

Extrusion of Polyhydroxyalkanoate Filament For Use in 3D Printers

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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Date: April 22, 2016

Abstract:

This paper addresses the problems associated with the extrusion and 3D printing of polyhydroxyalkanoates (PHA). PHAs are a family of biosynthetic, biodegradable molecule that in recent years has garnered much attention. One particular area of interest is the manufacturing of escape panels for marine wildlife. Although the potential impact of these panels on fishing is great, a slow manufacturing process limits their production. Various attempts have been made to speed up the production of PHA panels using a 3D printer but have largely failed due to an inability to extrude a consistent filament. The experiments included in this paper demonstrate that, using the EX2 Filabot with variable drill speed, PHA can be extruded into a consistent filament at 170 °C and a drill turning at 15 revolutions per minute. The filament can also be spooled using an automated spooler set-up in conjunction with a water bath.

Introduction:

Polyhydroxyalkanoate (PHA) is a useful material with numerous applications, particularly in the fishing industry. Both biosynthetic and biodegradable, PHA is attractive as a material because it will biodegrade in the ocean on a much shorter time scale than most other plastics, which degrade on the order of decades¹. It is this characteristic that could help alleviate a significant problem in one of the world's most crucial industries. Fishing, particularly of crab and lobster, involves leaving crab pots, essentially large cage traps, at the bottom of a body of water. Fishermen then wait for crabs, lobsters or other species to accumulate in the trap. Fishermen then collect both the trap and the marine life inside.

While most of this fishing is done intentionally, it was discovered recently that crab traps continue to kill animals when left at the bottom of the ocean. This is known as “ghost fishing” and occurs when these crab and lobster traps are lost by fishermen and left at the bottom of a water body. Rather than falling apart or going into disuse, the traps often remain intact for years while continuously trapping and killing marine life over their life span. The extent of the problem has only recently been investigated, but it is estimated that fishermen lose anywhere from 10-70% of their traps annually.² In the Chesapeake Bay fishing industry, that equates to a lot of lost revenue and needless loss of marine life.

One possible solution to “ghost fishing” involves PHA. Using a member of the PHA family, researchers at the Virginia Institute of Marine Science (VIMS) have successfully developed prototype biodegradable panels that can be built into these

¹http://des.nh.gov/organization/divisions/water/wmb/coastal/trash/documents/marine_debris.pdf

² Bilkovic, D. K. Havens, D. Stanhope, K. Angstadt. 2012. The use of fully biodegradable panels to reduce derelict pot threats to marine fauna. *Conserv. Biol.* 26(6): 957-966.

traps. It is these panels that provide an escape hatch for the marine life that find themselves stuck.

Fishermen need not worry much about lost catches either. The time scale on which a PHA panel can dissolve can be controlled by the thickness of the panel (i.e. the amount of PHA present). In an experiment where different weights of PHA were added to sediment in incubation bottles for 42 days, 0% of a 0.25 mg sample and 65-75% of a 15 mg of PHA remained. It is also important to note that the rate of this degradation is both heavily influenced by the type of PHA being used and if certain microbes, sulfate-reducing bacteria in particular, are present.³ Although these sulfate-reducing bacteria are important to degradation, many bacteria have the enzymes needed to hydrolyze the polymer ester bonds to produce water and carbon dioxide gas.⁴

Another important characteristic of the bacteria responsible for dissolving PHA is their sensitivity to ultraviolet light. This means biodegradation of PHA, which itself is resistant to degradation by UV light, will only commence in places with little UV radiation. As a result, panels kept out of the water will remain intact for longer times, and even submerged traps can be reused if they are harvested early enough. Couple this with the fact bacteria degrade different members of the PHA family at different rates and it means these PHA panels can be customized to survive a wide range of conditions and be used for an even greater range of needs.

To test what set of conditions are best for addressing the problem above, it would be extremely beneficial to be able to easily and quickly produce prototypes of these panels. One of the ways to do this, with minimum human labor involved, is to use a 3D printer. The basic premise of a fused deposition modeling (FDM) 3D printer is straightforward: melt down a plastic to extrude it into a thin filament, spool the new filament, and feed that filament into the 3D printer to melt down the plastic again. In the 3D printer, the printer head moves in three spatial directions building the object one layer of plastic at a time. The key to this entire process, however, is making sure to print a filament with a consistent diameter that fits the specifications of the 3D printer.

With more fickle plastics, meeting these specifications can be a difficult challenge. 3D printers such as the Ultimaker can only tolerate a range of 2.75-2.95 mm, a +/- 0.1 mm change, in the diameter of a filament. It is also necessary, from both a functional and practical standpoint, to spool the filament soon after it is extruded — assuming the filament can easily be extruded at all. PHA falls into this category of fickle plastics. It is not easily extruded into a filament, and it is not unusual for extruders to have trouble extruding PHA. Here in lies the aim of the

³ J. Mas-Castellà, J. Urmeneta, R. Lafuente, A. Navarrete, R. Guerrero, Biodegradation of Poly- β -hydroxyalkanoates in anaerobic sediments, *International Biodeterioration & Biodegradation*, Volume 35, Issues 1-3, 1995, Pages 155-174, ISSN 0964-8305, [http://dx.doi.org/10.1016/0964-8305\(95\)00066-E](http://dx.doi.org/10.1016/0964-8305(95)00066-E).

⁴ Corre, Y., Bruzaud, S., Audic, J., & Grohens, Y. (2012). Morphology and functional properties of commercial polyhydroxyalkanoates: A comprehensive and comparative study. *Polymer Testing*, 31(2), 226-235.

current research: develop a way to consistently produce, spool and ultimately 3D print PHA to produce biodegradable panels.

Methods:

The ability to extrude filament with a consistent diameter required first finding the ideal temperature range in which extrusion of certain plastic could occur. For each plastic, a range of melting temperatures was known and could be used to narrow down the ideal temperature. Starting at the lower end of the range, the extruder drill in the Filabot was turned on and we recorded if any filament came out. The temperature would be increased by increments of 10 °C until filament of a consistent diameter were produced. From there, smaller increments of 5 °C were used to zero in on the extrusion temperature that would produce the best filament.

Once a consistent filament was extruded, a standardized method was used for measuring the diameter of every filament over its entire length. Starting at the newest end of the filament (the last piece of the filament to emerge from the extruder nozzle), marks were made along the filament every 6 inches. At each mark, the diameter of the filament was recorded using digital calipers.

This extrusion process was used to produce ABS, PLA, and PHA filaments. The first two plastics are widely used for 3D printing, and thus served as good tutorials for the extrusion process. These plastics helped determine what conditions were necessary to extrude filament at a constant diameter.

When it came time to extrude PHA, initially a Filabot Wee was used. Over the course of many extrusion sessions, however, it became clear that extrusion of PHA filament would benefit greatly from speed control of the extrusion drill. Therefore a Filabot EX2 with a speed-controlled drill was used to produce all PHA filaments for the rest of the experiment.

Discussion:

This section will be broken up into four areas of interest that were addressed over the course of research: Initial extrusion with ABS and Polylactic Acid (PLA), PHA extrusion with Filabot Wee, PHA extrusion with Filabot EX2 and spooler design.

Initial Printing with ABS and PLA

In order to familiarize ourselves with the 3D printing process we began by extruding ABS filaments. This type of plastic is widely used for 3D printing, and the fact that it is generally user friendly makes it a perfect way to practice extruding filaments with a consistent diameter. All printing of ABS was done with the Filabot Wee. In total, 18 filaments were produced with lengths between 36 inches and 420 inches. It was found that the ideal extruding temperature was 190 °C and six filaments were produced at this temperature. The diameter of these filaments as a function of length is given in Figure 1.

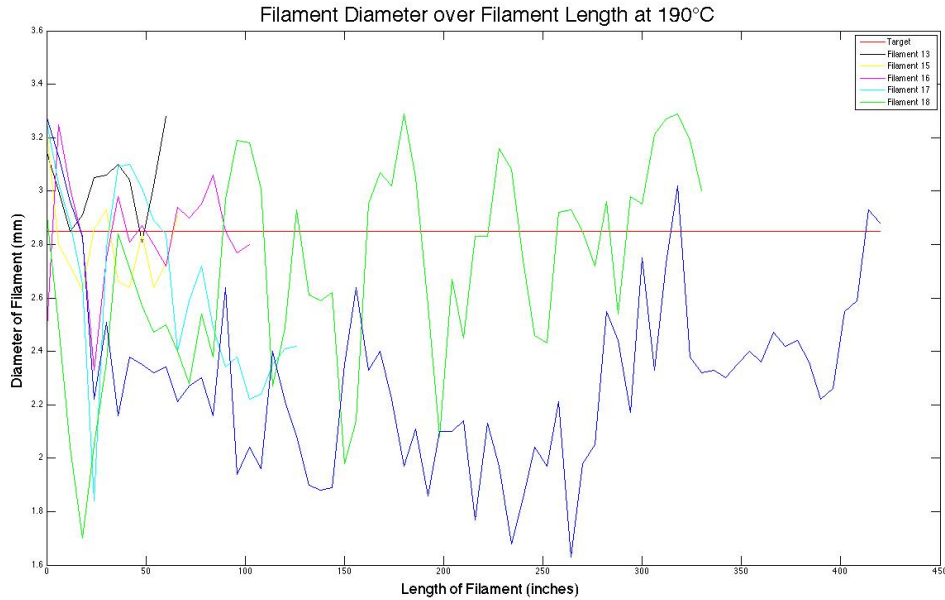


Figure 1: Diameter of ABS filament over length for six filaments. Diameter can vary wildly over the length of the filament due to inconsistency in spooling. This highlights the need for an automated spooling process with feedback loops.

PLA, the closest chemical cousin to PHA readily available for use, was also used to practice extruding filaments and show it could be done to produce a filament with a consistent diameter. Again, all printing was done using the Filabot Wee. A total of 9 filaments were produced with lengths between 12 and 48 inches. The ideal temperature range to produce PLA filament with consistent diameters was between 145 °C and 150 °C. The diameter of PLA filaments as a function of length is given in Figure 2.

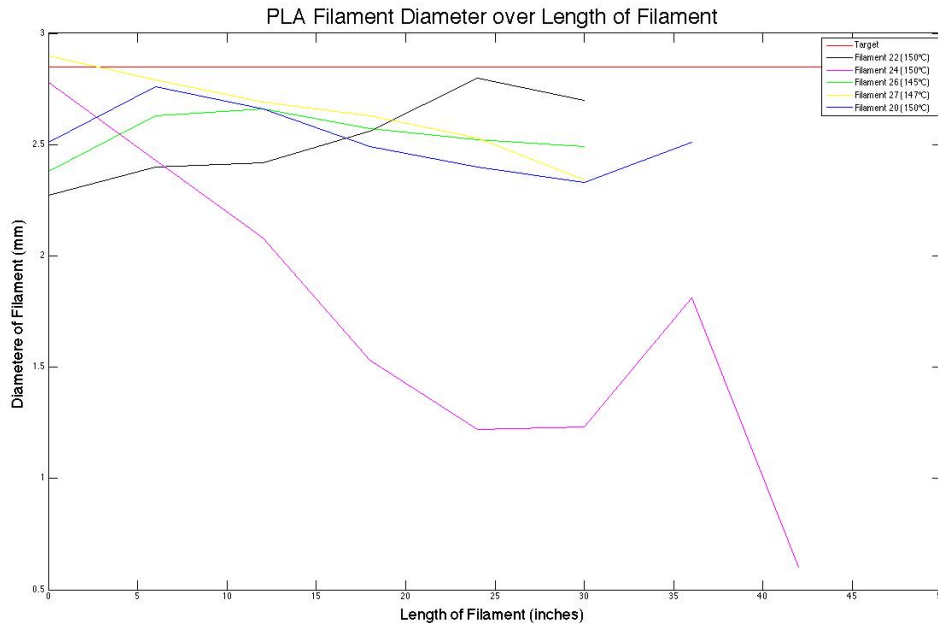


Figure 2: Diameter of PLA filament over length for five filaments. Diameter can vary wildly over the length of the filament due to inconsistency in spooling. This highlights the need for an automated spooling process with feedback loops.

Trials with both ABS and PLA highlight the need for an automated spooling process. Having a motorized spooler pull the filament at a constant tension could mitigate many of the issues with inconsistent diameters. Also, constructing a feedback loop between the spooler motor and a diameter sensor will help achieve not only a consistent diameter but also a diameter within the tolerance of the Ultimaker. Specifics of the spooler design are given in a later section.

PHA Extrusion with Filabot Wee

As expected, extrusion of ABS and PLA proved to be much easier than extrusion of PHA, specifically Metabolix-produced PHB. The extrusion difficulties were in large part due to finding a temperature PHA would extrude at and be solid enough to form a filament. The Metabolix safety sheet listed the melting temperature of the pellets to be between 100 °C and 190 °C, and most other sources put the melting temperature of PHB near the higher part of the range. When it came time to actually extrude, however, there seemed to be no temperature that could consistently produce PHA filament. Below 170 °C the extruder nozzle would become clogged and be unable to produce PHA; above 170 °C the PHA produced would be too melted to form into a filament. Even when one temperature was found to produce decent filament, attempting to replicate the good results proved almost impossible.

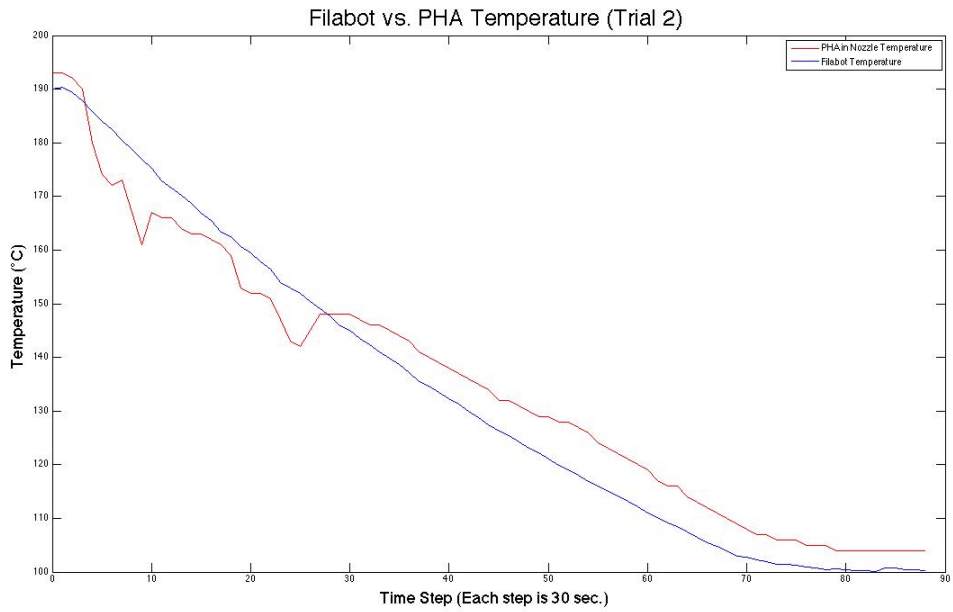
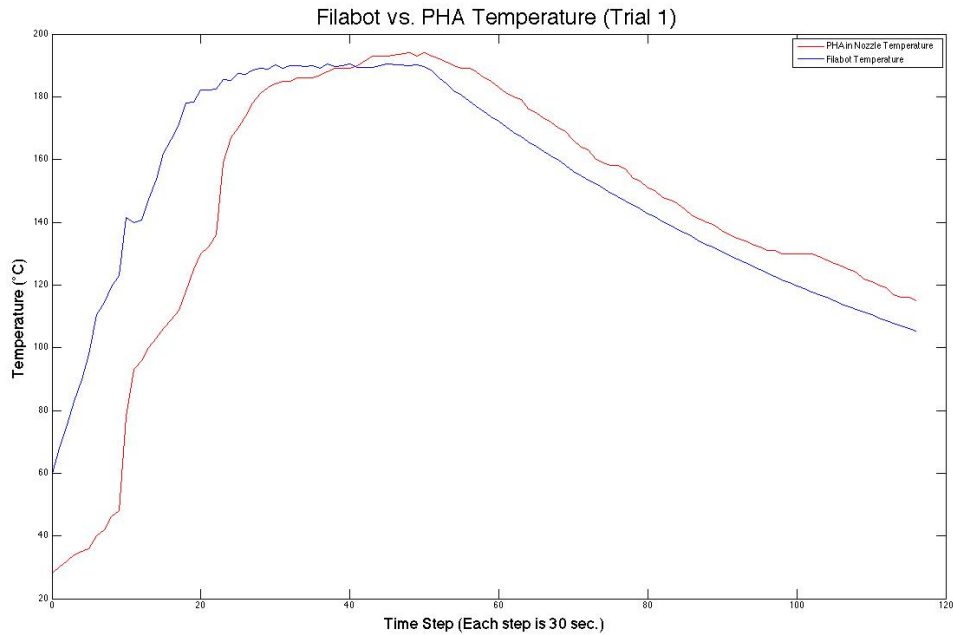
One of the main issues was the temperature lag between the LCD display of the Filabot. The display showed one temperature that was not equal to — and sometimes drastically different — from extruder nozzle temperatures of PHA.

An experiment was conducted as the Filabot was heated up or cooled down by simultaneously reading the LCD display and measuring the temperature of PHA in the nozzle. The experimental procedure was relatively simple. For the first trial, we began with a cold Filabot (i.e. not previously turned on) and set the target temperature to 190 °C. As the temperature of the Filabot slowly began to increase to reach the desired temperature, the temperature on the LCD display and in the nozzle was recorded every 30 seconds. Once enough time had passed that both the LCD temperatures and PHA temperatures agreed, the target temperature was set to 100 °C and the procedure was repeated but with the temperature decreasing with time. In a second trial we started with the Filabot at 190 °C and recorded the temperatures as we let the Filabot and nozzle cool to 100 °C.

The experiment itself is simple, but the results help us better explain why printing was so difficult and why different trials at the same temperature yielded different results. Starting with a cool Filabot, the temperature difference between the LCD display and the PHA in the nozzle is, on average, 28.86 °C. A temperature range of this can span two completely physical states of PHA. This can explain why the filament can be extruded at a temperature during one session, and then be too solid during another session.

The temperature difference when allowing the machine to cool down is equally enlightening. As the temperature of the Filabot is allowed to decrease, the average difference is much closer at 5.05 °C. When we decrease the temperature the PHA temperature typically remains higher than what the LCD panel displays. Thus if we allow the Filabot to reach a high temperature and then let it cool to the temperature we wish to extrude at, the extrusion temperature will be much closer to what the Filabot says it is than if we started from a lower temperature. Figure 3a and 3b show this visible lag between the display and the extruder nozzle.

Figure 3a: Starting at a low temperature setting on the Filabot, the temperature difference between Filabot LCD display and the extruder nozzle is shown below. The temperature in the nozzle does not actually equal that of the LCD display until the target temperature is reached. Until this point, the nozzle can be as much as 30 °C. cooler than the temperature shown on the display. Figure 3b: When the machine is allowed to cool down after the display and nozzle reach the same temperature, the temperature in the nozzle typically stays 5 °C then the LCD display.



After accounting for this temperature lag, the extrusion of PHA filament became relatively successful. More than 12 linear feet of filament was produced thus far with diameters between 1.3 mm and 2.9 mm, and an average diameter of 2.01 mm. The longest individual filament is 4 feet and 5 inches long.

Each filament produced followed an identical procedure. The temperature controller on the Filabot is set to 180 °C. Once the LCD display on the Filabot displays this temperature, it is then necessary to wait another 5-10 minutes to allow the temperature in the nozzle to reach this temperature. The temperature in the hopper seems to affect the consistency of the filament, so a plexiglass door was placed over the hopper opening to limit the loss of heat. After the short warming up period, one person stood near the Filabot to turn it on and off, and another stood ready with a pair of tweezers to pull the filament. When the drill is started and the extrusion process begins, the individual with the tweezers grabs the filament and pulls it steadily through a short, 8-15 °C water bath. It seems this has been another key to successfully producing filaments: at 180 °C the filament is too runny to work with by itself, but running the filament through the bath cools it immediately and allows it to be pulled without tearing. Currently the filament is pulled through the entire 15" length of the water bath and up and out onto the spooler.

Despite the newfound success, there were still issues in the extrusion process. One concern is the consistency of the filament extruded, particularly when the filament comes out of the nozzle in chunks. These chunks not only result in inconsistent diameter filaments, but also weaken the filament and hinder the printing process. Although the exact mechanisms for this are unknown, it is suspected that an inconsistent temperature in the hopper in conjunction with the volume of the pellets being more than double that of previously used pellets may be to blame. Attempts have been made to produce smaller size pellets using a blender have been unsuccessful.

PHA Extrusion with Filabot EX2

In comparison to the original Filabot, the Filabot EX2 is a significant improvement. For one, the temperature range for extruding PHA filament in the EX2 is much greater. Where the original Filabot could not produce PHA filament below 160 °C without clogging the nozzle, the EX2 can produce PHA filament at temperatures as low as 130 °C. Part of what makes this temperature range so large in the EX2 is the speed-controlled drill. A feature the original Filabot was sorely lacking, the EX2 can increase the speed of its drill bit to 35 revolutions per minute. Having the ability to control how fast the drill bit revolves allows the PHA pellets more time to melt in the hopper, and thus avoid a chunky filament consistency.

In fact, the EX2 seems to fix many of these filament-consistency problems. Not only has the filament become less chunky, but we can also run the extruder for greater length of time to produce much longer filament. The EX2, at 170 °C and 15 rpm, produces PHA filament of one meter or longer consistently. Unfortunately, the inconsistencies with the diameter of the filament remain. To build the spooler apparatus to ensure a consistent tension on the filament will be the best way to address this.

Spooler Design

With the help of the EX2, the ideal temperature and rotational speed for PHA extrusion has been determined and now most of the remaining work can be on building the spooler set-up. The automation of the spooler should ensure the filament is spooled at a constant tension. Furthermore, the Filimeasure will measure the diameter of the PHA filament during this process to determine if that spooler tension is too high or too low.

The initial spooler apparatus features only the most critical design elements. The assembly begins on one end with the Filabot and the welding fume hood. As PHA vapor is an irritant, the fume hood is a necessary part of the entire apparatus. A thin metal ramp, extending from the nozzle of the Filabot, allows the filament to have a controlled descent to the first set of V-wheels. These V-wheels lie on thin, foot-long metal rails and direct the now-cool filament to the diameter gauge. The apparatus used to measure the diameter of the filament is the Filimeasure and has proved itself to be incredibly useful in measuring filament diameter without interrupting the movement of the filament. The final step of the process, and an indicator of a successful apparatus, is a spooled filament. This involves a piece of the assembly that deserves particular acknowledgment — the spooler.

The spooler consists of two upright metal strut channels to serve as the stand for the spooler. Inside the hollowed portion of the spooler is a wooden dowel, cut to the width of the spool, with a metal disk screwed into either side; these disks are themselves attached with two screws to the strut channels. Turning the metal disks provides the torque on the wooden dowel, and consequently the spool, necessary to spool the filament. At this early stage, spooling would be done by hand, but the ultimate goal of the apparatus is to have the spool motor controlled. This control over the spooler, however, hints at an important part of the setup that is still lacking.

This first assembly is currently without any feedback loops. The original design called for feedback loops controlled using simple Arduino circuits. One circuit will provide feedback between the Filameasure and spool and another between the Filameasure and temperature controller of the Filabot. The first feedback will control the rate at which the spooler turns, slowing down if it draws the filament out to thin. The second feedback loop would allow the temperature of the Filabot to be changed depending on the diameter of the filament. If too thin, the filament is likely too hot and the temperature of the Filabot needs to be decreased. Alternatively, if the filament is thicker than the desired diameter at the Filameasure, then the temperature of the Filabot needs to be increased. For future research, a feedback system should be used to control the tension of the spooler based on the diameter value recorded by the Filameasure. The extruder diagram is shown in Figure 4.

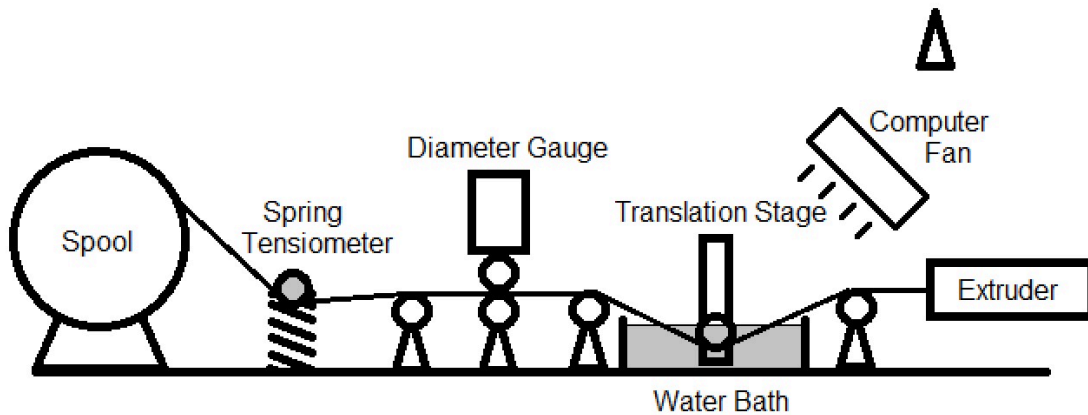


Figure 4: Spooler apparatus. Feedbacks controlled using Arduino circuits would be used to control the rotation speed of the spooler and temperature of the Filabot based on the thickness of the filament measured by the Filameasure.

Future Directions

The ultimate goal of PHA extrusion is to produce a filament that over its entire length has a diameter within ± 0.1 mm of 2.85 mm. That is, the project will be successful when a consistent PHA filament can be created that meets the necessary tolerance of the Ultimaker and prototype PHA panels can be printed. At the end of this project, the PHA filaments extruded will not be in this narrow tolerance. For future efforts with printing PHA filament, it will be necessary to first finish developing a motor-controlled spooler. The motor control will better ensure that the filament is pulled with a constant tension over its length and thus remove the human error associated with pulling and spooling the filament. Current attempts at automating the spooler with a drill motor have been unsuccessful because the spooler spins at 30.3 revolutions per minute at the lowest speed, more than 10 times faster than what is needed. It will be important in future projects to make sure the spooler will spin close to the rate filament is extruded out of the Filabot, which is about 2.86 spooler revolutions per minute. The spooler automation will also be important part of the feedback loops that were introduced in the previous section. With the introduction of feedbacks and automation, PHA filament can be more easily created and thus make the goal of producing PHA panels attainable.