

# PHA Biopolymer Filament for 3D Printing

A thesis submitted in partial fulfillment of the requirements for the degree of Bachelor of Science degree in Physics from the College of William and Mary

by

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## **Abstract**

Polyhydroxyalkanoate, or PHA, is a bioplastic that biodegrades in aerobic and anaerobic environments over a wide range of timespans<sup>1</sup>. Researchers have had considerable difficulty forming PHA into precursor material for 3D printing. We investigated ways to create PHA bioplastic filaments as precursor material for 3D printers. We carefully examined the temperature control elements of our filament extrusion machines, as well as the thermal properties of the PHA material itself. We also experimented with different post-extrusion processes for creating useable filament. We found that, with careful filament extrusion speed control and a water bath, we could create useable filaments with PHA bioplastic.

## **Introduction**

Since its invention in the early 1980's by Hideo Kodama, 3D printing has promised to revolutionize manufacturing and prototyping. Kodama's original printers used directed ultraviolet light to harden photosensitive liquids into plastic models<sup>2</sup>. Currently, 3D printers come in many diverse forms, all which fall under the broader category of additive manufacturing; this diversity in variety allows scientists, engineers, doctors, and artists great freedom in how they use 3D printing. 3D printers have been used in applications from light manufacturing to architectural prototyping. Custom printers have even been used to create living tissue out of biological material<sup>3</sup>. The most common 3D printers use a heated, motorized nozzle to melt plastic precursor. The nozzle will then slowly deposit the melted plastic layer by layer to build up the specified object, much like frosting bags deposit frosting on to cakes. With the increasing usefulness of 3D printing technology, the importance of having a wide variety of precursor materials to print with has greatly expanded.

The Virginia Institute of Marine Science (VIMS) has been attempting two experiments that rely on 3D printing. The first is to use 3D printing to rapidly prototype biopanel, or biodegradable locks for crab and lobster traps. Fishermen commonly lose anywhere between 10-70% of their total traps each season; these traps remain active, but are never hauled in<sup>4</sup>. Animals will enter these lost traps and die when the traps are not removed and they cannot escape. Dead animals in the traps entice new scavengers to enter the traps looking for food, who themselves become trapped and caught in the vicious cycle<sup>4</sup>. VIMS found that, over four winters, fishermen hired to recover lost traps from the Virginia portion of the Chesapeake Bay recovered 32,000 traps and roughly 32,000 animals which could not escape from the abandoned traps<sup>4</sup>. By equipping traps with biodegradable locks that decompose and break open in the time span of a few months to a year, the traps would be neutralized and no longer pose a threat to the aquatic environment while still remaining useful to fishermen.

The second project involves weaving a web of biodegradable plastic filament into a mat that can be used to filter water. Researchers from VIMS identified PHA plastic as a material that fulfills their needs regarding both projects. PHA plastic is biodegradable on the time span of a year, breaks apart in an anaerobic environment, and decomposes into environmentally safe particles. However, researchers have encountered considerable difficulty producing or procuring PHA plastic precursor filaments for 3D printing. The plastic's properties make it difficult to extrude into useable strands: they reported that it would come out of the extruder as a liquid or too clumpy and brittle to use. This project seeks to overcome these challenges and produce useable PHA filament.

Last semester, we left off at our first attempted print of PHA. We had designed a modular system to automatically spool the filament. We proposed several types of feedback control

mechanisms to spool the extruded filament at a fixed diameter with little variation so it could be used as precursor material for 3D printers. The first run of PHA did not yield any product, so we began this semester investigating the cause or causes why.

## **PHA Information**

Plastics can generally be placed in three categories: thermoplastics, which are composed of individual long chained polymers; thermosets, which are made of a highly ordered three dimensional crystalline network; and rubbers, which are made of a more loosely ordered three dimensional network<sup>5</sup>. Of the three categories, thermoplastics are the most ideal for 3D printing, as they reform back into the same physical condition they were before melting or other reformations. With rubbers and thermosets, heat breaks apart the crystalline structure and ruins the plastic<sup>5</sup>. PHA (polyhydroxyalkanoate) is a relatively new type of thermoplastic that is both produced and consumed by bacteria. Bacteria produce PHA as a way to store energy in certain conditions. Bacteria can later consume the PHA, thus biodegrading it<sup>6</sup>. PHA has a very short biodegradation time span (often a few months to one year), making it much more useful in short time span applications than other, more popular biodegradable plastics (such as PLA, which biodegrades on the order of hundreds of years). PHA plastic can also be broken down by bacteria underwater, in an anaerobic environment, making it useful for aquatic applications. Researchers have found that plastics from the PHA plastic family mirror the properties of many common plastics well, making it easier to work with and predict its behavior<sup>6</sup>.

VIMS reported to us that their PHA plastic began to melt at 140 degrees Celsius; our fact sheet indicated that the range would be between 150-170 degrees Celsius<sup>1</sup>. Our PHA was

manufactured by Metabolix; it is a mixture of two different PHA plastics: PHB and P(3HB-co-4HB).

## Extrusion Experimentation

We used a Filabot Wee filament extruder in our first attempts to extrude PHA plastics. To extrude filament, plastic pellets are fed into the top of the machine. A screw drives the pellets through a heated barrel and out a nozzle as a plastic filament. When we first attempted to extrude the PHA plastic, we started at 140 degrees Celsius. However, at this temperature, we were unable to produce any filament at all.

Figure 1: The Filabot Wee filament extruder



We began to attempt successive extrusions at higher and higher temperatures until we found the correct temperature (a trial and error method). At 160 degrees Celsius we began to observe some extruded filament (all degree measurements will be in Celsius for the remainder of this paper). However, this filament was very brittle, chalky, and clumpy. We speculated that these clumps were unmelted plastic precursor pellets. We increased the temperature, expecting

there to be a certain temperature at which the PHA extruded smoothly. This was a standard procedure last semester in our experiments with PLA and ABS, and we previously found it to be a very effective way of honing in on the correct temperature at which to extrude. However, we never found this point. As soon as the temperature rose above the level where it was extruding in a clumpy, chalky, brittle state, it would begin extruding as completely melted liquid. Further adding to the confusion, we observed there were no set temperatures at which transitions between not melted, semi-melted (chalky), and melted would occur. Each new experimental session produced different results. Temperatures that would melt the plastic completely one day would not melt the plastic at all the next.

<b>Trial</b>	<b>Observation</b>
160 Degrees (Trial 1)	Little Compound Initially, but still gets clogged
160 Degrees (Trial 2)	Good, dries quickly
160 Degrees (Trial 3)	Nozzle clogged, too cold

Figure 2: Sample Selection of Observations at 160 Degrees from our Data book. This shows that even at the same temperature there is vastly varying results. Note: data table presented only contains selected entries to illustrate behavior at one temperature.

To find the cause of this discrepancy, we tested the filament extruder for lag between the temperature read-out and temperature in the barrel. Lag time in the heating would explain some of the discrepancies in the results from session to session. Because we did not account for barrel heating time, a lag could mean that a barrel heated for 30 minutes would be much hotter than a barrel heated for 10, though it would appear the same temperature to us. This testing would also reveal if there was some thermal property of the plastic itself that would cause the lag in heating (i.e. it takes a very long time to heat up compared to other plastics.) To test this, we recorded the temperature inside the barrel of the extruder with a thermometer as we varied the temperature up and down. We compared the thermometer readings to the readings on the machine's read out. We took a data point every 30 seconds; the results are displayed on the graphs below.

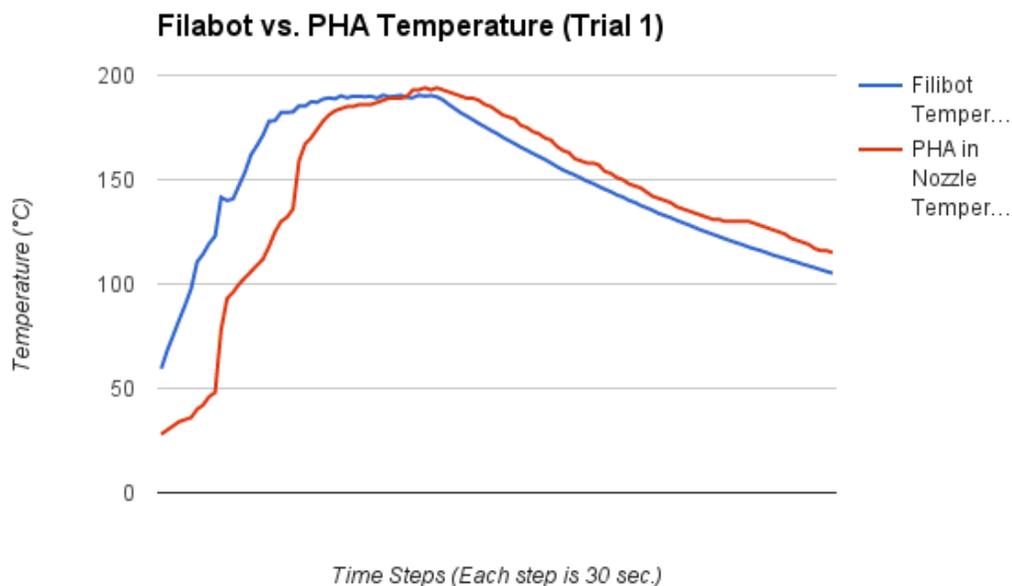


Figure 3: Filabot Temperature v. Time. Notice the lag between the Filabot temperature display (blue) and the true temperature (red)

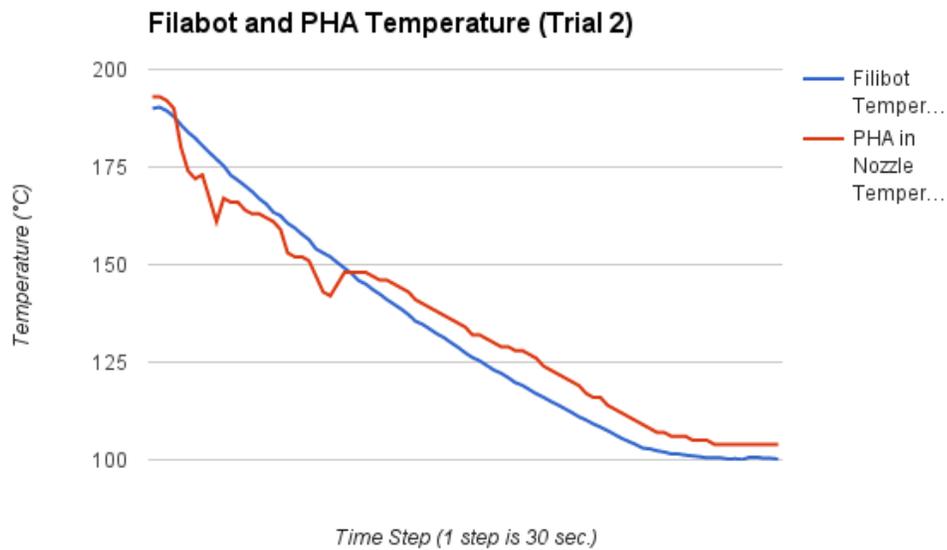


Figure 4: Filabot Temperature v. Time. Lag in both the heating and cooling is observed here as well, although the trend is less clear. Display temp is blue and measured temp is red.

Based on the data collected, we did observe a considerable amount of lag in heating and cooling. This is because of the thermal properties of the PHA plastic itself, rather than the extruder, because we did not notice any lag when using the same extruder with ABS and PLA last semester.

Even accounting for the lag by allowing long heat up and cool down times between temperature adjustments, we could not produce useable filament at any one temperature. The same behavior continued, with the plastic either not melting, extruding in a brittle, clumpy filament, or extruding as pure liquid. Additionally, even liquid plastic extrusions would extrude clumpy after only a few minutes. This is due to the same properties of the plastic that caused the lag. The plastic would reach a useable state, but once it was all extruded from the barrel of the

Filabot the new pellets fed in from the top would not have enough time to reach the same temperature.

We began to explore post-extrusion methods to produce useable filament. We attempted to use a cold water bath. When heated past its clumpy state, air cooling could not cool the liquid plastic fast enough to form a useable filament. Whereas ABS plastics would come out of the nozzle semi-melted (gel-like) but immediately cool into a firm, useable filament, PHA ran out of the nozzle and puddled, taking minutes to harden. However, when we liquefied the plastic by heating it to 180 degrees Celsius (much hotter than its melting point) and dropped the liquid plastic directly from the nozzle into the cold water bath, we could produce useable PHA filaments. The cold water bath would immediately cool the liquid plastic still in its filament shape, regardless of how fluid it came from the nozzle.

Using this new method (which circumvents having to find an appropriate temperature at which to extrude filament that is between the solid and liquid states), we began to produce longer and longer test filaments. We would drop the liquid filament into the bath, then drag it through the cold water as it extruded. However, we soon encountered a problem: the Filabot Wee does not come with built in speed control. It quickly extruded liquid plastic at a constant temperature, but could not melt the new plastic pellets that filled the barrel fast enough to continue this rate, so it would begin extruding clumpy strands after a short amount of time. This made producing useable, non-clumpy, even filaments longer than 2 or 3 feet impossible. Because the Filabot Wee has no speed control, we had to purchase a new filament extruder machine that does to overcome this problem.

We obtained a Filabot EX2, which has a speed control function. The Filabot EX2's speed manually varies during use, and can be adjusted from 0 to 35 RPM. We slowed it down to a very

low speed, roughly 15 RPM. We began repeating our previous water bath experiment with this new filament extruder. We found that we could produce filaments at any length we desired without the strand becoming unusable.

We then began to attempt to control the thickness of the extruded filament. We obtained a thickness gauge measuring device, which allowed us to measure the diameter of the filament as we printed. We found that the machine produces filament at values both at, above, and below our desired value of  $2.85 \pm 0.10$  mm, largely as a function of how hard we pull on the filament as it extrudes. Using two people to simultaneously measure and pull the filament, we could produce short filament which fits in the tolerance range by hand. Though the test filament produced in this way is itself too short to use in 3D printing, it still proves that PHA filament can be produced within the necessary thickness range.

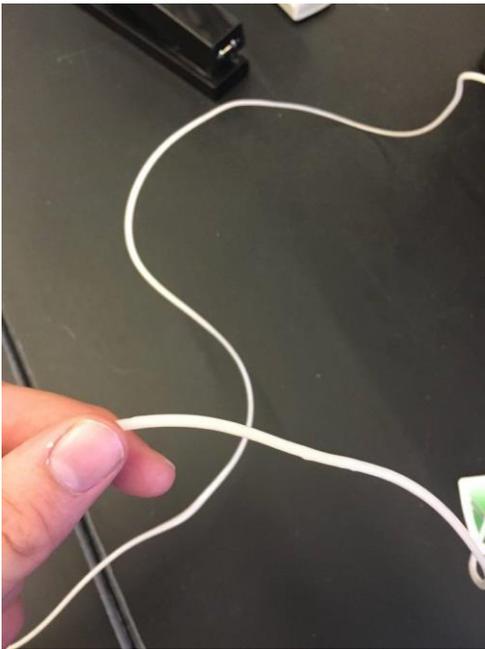


Figure 5: Useable PHA filament extruded within the tolerance range

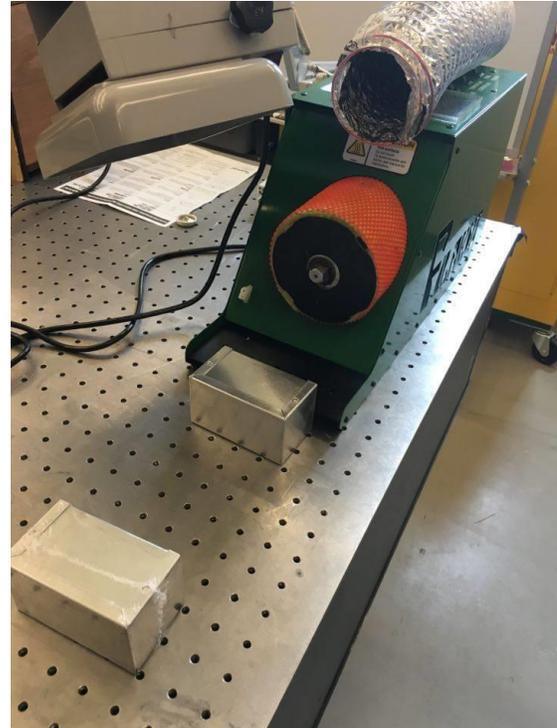


Figure 6: The Filabot EX2 and ventilation snorkel (pictured right) and excess PHA filaments extruded in a variety of diameters (left)

To complete the process of creating 3D printer precursor material, we needed to twist the filament onto a spool that can be fed into a 3D printer. Although this is theoretically possible (albeit extremely difficult) to do by hand, it can be done efficiently with a motor. We built two separate test mechanisms for spooling the filament. The first is an Arduino controlled motorized spooling mechanism based on a design in the Arduino microcontroller manual. By using a filament extruder with manual speed control, we eliminated the need for feedback to a motor that was present in the original design to ensure the filament was extruded at a constant thickness. This design currently functions, although it still must be tuned to the proper speed to spool the filament. The second is a DC motor attached to a belt, which allows us to spool at a slower speed than the motor would normally spool at.

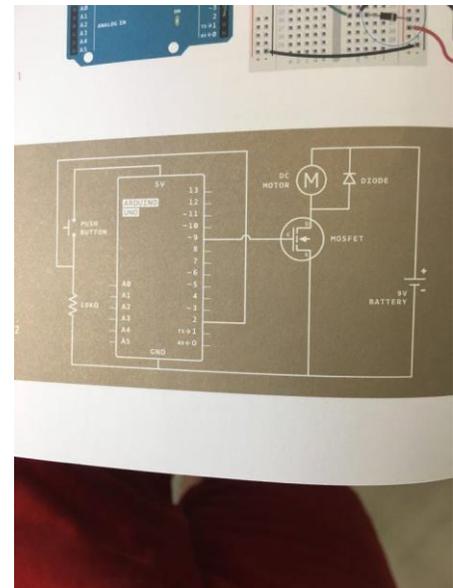
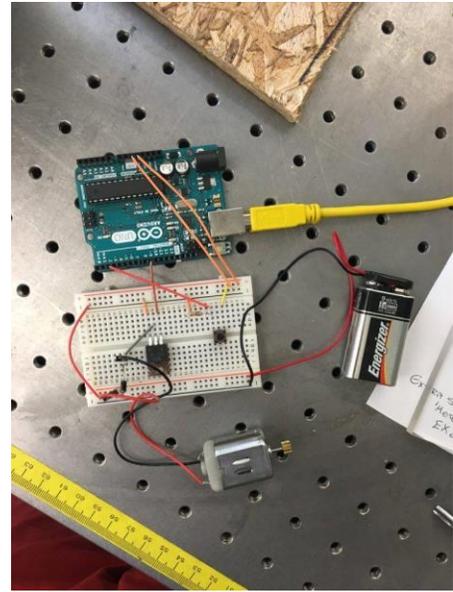
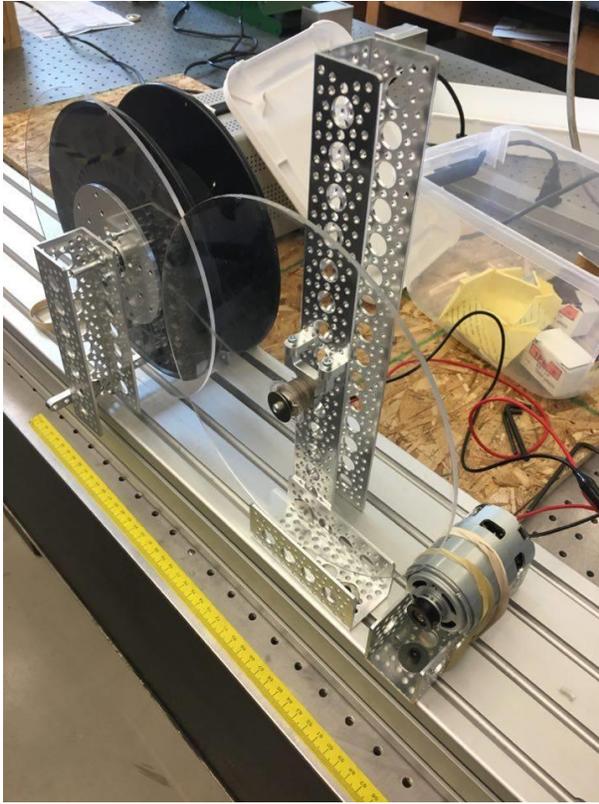


Figure 7: The belt driven spooler (left), the Arduino controlled spooler (top right), and the designs for the Arduino controlled spooler (bottom right)

By using a belt and clear plastic disks to reduce the gear ratio, we can get the motor to spin the spooler at more appropriate speeds for spooling. Though both of these systems function correctly, they have not yet been used to spool any filament.

## **Conclusion**

We have created PHA biopolymer filament for use in 3D printing applications. By carefully examining the thermal properties of both the PHA and the extruder, and by experimenting with post-extrusion processing, we were able to produce short filaments of PHA plastic within the necessary tolerance range for a 3D printer. With the correct extrusion and spooling mechanisms, researchers could produce PHA precursor filaments of any length in their own labs using the methods described in this project. Hopefully, VIMS and other institutions can use these techniques to help reduce the impact humans have on the environment.

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