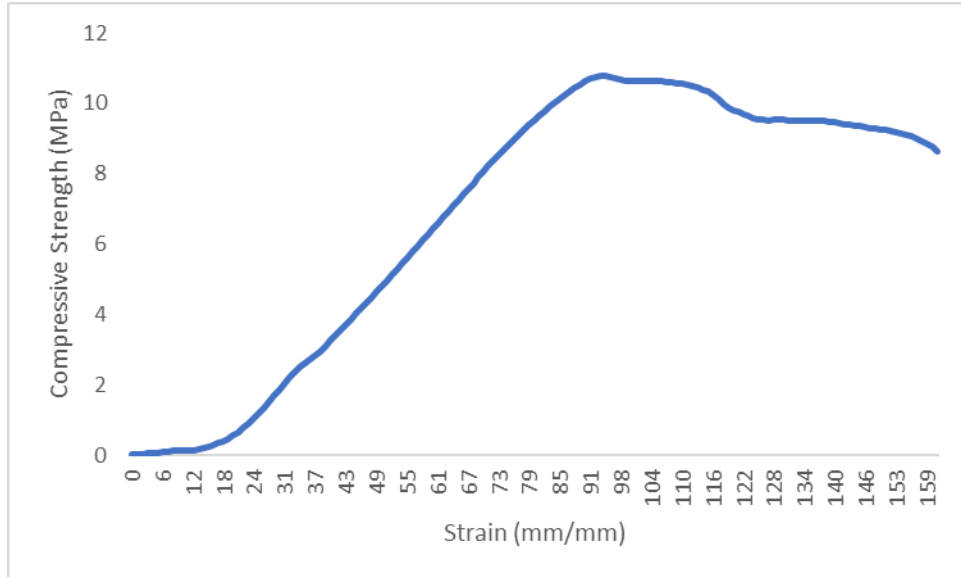
Sample 55



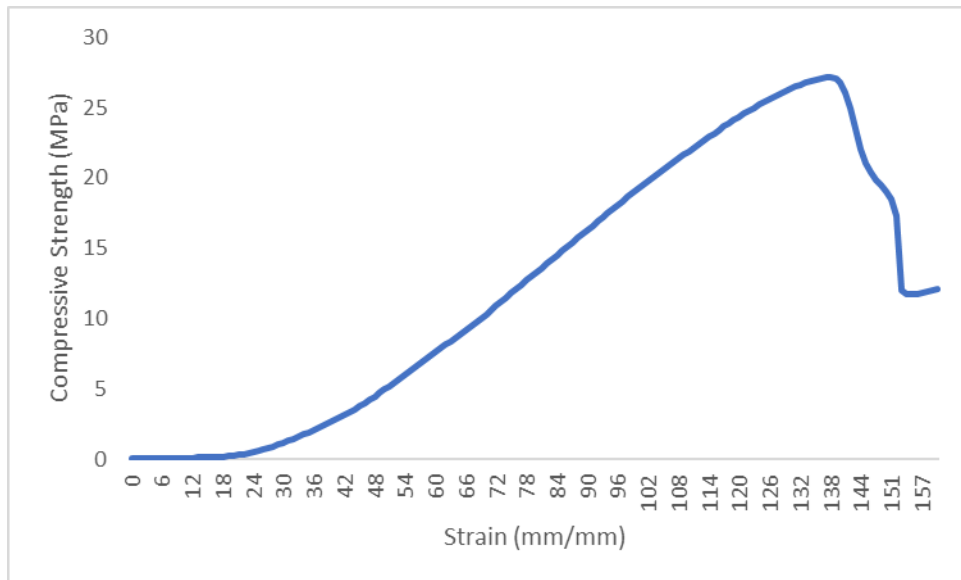
Sample 56



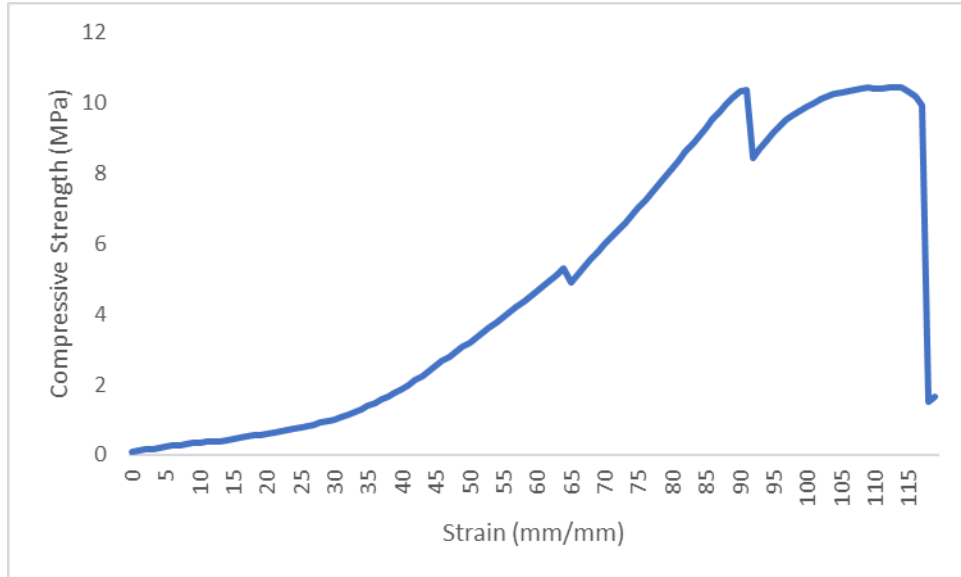
Sample 57



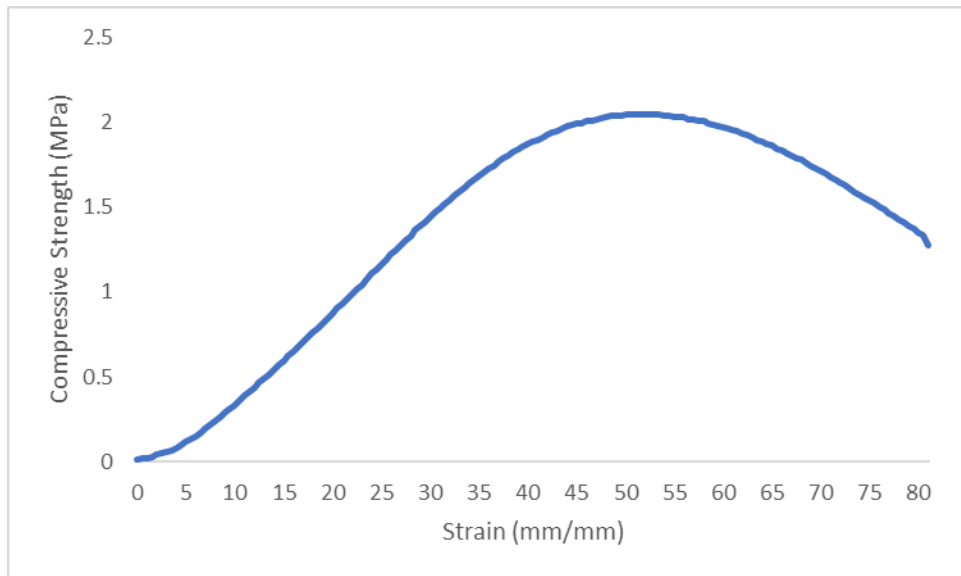
Sample 58



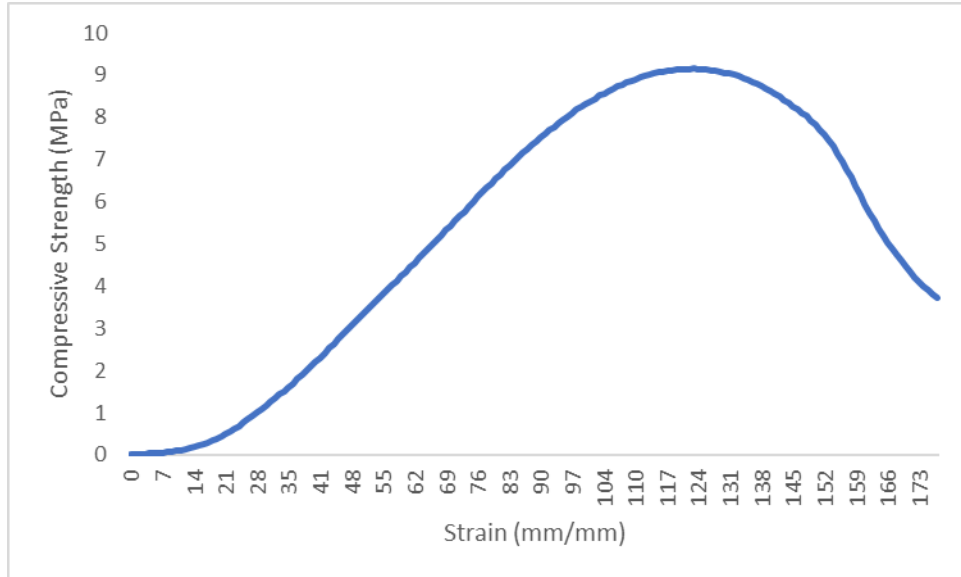
Sample 59



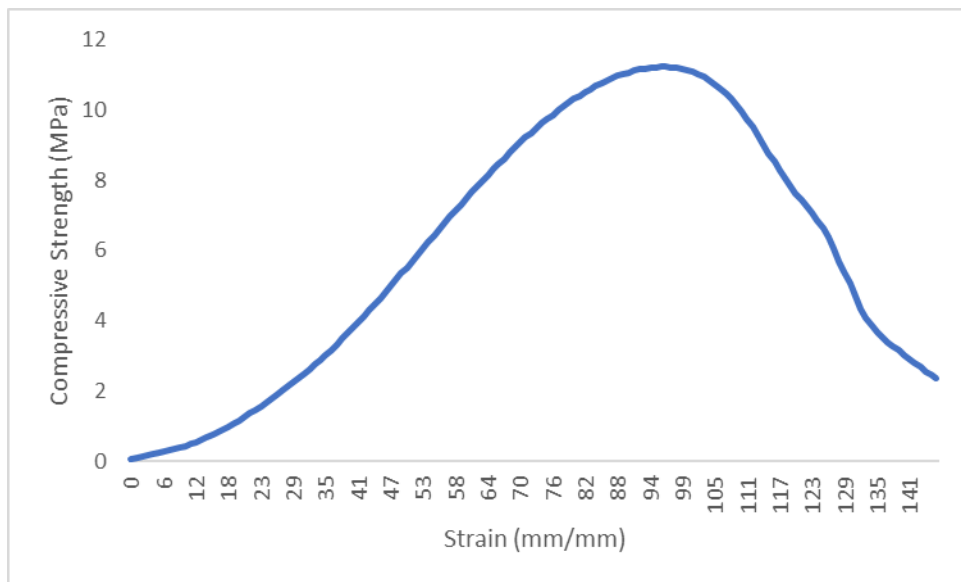
Sample 60



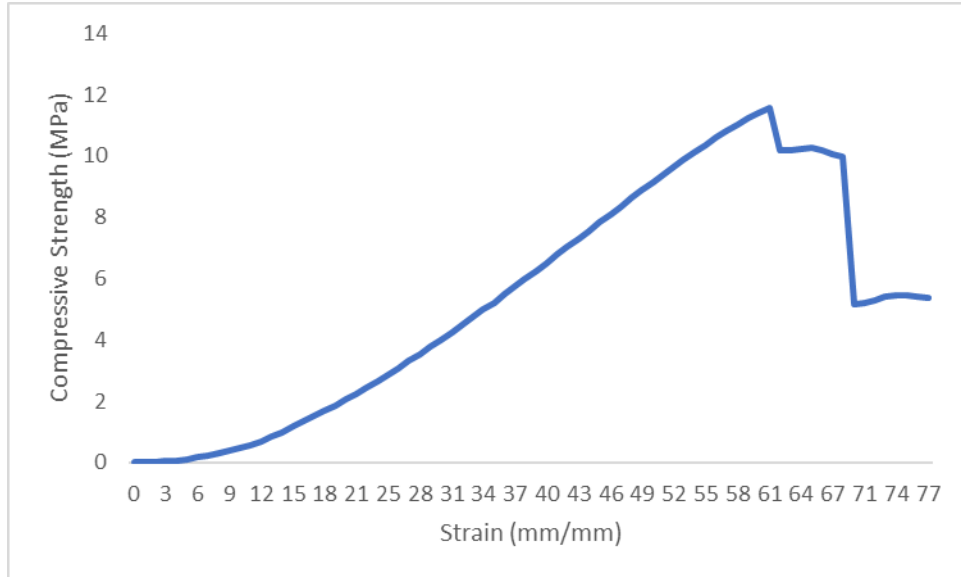
Sample 61



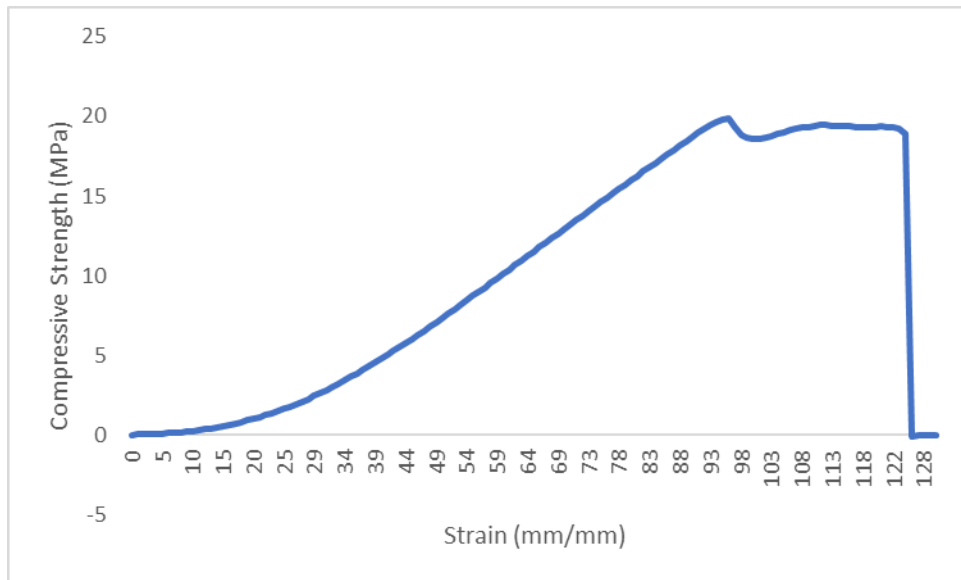
Sample 62



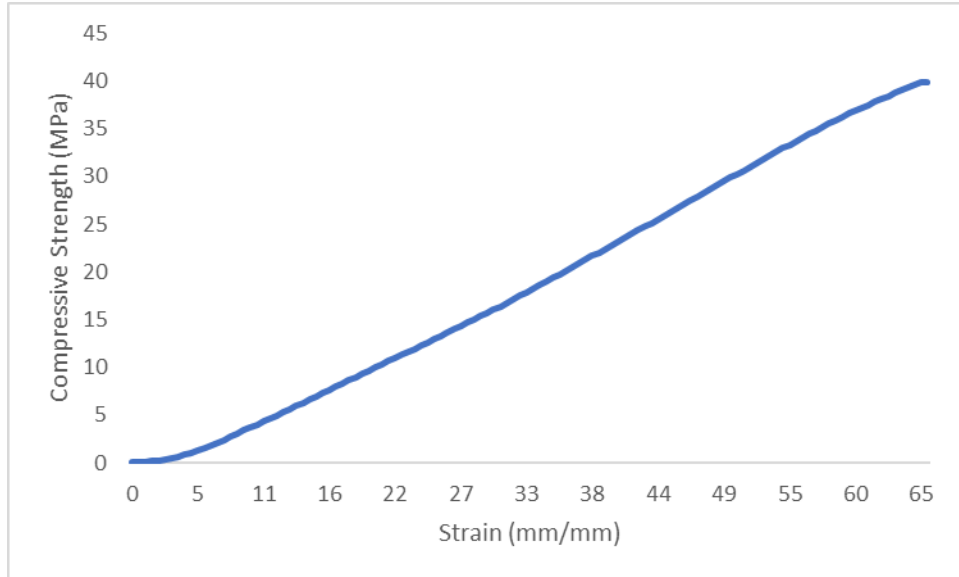
Sample 63



Sample 64

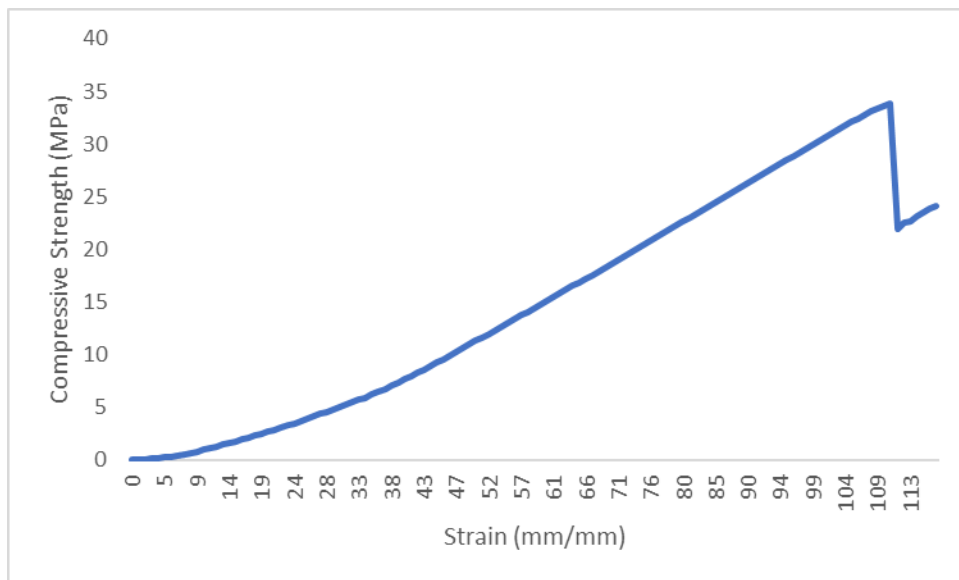


Sample 65*

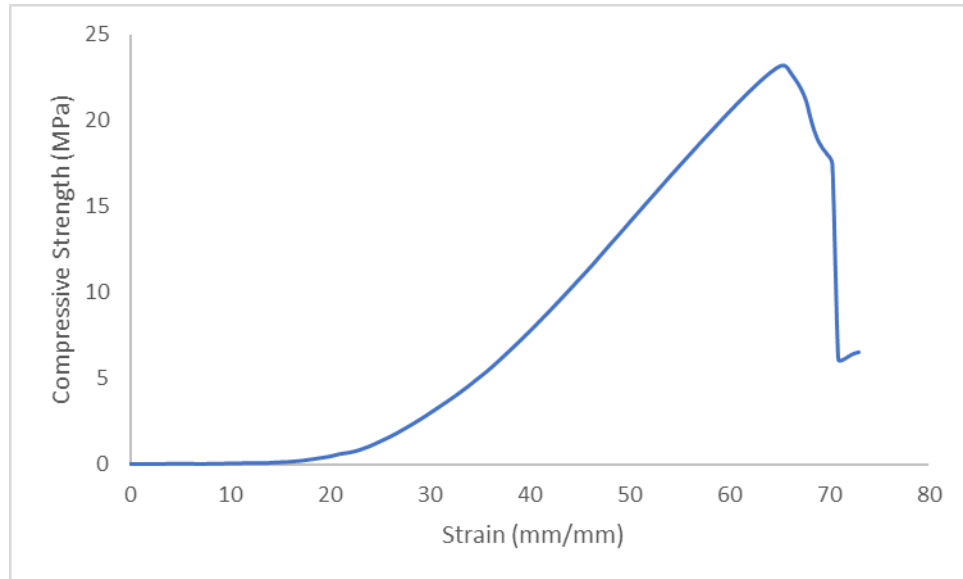


*Note: The mechanical testing system stopped mid run; this sample may be stronger

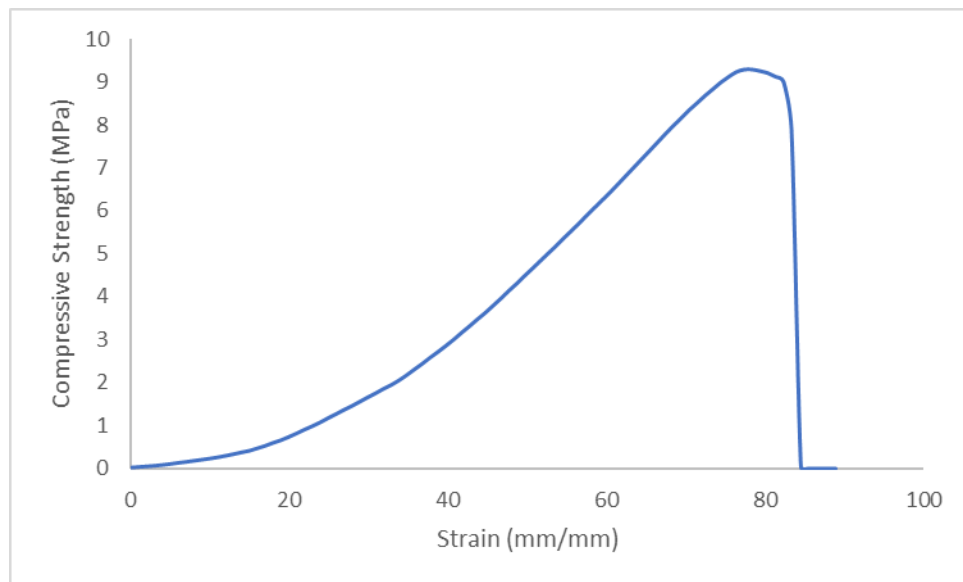
Sample 66



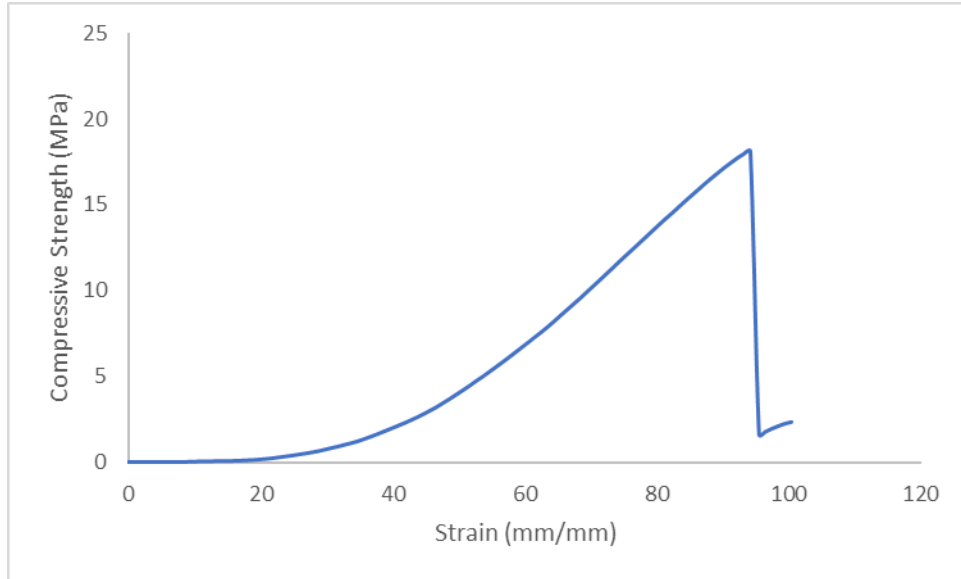
Sample 67



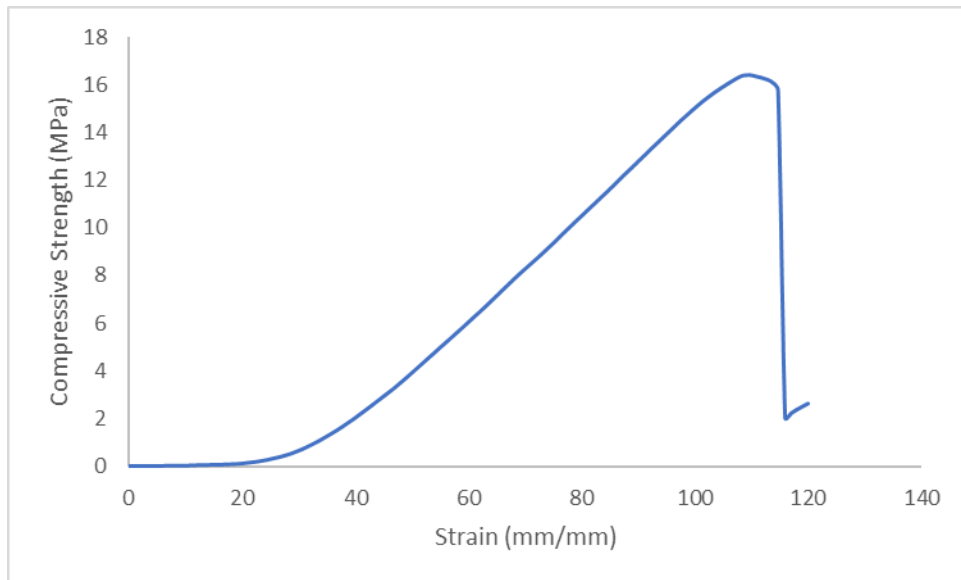
Sample 68



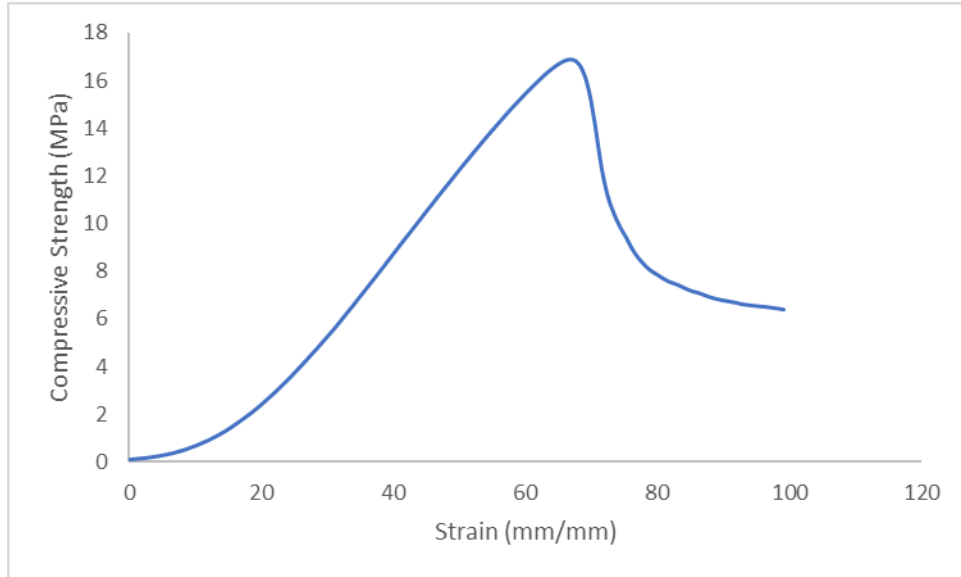
Sample 69



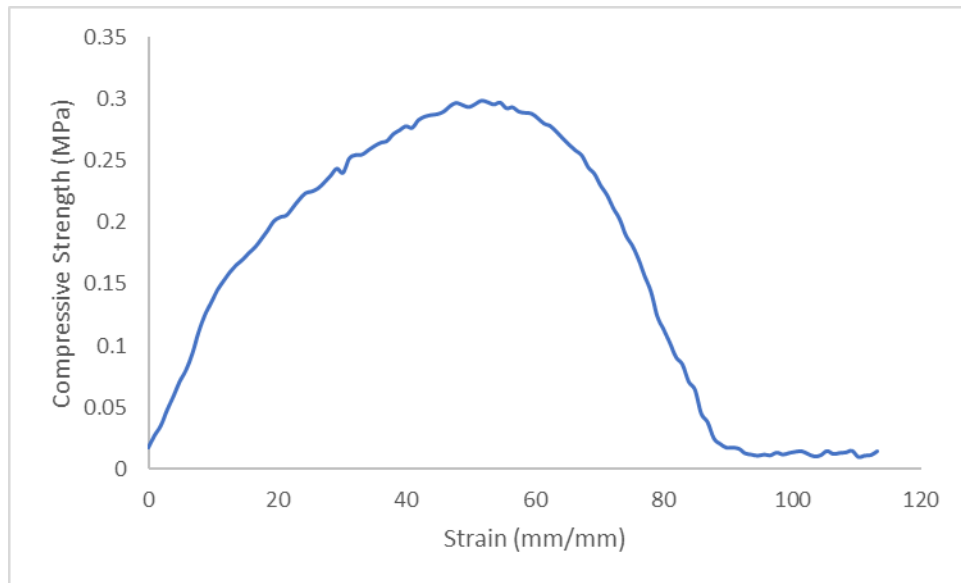
Sample 70



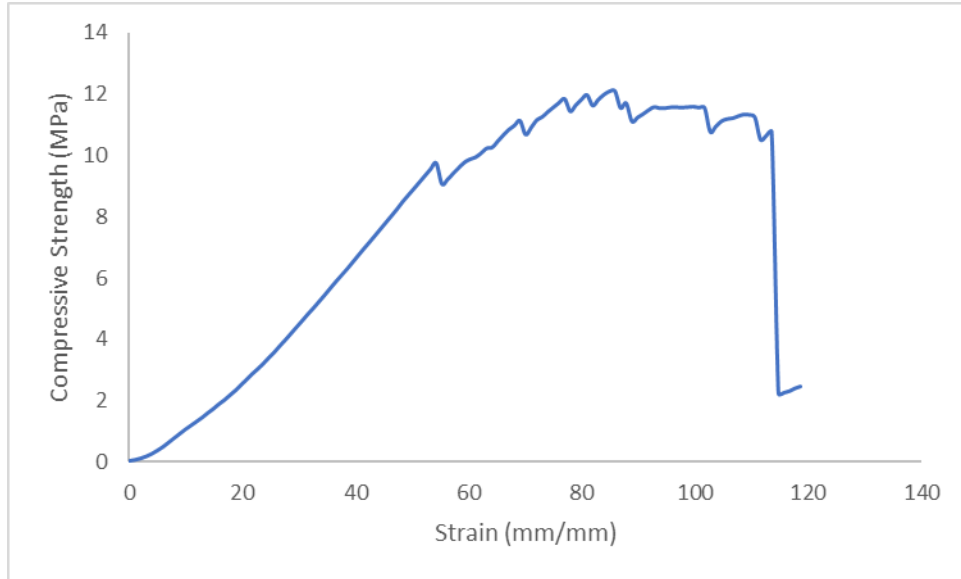
Sample 71



Sample 72



Sample 73



Sample 74

