AC 2011-2913: DESIGN AND DEVELOPMENT OF A 3D PRINTER WITH RECYCLING SYSTEM

R. Radharamanan, Mercer University

Dr. R. Radharamanan is currently working as Professor of Industrial Engineering and Director of Mercer Center for Innovation and Entrepreneurship (MCIE) at Mercer University in Macon, Georgia. He has thirty eight years of teaching, research, and consulting experiences. His previous administrative experiences include: President of International Society for Productivity Enhancement (ISPE), Acting Director of Industrial Engineering as well as Director of Advanced Manufacturing Center at Marquette University, and Research Director of CAM and Robotics Center at San Diego State University. His primary research and teaching interests are in the areas of manufacturing systems, robotics and automation, innovation and entrepreneurship, quality engineering, and product and process development. He has organized and chaired five international conferences, co-chaired two, and organized and chaired two regional conferences. He has received two teaching awards, several research and service awards in the United States and in Brazil. His professional affiliations include ASEE, IIE, ASQ, SME, ASME, and ISPE.

Design and Development of a 3D Printer with Recycling System

Abstract

This paper presents the design and development of the Cupcake 3D CNC printer, a special class of machines designed for the automated construction of physical objects using additive layer manufacturing technology. The printer system is great for fabricating parts and designs that are not available on the open market. It prints with Acrylonitrile Butadiene Styrene (ABS), High-Density Polyethylene (HDPE) and Polylactic Acid (PLA) plastics. To print a design, the printer platform moves in the X-Y plane and the extruder along the Z-axis with precision stepper motors while the extruder continually places a small stream of melted ABS. The recycler's addition to the printing system provides a way to reduce cost and make the system more environmentally friendly. A rotating auger bit inside an enclosure barrel forces the particulate down the tube. An electric motor turns the auger which grabs the material to move it down the barrel. Prototype of this design and the 3D printer were fabricated and tested to determine proper functionality.

The 3D printer and the recycling system are currently being used to: teach additive layer manufacturing and rapid prototyping to students enrolled in manufacturing courses; print prototypes for new, difficult to find or expensive parts for research/design projects; and recycle the scrap ABS from the Cupcake 3D printer to a 3 mm filament and reuse it for printing new parts and prototypes. Samples printed using the 3D printer, the advantages of the recycling system, the difficulties encountered during the design and development, and recommendations for future recycling system design are presented and discussed.

1. Introduction

Rapid prototyping (RP) consists of a family of unique fabrication processes developed to make engineering prototypes in a minimum possible lead times based on a computer–aided design (CAD) model for the item[1]. The variety of rapid prototyping technologies arise because product designers would like to have a physical model of a new part or product design rather than a computer model or line drawing[2]. Three-dimensional (3D) printing builds the part in a usual layer-by-layer fashion using an ink-jet printer to eject an adhesive bonding material on to successive layers of powders[3].

The MakerBot Cupcake CNC 3D printer is of a special class of machines designed for the rapid prototyping and manufacturing of physical objects using additive manufacturing technology. The Cupcake is one of many models available in the open source community. The main purpose of designing and developing a 3D printer is to demonstrate additive manufacturing technology to students. The Cupcake was chosen over more reliably printing and accurate commercially available CNC printers because of a very significant price difference. Currently, the most affordable commercial additive fabrication machine is available from Hewlett Packard (HP) and Stratasys called the uPrint personal 3D printer. These HP-Stratasys printers were released in

Europe on April 19, 2010 with a basic price at $14,900[4]. The ABS refills for these machines cost around $200[5]. The MakerBot Cupcake currently costs $750 for the basic kit and 1 lb of ABS filament costs $15 for any color[6]. The initial cost of a MakerBot Cupcake is 5% of the initial cost of the uPrint. Also, the continuing costs of ABS refills are only 7.5% of the cost of refills for the uPrint. This drastic cost difference makes the difficulties involved with using the MakerBot worthwhile[7, 8].

MakerBot uses high quality laser precision cut parts as well as parts fabricated by the Cupcake. The build platform and extruder move with precision stepper motors and the extruder continuously places a small stream of melted Acrylonitrile Butadiene Styrene (ABS). Any model, within the build limitations of 4in x 4in x 6in, generated in a CAD program that exports a Stereo Lithography file (.stl) can be converted to G-codes using Skeinforge[6]. Like most CNC machines, the Cupcake is driven by G-codes. The program ReplicatorG is freeware that is designed to drive the Cupcake. The ReRap (Recycling System for Rapid Prototyping) addition presented is based on an external ABS recovery system that complements the Cupcake 3D printer by converting scrap ABS to a 3mm filament to be used by the Cupcake 3D printer. The ABS recovery system's addition to the 3D printing system provides a way to reduce cost and makes the system more environmentally friendly[7].

The ReRap student team successfully designed, fabricated, and tested the Cupcake 3D printer and the recycling system for proper functionality and use. They are placed in the Mercer University School of Engineering (MUSE) manufacturing lab. There the printer is being used to teach additive layer manufacturing and rapid prototyping to students enrolled in manufacturing courses (ISE370: Manufacturing Processes; ISE425: Computer Assisted Manufacturing Systems) and to create prototypes for new, difficult to find or expensive parts needed for the students' research/design projects. The recycling system is used to convert the scrap ABS from the Cupcake printer to a 3 mm filament for reuse and print new parts.

2. Background

In the year 2005 the RepRap Initiative was launched by Dr. Adrain Bowyer from the University of Bath with the intention to make 3D self replicating machines 'freely available for the benefit of everyone'. The first open source 3D printing machine was released in March 2007 by the RepRap initiative (RepRap.org). Many companies have developed affordable 3D printers and supplies using the information provided from the RepRap initiative. One of these companies is MakerBot, Inc. MakerBot (founded in January 2009) developed a desktop 3D printer called the Cupcake[6]. MakerBot Cupcake number 489 was purchased for the Mercer Engineering Education Entrepreneurship Program.

The ReRap student team[7] researched the 3D printing alternatives to learn about how 3D printing is accomplished, what resources are required to maintain it for the user, and which 3D printing system is the most reliable. One of the major unaddressed concerns of the owners of open source 3D printers was the waste associated with printing and how the waste can be recycled or reused. Even if a print comes out perfectly there are support materials for any overhang structures and a grid that helps the part grip the surface that it is printing on. In the learning process also many misprint can occur (Figure 1).

(a) (b) (c)

Figure 1. Waste in 3D printing: (a) support materials; (b) misprints; and (c) grid material.

The overall learning objectives for the ReRap student team include the following:

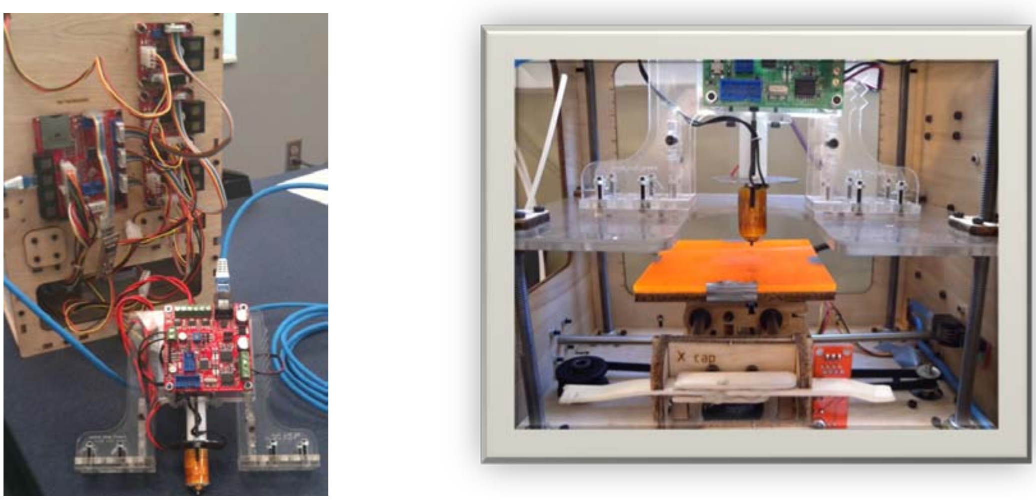
- Design, build, and test the MakerBot Cupcake 3D CNC printer.
- Print prototypes of complex and difficult to machine parts using the 3D printer.
- Design, build, and test a recycling system to convert the scrap ABS from the Cupcake printer to a 3 mm filament for reuse and print new parts and prototypes.
- Install the Cupcake printer and the recycling system in the MUSE manufacturing lab.
- Provide easy to use operating instructions for the 3D printer and the recycling system.

The Cupcake printer and the recycling system will then be used to:

- teach additive layer manufacturing and rapid prototyping to students enrolled in manufacturing courses;
- print prototypes for new and difficult to machine complex parts needed for the students' research and design projects; and
- convert the scrap ABS from the Cupcake printer to a 3 mm filament for reuse and print new parts and prototypes.

3. MakerBot 3D Printer

The MakerBot consists of a wooden frame, a build platform with X and Y pulleys for movement, and a Z platform on which the extruder sits. The extruder, and the X, Y, and Z stepper motors all have a circuit board which is connected to the Cupcake's motherboard (Figure 2).



(a) (b)

Figure 2. MakerBot: (a) circuit board details; and (b) assembly.

Cupcake uses additive technology to form 3-D parts, which is ideal for prototyping and manufacturing a small number of parts. Additive technology allows the capability to print interior structures.

The following steps were taken to achieve successful operation of MakerBot:

- Downloading software
- Testing motors independently for vibration and backlash
- Testing extruder for idler wheel and heater barrel
- Printing: misprints or successful prints

Throughout this process of testing it was necessary to troubleshoot several issues. This involved constantly verifying the assembly by referencing the MakerBot website[6]. Adjustments that are unique to this machine, such as the idler wheel grip, were also determined on an ongoing basis.

Downloading Software

To use the Cupcake, any 3D modeling software that can export a stereo lithography file (.stl) may be used. AutoCAD and ProENGINEER programs can export this file type. Free software for 3D modeling that many in the MakerBot community use is Blender. The software can be found at http://www.blender.org/. The only limitation is that the 3-D model be within the 4in x 4in x 6in build area.

From the stereo lithography file, G-codes are produced. The G-codes drives the machine. To convert the stereo lithography to G-codes, Skeinforge is used. Skeinforge will automatically center a model on the X, Y and Z axes and determine the raft size for the print. It will maintain the same orientation within the X, Y and Z planes. Skeinforge has several settings which can be changed to optimize the performance. The version downloaded was optimized for a MakerBot Cupcake CNC in general, but not adjusted for optimization of this Cupcake machine. ReplicatorG is used to control the machine by delivering the G-codes to print the parts and perform test extrusions. Both ReplicatorG and Skeinforge may be downloaded at http://replicat.org/download. ReplicatorG was downloaded to test the MakerBot Cupcake through its control panel. The G-codes for the whistle was downloaded directly and the whistle was printed successfully. This was the first object printed[9]. The next step was testing Skeinforge. For the rest of the prints, stereo lithography files were downloaded, converted with Skeinforge, and then printed through ReplicatorG.

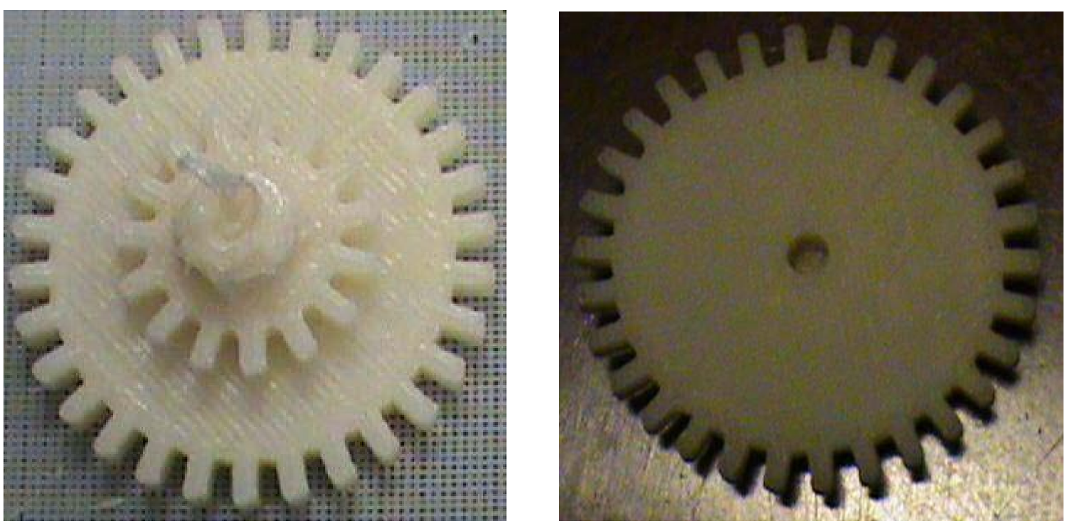
Testing Motors Independently

After downloading ReplicatorG and connecting the MakerBot Cupcake, the control panel was used to test the X, Y, and Z motors. This testing revealed that the X and Y motor control hardware was switched, so the necessary connections were changed so that the motors were all connected to their proper controllers. Further testing revealed that both the X and Y motors were running in reverse. The motors were inverted by using the ReplicatorG software so that after testing all motors moved the correct platform in the correct direction when prompted by the ReplicatorG control panel. To test full functionality of the motors, a simulation print was performed.

Vibration: The G-codes for the whistle was downloaded and a simulation was run to test the motor performance. The extruder was disconnected to isolate the testing to the movement of the platforms. Loud and visible stuttering and excessive vibration were noted during the test run. The tension on the X-direction pulley belt was adjusted and this reduced stuttering. Vibration has continued to be an issue. Vibration decreases precision of the filament placement, so a clean print is not achieved. The inherent vibration of the stepper motors over time loosens the nuts on the pulley system. The pulleys have been repeatedly checked for tension, and adjusted as needed. Lubrication was added to the rods to aid in vibration reduction.

Backlash: Tightening pulleys has reduced vibration, however since one side of the pulley remains slack, there are also backlash issues. A test to determine how much backlash was performed by moving the platform in one direction until it was fully taunted and then reversing direction with a small jog size. The number of steps that were required before the platform moved equated to the backlash distance. It was found that in both the X and Y pulleys there were 0.4mm to 0.5mm of backlash respectively. Research revealed that the Skeinforge default for backlash, which it calls ‘lash’, is 0.2mm[10]. This explains why a cleaner print was not achieved. The pulleys were tightened so that both sides were taunted and have 0.2mm backlash. Each MakerBot Cupcake machine has its own optimal settings, and vibration can further be reduced by determining the optimal pulley tension, resulting backlash, and editing software settings.

An example of how vibration and backlash effects a print can be seen in Figure 3. Backlash is especially noticeable when there are several back and forth movements consecutively, as in the top cylinder on the double gear - Figure 3 (a). The backlash causes the small hollow cylinder to be printed with the extruded material offset from the intended placement. The center hole, which can be seen in the rear view of the gear, was not maintained, and the outer edges of the top are not clean – Figure 3 (b).



(a) **(b)**

Figure 3. Effects of backlash on printed double gear

Testing Extruder

After initial testing of the motors, the extruder was tested independently. First, the physical set-up within the MakerBot was checked. It was noted that the laser-cut openings in the acrylic for the screw heads were too small. This prevented the screws from being pushed in flush and a nut to be attached on the other side for stability. Sandpaper was used to slightly enlarge each hole so that the screw-heads could fit, and when attached, the extruder could be safely bolted for stability, and the vibration of the stepper motors would not cause extruder motion.

Once the extruder was securely attached to the stage in the MakerBot, it was connected to the MakerBot motherboard with an Ethernet cable. The ReplicatorG control panel was used to test the extruder. The temperature was set at 220 degrees Celsius and the NiCr wire began to heat the heater barrel. The temperature measured by the thermistor is also shown in the control panel as "current temperature". Once the control panel indicated that the heater barrel was at operating temperature, the motor was turned on and a filament fed in to begin extrusion. Alignment issues with the feeding assembly caused the filament to have difficulty in feeding, all the way down to entering the portion of the assembly. An attempt to determine if the thermistor was properly calibrated was made. The temperature was raised in 5 degree increments to 240 degrees Celsius according to the ReplicatorG control panel to see if this aided extrusion. The motor idler wheel was aligned properly and the heater barrel was thoroughly cleaned. After all of the above fixes, the extruder was tested and successfully extruded a continuous extrusion without difficulty or manual aid. Since extrusion was achieved, and the motors had been verified to move correctly during a simulation print, the next step was to run a trial print.

3D Printing

The previously downloaded whistle code was loaded into ReplicatorG to be printed. The first thing that must be done before printing is setting the zero point. This is a simple matter for the X and Y axes as the nozzle simply needs to be aligned with the center cross mark on the build platform. The Z position has a greater effect on build performance. Using a piece of paper on the build platform, the nozzle is lowered until the paper cannot be moved. The nozzle is then raised by 0.25 mm, which is approximately half of the extrusion diameter. Next, the print is started by clicking G-code->Build in ReplicatorG. The first thing the program will do is to lift the Z platform and heat the heater barrel to operating temperature. After heating to the proper temperature, a small amount of filament will extrude. Remove this test filament with tweezers, and click 'OK' on the dialog box. The Z platform will then lower and the raft will print. The platform will move in an outer rectangle before beginning extrusion. The initial prints encountered issues, and there were three failed prints before a successful print was achieved.

A whistle was successfully printed as shown in Figure 4. The interior ball did not come free from the bottom wall, and it is possible that this is a complication of the nozzle being too close to the Z platform at the start of the build, or an error in the G-codes. The whistle is a good example to print because of its interior features. The whistle is hollow with an interior ball, which cannot be achieved using a traditional milling machine.

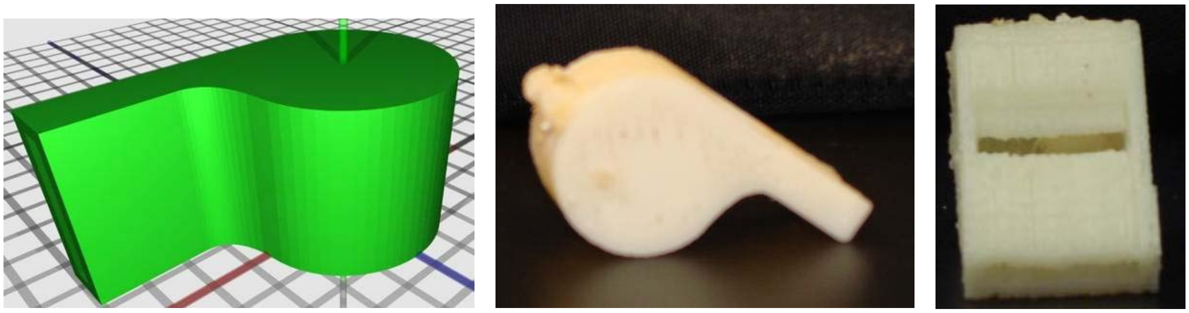
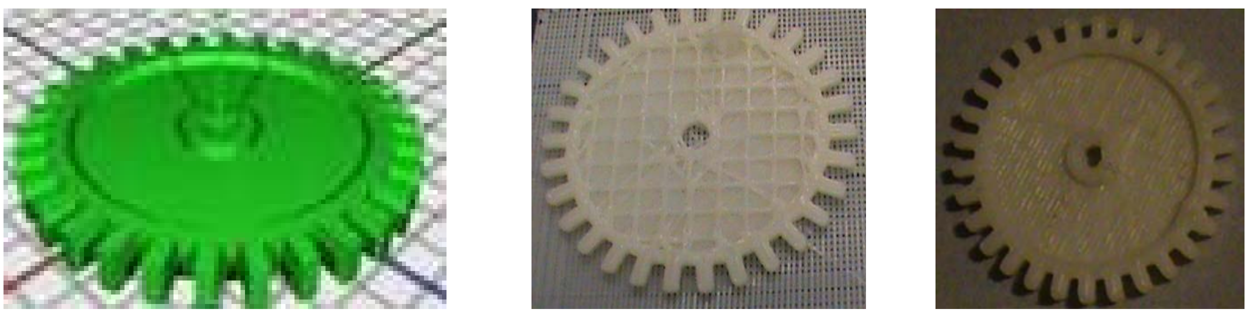
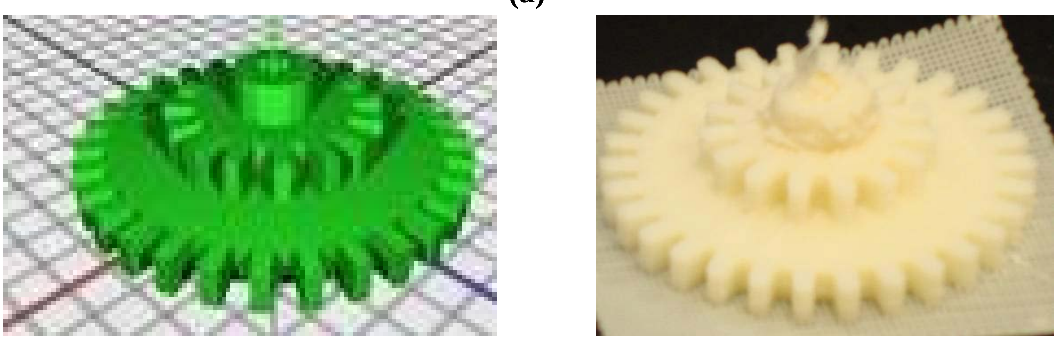


Figure 4. Printed part - different views of the whistle.

For the rest of the prints, stereo lithography files were downloaded from Thingiverse.com. The files were converted with Skeinforge and the G-codes were loaded into ReplicatorG. The gears printed have a hollow honeycomb interior, which reduces use of unnecessary ABS filament. This can be seen in the interior of the gear. Both the single and double gear[11] were printed and different views of the gears are shown in Figure 5.



(a)



(b)

Figure 5. Different views of (a) single gear and (b) double gear.

4. Recycling System Design[7]

The ReRap Recycling System can be broken down into 3 main components; The ReRap Control software, the ReRap Electronics System, and the ReRap Body. The ReRap basically functions by taking in scrap plastic, feeding it down a metal pipe using an auger, heating pipe at one end, and forcing the plastic through a 1/8 inch nozzle. The ReRap is completely controlled with software to make interaction with it simple and user friendly.

The ReRap is optimized for use with the Cupcake 3D printer. There are many plastics which ABS is commonly mixed with to improve certain properties. The ABS mixture that the Cupcake 3D printer uses begins to burn at 250^{o} Celsius. Though ABS is not classified as a carcinogen, all chemicals that compose it are known carcinogens[12]. Therefore a thermal failsafe was implemented to cutoff the ReRap if the temperature goes above 240^{o} Celsius.

The 'brain' of the ReRap is an Atmega 328 microcontroller. The microcontroller communicates with the ReRap Control Software through the USB port of a computer. The microcontroller reads the signals from the thermistors and sends the information to the ReRap TempMon, it controls the motor speed, and it controls the temperature by using feedback from the thermistors. The ReRap TempMon sends the values of the desired motor speed and temperature to the microcontroller. The microcontroller uses the values set by the user to then obtain the desired speed and temperature. The speed and temperature are controlled by pulse width modulation (PWM).

The power supplied to the heater, motor, and heat sink fans comes from a 12 Volt, 10 Amp computer power supply. With all the electronics fully on about 6 Amp of power is used. The fuses are in series on the 12 volt line. The electronics consist of 4 main components: insulated 80/20 Nickel Chromium wire to heat the nozzle area, 100K thermistors to read temperature, DC motor to push plastic through, and fans to increase the efficiency of the heat sink[7].

For both the motor and heater a MOSFET is used to translate the 5 volts PWM from the Arduino into a 12 volt PWM. Due to the earlier stated hazards of temperatures over 250^{o} Celsius, the circuit was carefully designed to never provide power to the heater and motor unless the Arduino (microcontroller) is 'on' and told to run. This way the ReRap will not function unless values are set for the temperature and motor.

The heating element is two insulated 80/20 nickel chromium wires which are secured directly on the 3/8 inch brass heating barrel section. Both wires must be cut the 4.5 ohms for the ReRap to be able to reach up to 240^{o} Celsius. To secure the wire, a Kapton tape is rated to handle up to 260^{o} Celsius was used.

The temperature sensing on the ReRap control system functions by reading the voltage division between resistors. One resistor is a known value and the other is a thermistor. A thermistor’s resistance varies inversely with temperature. The voltage signal is read across the thermistor and put through an analog to digital converter to feed a value to the software that corresponds to the temperature.

To protect the electronics a 10 Amp fuse was added so that a short in a wire will not melt the hardware. The 10 Amp fuse is in series with the thermal switch. It is the 12 volt line from the computer power supply which is opened to turn off the heater.

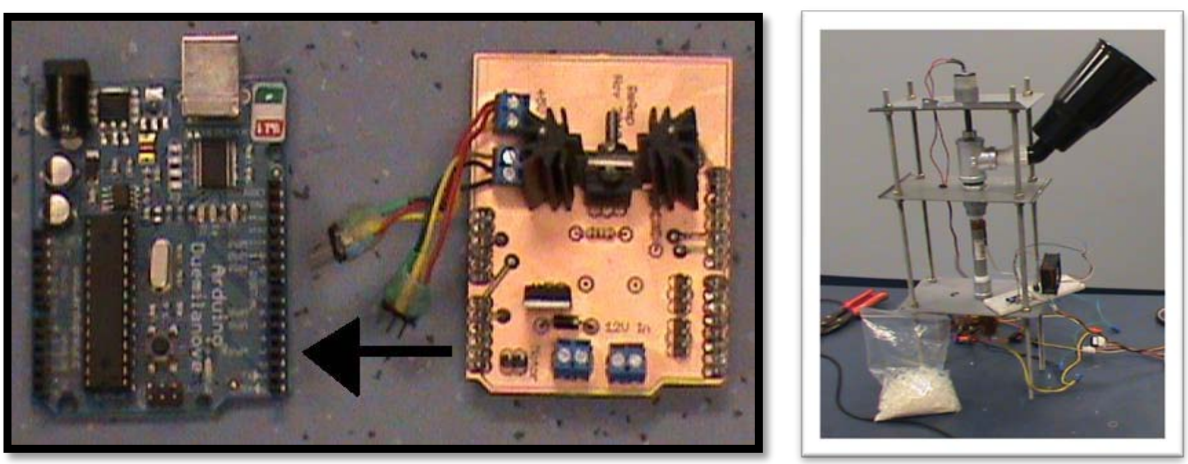
The desired motor characteristics were that it had to have high torque and low speed to slowly apply pressure to the molten thermoplastic and move the plastic down the pipe. The motor chosen is a 12 Volt DC gear motor which has a no load speed of 29 revolutions per minute (rpm).

The ReRap body consists of threaded steel pipe, along with a bevy of other components, which screws together and is supported by 3 sections of sheet steel. The body was intentionally constructed so that it would be easy to disassemble in case troubleshooting is required in the future. Each section of the system may be removed for any reason except for the heated section. The attempted removal of the nickel chromium would remove the insulation from the wire.

The biggest difficulty in forming a working product was the struggle between heating up the nozzle and brass nipple while still maintaining a room temperature environment in the barrel that the ABS travels down. Due to axial heat conduction from the brass nipple to the steel nipple barrel, it was hard to apply heat to just one area as the surrounding area where adversely affected. In fear that the heating the steel nipple at all would gunk up the assembly and cause blockage, a decision was made to apply heat sinks. The problem is the heat sinks dissipated large amount of heat and created too much of an area for the heat to conduct to. This increase in area caused the overall temperature to go down and the system would not reach the desired temperature of 240^{o} Celsius.

Another problem the design team came across was trying to determine the properties of the thermistor which was used for temperature measurement. Ultimately, since the manufacturer provided no specifications or details about the item, it was tough to determine the characteristics of the thermistor and difficult to find other sensors to compare it to. In the end, a thermocouple of one of the digital multi-meter was used to form a range for the thermistor and this was extrapolated to the operating temperature needed for the design.

Some parts that were made entirely out of scrap metal were the two thermal switch mounts, the two heat sink mounts, and the five thin plates for the body of the machinery. The auger had to be physically altered in order to directly mount it to the motor. In total, ten mechanical parts were either altered or constructed for this design.



(a)Arduino and ReRap board **(b) Extruder for recycling**

Figure 6. Recycling system to convert the scrap ABS into a 3 mm filament[7]

The following changes were made to the ReRap to bring the extruder up to temperature. First the heat sink was completely removed. One fan from the heat sink was used to keep the barrel cool. Also the barrel size was reduced from ¾ inch to ½ inch. Consequently A half inch to half inch coupling and a half inch to ¾ inch coupling were purchased to fit the ½ inch barrel to the extruder. In edition a thin Teflon coating was applied at all joints where heat conduction was undesired. The Arduino and ReRap board and the final functional extruder built and tested to convert the scrap ABS to a 3 mm filament are shown in Figure 6.

5. Conclusions and Recommendations

The Cupcake has been brought to operational status, successful prints were achieved, and user instructions were written. The equipment is sensitive and can easily be damaged by misuse, so use of the Cupcake should be closely monitored. Since the software is Beta, failure of or damage to the machine can occur due to glitches. There are several opportunities to improve the MakerBot Cupcake in the future.

The current solution for converting scrap ABS into 3 mm diameter filament is a screw fed system with sensors monitoring the temperature of the ABS. The components that make up the system function as they should separately. The completely assembled solution is able to obtain target temperature and maintain a temperature within 15 degrees of the range. The ReRap team believes the auger fed extruder system still provides the best solution for recycling the reusable ABS. This device functions but does not produce a filament continuously because the device has trouble reaching the required temperature. Future revisions of this machine should have a more powerful heater that is removable without compromising the heating element. The code for maintaining constant temperature should be further optimized to stay nearer to the target temperature. A better power supply should be used for ease of use. The current screw extruder could still provide an excellent teaching tool for a classroom setting as it showcases the workings of common plastic extrusion processes.

The purpose of this project was to improve upon the MakerBot 3D printer and after working with the printer the ReRap team has more ideas on alternative ways to improve the 3D printing system. First, build a more reliable extruder for the Cupcake 3D printer. The current extruder model has a high failure rate and is often in need of troubleshooting. The ReRap team suggests development of an automated printing system that is capable of printing parts in succession. Currently the user must remove the part by hand and go through a 5-10 minute process between printings. A laser could be added for auto position of the extruder at the origin point slightly above the building platform. A vast number of modifications could be made to improve reliability, ease of maintenance, and add functionality.

The learning objectives of this project were successfully accomplished by the ReRap student team: MakerBot Cupcake 3D printer was built and tested; prototypes and complex parts were designed and made; recycling system was built and tested for processing scrap ABS and extruding 3 mm filament for reuse in the 3D printer; and the Cupcake 3D printer and the recycling system were placed in the MUSE manufacturing lab for teaching additive layer manufacturing and rapid prototyping to students enrolled in the manufacturing courses and print prototypes for senior design projects and research projects.

The MakerBot Cupcake 3D printer has already been used by a number of student teams working on their senior design/research projects to print their parts and prototypes. A lab module on 3D printing and rapid prototyping has been developed to introduce additive layer manufacturing and rapid prototyping to engineering students enrolled in the manufacturing courses. The feedback from the students were positive and a 3D scanner has been purchased to provide training to engineering students in 3D scanning, 3D printing, and reverse engineering. The added lab facility helps to enhance the hands-on rapid prototyping experience to engineering students at MUSE.

References

[1] Groover, M. P. (2002), Fundamentals of Modern Manufacturing: Materials, Processes, and Systems. 2nd Edition, John Wiley & Sons, Inc., New Jersey.

[2] Pham, D. T. and Gault R. S. (1998), A Comparison of Rapid Prototyping Technologies. International Journal of Machine Tools and Manufacturer. Vol. 38, pp. 1257-1287.

[3] Kochan, D. C., Kai, C. C., and Zhaohui, D. (1999), Rapid Prototyping Issues in the 21st Century. Computers in Industry, Vol. 39, pp. 3-10.

[4] Stratasys, Inc. uPrint Personal 3D Printer. (2010) Retrieved from http://uprint.dimensionprinting.com/ppc/?adver=google&type=cpc&camp=google_Printing_3D_Printer&gclid=CODW0cvzlqMCFQ4TswodbzgntA

[5] Palmisano, John. (2010). 3D Printers Go Mainstream. Retrieved from http://spectrum.ieee.org/automaton/consumer-electronics/gadgets/3d-printers-go-mainstream-with-hewlett-packard

[6] MakerBot, Inc. (2010). Build Instructions. Retrieved from http://wiki.makerbot.com/cupcake-cnc-0:build-instructions

[7] Dawson, S. N.,Coonce, A. M., and Cox, L. J. (2010), Recycling System for the Cupcake 3D Printer. Critical Design Review, School of Engineering, Mercer University.

[8] Dawson. S. N., and Wheeler, C. (2010), Report on: “Rapid Prototyping”. Independent Study, Mercer University School of Engineering, Summer 2010.

[9] Zaggo. (2009). Whistle by Zaggo. Retrieved from http://www.thingiverse.com/thing:1046

[10] BitefromBytes. Skeinforge Lash. Last edited on 31 January 2010. Retrieved from http://www.bitsfrombytes.com/wiki/index.php?title=Skeinforge_Lash

[11] Catarina. (2009). OpenSCAD Spur Gears by Catarina. Retrieved from http://www.thingiverse.com/thing:1336.

[12] PVC Alternatives Database. In Greenpeace.org. Retrieved 02:49, January 18, 2010, Retrieved from http://archive.greenpeace.org/toxics/pvcdatabase/bad.html