ABS Plastic Cannot Be Recycled Infinitely;
Chemical and Mechanical Analysis of Recycling 3D Printing ABS

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Executive Summary

3D printing technologies allows for rapid prototyping using extruded polymers to create complex shapes. The nature of 3D printing creates waste in the form of failed parts and support material.

Recycling the waste from 3D printing reduces the cost of production and lowers the amount of polymers entering the environment.

ABS (Acrylonitrile Butadiene Styrene) is common in both 3D printing and larger scale manufacturing, which is the focus of this research. Recycling ABS in 3D printing additionally gives insight into larger scale recycling.

Samples were created with 3D printing to be tested and recycled with thermomechanical extrusion. The recycled ABS was then printed and tested again to analysis mechanical and chemical differences.

Mechanical testing included Tension Testing and Density Measurements, with chemical analysis being conducted with Fourier Transform Infrared Spectroscopy and Melt Flow Index testing.

Recycling the ABS polymer caused ultimate strength and Young’s Modulus to decrease, with the elongation before break and fracture strain to increase.

Chemical analysis revealed reductions in absorption peaks from the breaking of bonds and chemical reactions yielding IR inactive species. Melt Flow Index testing demonstrated a decrease in viscosity.

The change to the ABS polymer after recycling does have worse properties than virgin material. The use of recycled ABS in blends is still viable for manufacturing at any scale.

Tests into the additives and the effect of further recycling will improve the understanding as to the ways that recycled ABS can be used.

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Introduction

Polymers are integral to modern manufacturing technologies as replacements to metal, wood, and ceramics. Polymers are favorited for myriad reasons over the aforementioned materials and have had ever-expanding use cases since the 1950's (6). In this time, more advanced polymers with favorable properties like extended lifetimes have created a growing problem of waste. The ubiquity of polymers in all aspects of life has only supercharged the problem. Recycling is an obvious solution as already used for materials like glass and metal, the unique chemistry of polymers makes recycling challenging.

The focus of this investigation was to study the effects of recycling on the properties of the polymer to assess if using recycled polymers is feasible.

To keep this investigation narrow and specific, Acrylonitrile Butadiene Styrene was chosen for its use in a variety of applications. Additive manufacturing, specifically fused deposition modeling, was the manufacturing technology used. Additive manufacturing exists in the intersection of hobby and industry, with similar materials and processes. Using ABS with fused deposition modelling enables rapid testing and iteration of the methodology (10).

Mechanical testing was used to assess the tangible changes that recycling has on the end product made with recycled material. Tensile testing was used to primarily determine the changes in ultimate strength and Young's Modulus after recycling. Secondary mechanical tests included density and melt flow index. Density affects the viscosity of the molten polymer during injection molding and additive manufacturing, which is directly assessed with melt flow index testing.

Chemical tests were conducted to explain why changes to the mechanical properties occur during recycling. Fourier Transform Infrared Spectrocy was used to quantify any changes to the chemist that occur during additive manufacturing and the recycling process.

The nature of this investigation was a preliminary quantification of changes to determine if further investigations would expand the knowledge surrounding the use of recycled polymers in additive manufacturing.

Background

Additive Manufacturing

Additive Manufacturing is a catch all term that encapsulates various technologies that produce parts by stacking individual layers of material on top of each other to create objects that could not otherwise be manufactured with traditional subtractive manufacturing. Additive manufacturing is most commonly known as 3D-printing and carries a connotation of desktop systems that take plastic filament and extrude it onto a build surface, which does not fully reflect the vast capabilities of additive manufacturing. For this investigation fused deposition modelling is used, meaning the distinction between technologies is moot. Fused Deposition Modelling, or FDM, is the stereotypical desktop machine used by hobbyists and industry alike. A 3D printer is fundamentally a three-axis motion system with a motor driven, self-heating extruder which heats a plastic filament to its molten temperature before depositing the molten filament onto the build surface or previous layer. 3D printing is the most accessible manufacturing technology, with entry level machines retailing for less than $200. The major appeal of 3D printing is three-fold, the cost is low, the technology can produce part not otherwise possible, and the time to make a part is hours instead or months or weeks. The two major drawbacks of 3D printing are the limitations of available material types, and the layer-by-layer nature cannot produce a part that is exact in strength to an injection molded part of the same material (11). The process of 3D printing starts with a 3D model, whether it's a file downloaded from the internet or created in computer-aided design, that model file is imported into a software which slices the 3D model into layers and encoded the instructions into a language that the 3D printer understands. The 3D printer is loaded with material and the print is started. 3D printing and other additive manufacturing processes are indispensable tools to production, R&D, hobbies, decentralized manufacturing, and an ever-growing list of applications.

Waste in Additive Manufacturing

Additive manufacturing produces substantially less waste than traditional subtractive processes, as material is precisely added where it is needed. Additive manufacturing still produces waste in the forms of failed parts and sacrificial material. One of the unique challenges of 3D printing is putting material on top of air. The molten polymer is prone to droop if insufficiently supported. To combat this, sacrificial material is used to support the molten polymer as it cools and solidifies, which is removed and discarded after the part has finished printing. The most common form of sacrificial material are supports, which take on a few different forms but ultimately are discarded. For highly complex geometries with material that overhangs the previous layer, supports are essential to the success of the print. These discarded parts could serve a second life if recycled.

Acrylonitrile Butadiene Styrene (ABS)

ABS plastic is a common thermoplastic used for its mechanical properties, versatility, toughness, low cost, and dimensional accuracy. ABS resins, like those used in the production of 3D printing filament are comprised of three distinct phases: polybutadiene rubber nodules, styrene acrylonitrile matrices and styrene acrylonitrile grafted polybutadiene (9). Each of the monomers plays a specific role, which together are stronger than the sum of its parts. Styrene is used for its rigidity and processibility. Acrylonitrile is used for its chemical resistance, from the carbon nitrogen triple bond and good thermal properties. Finally, Butadiene is used for its rubber toughness, impact resistance and as the backbone of the polymer. Different combinations of monomers determine the properties of the final product.

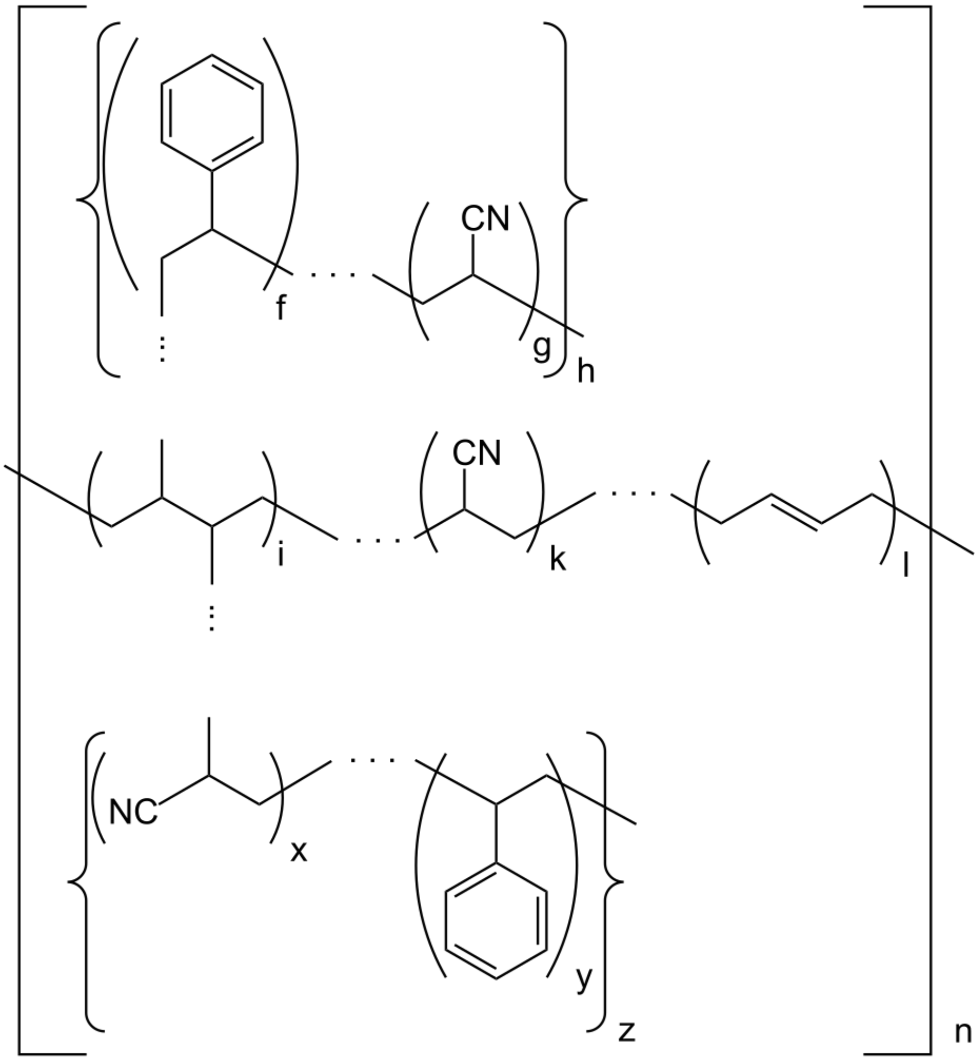

Figure 1: Common bonding motif between the different monomers

Literature Review

Several studies in the past seven years have investigated the effect of recycling on ABS used for 3D printing. Each found that the mechanical properties of ABS degraded after being recycled.

A joint study from several Australian institutions tracked the differences in thermomechanical properties between recycling processes found changes to the physical structure which reduce the melt flow index, an increased the glass transition temperature. They also found that the recycled ABS had continually worsened tensile and compressive properties for each recycling iteration. In their FTIR spectra, they found an increase in the formations of carbonyl groups, which they suggest is evidence for thermal oxidative breakdown of the monomers (10).

The only study investigating the impact of recycled ABS in 3D printing came from Karlsruhe Institute of Technology which focused on evaluating the thermomechanical degradability of multiple iteration of recycling on ABS for 3D printing. The researchers only investigated the mechanical properties of the recycled material, where the Australian study conducted chemical analysis in addition to the mechanical testing. They found a similar decrease in the tensile properties of the recycled material over the virgin material. In contrast to the previous study, the researchers argue that no major chemical changes are occurring despite doing no chemical analysis (1).

These two studies focused specifically on ABS recycling in 3D printing, but studies conducted using other polymers, namely PLA, also found similar results to the two studies using ABS (2).

Methods and Materials

Material Selection

ABS is becoming a less common material in the realm of 3D printing in favor of other materials with better mechanical properties or which are easier to use. ABS was the most common material used in the early years of non-commercial/DIY 3D Printing for its accessibility and range of colors. ABS has ultimately been dethroned in popularity by PLA and PETG as both do not require special heated beds and heated chambers and both PLA and PETG are less hazardous to print. ABS can be hazardous to 3D print with because of the fumes produced as the ABS heats up and some of the monomers become hot enough to volatize or are emitted as fine particulate (7).

ABS has some remaining staying power as it costs less than PLA or PETG, owing to the large production of ABS resin worldwide. ABS has also found a niche for making figurines and other boardgame characters as ABS can be vapor smoothed with acetone.

ABS was selected for this investigation because of the intersection between additive manufacturing and conventional manufacturing and complexity of the ABS chemistry made changes to the chemistry more obvious than polymers comprised of only one monomer.

The specific ABS filament used was Raise 3D’s Hyperspeed ABS V1 filament in natural coloring. It is advertised to be optimized for 3D printing by tuning the molecular weight and limiting stress causing temperature gradients in the material.

Sample Design and Considerations for Additive Manufacturing

The testing samples were designed in accordance with ISO 527:2-2012 1A specimen parameters (3). The 1A specimen parameters are intended to be used for injection molded test samples but was used as the other specimen types are used for metals or other dissimilar materials (4). Fusion 360 was used to create a 3D model of the test specimen which was exported into Simplify3D in the next step. One notable change made was the inclusion of text markings denoting relevant information used for sorting. This did not effect testing as force was not applied to the areas with text debossed into the surface.

Three orientations were initially created to investigate the impact of layer orientation on strength. Only the design which printed flat against the build plate with the thickness being added with subsequent layers was chosen as the other orientations did not have enough adhesion with the build plate and would fail mid-print. The chosen orientation has the best strength as the layer orientation is such that the tensile forces pull along the layers instead of pulling the layers apart as would happen with the other orientations. Producing the test samples as specified best demonstrates the changes in the ABS as it is recycled and not the geometry and production downfalls associated with additive manufacturing.

Layer orientation affects how stress is distributed within a part, as a 3D printed part is non-homogeneous like an injection molded part is. Designs intended to be produced with additive manufacturing are done so that compressive and tensile forces are parallel to the layer orientation and shear forces are perpendicular to the layer orientation. The intralayer cohesive forces are stronger than the interlayer cohesive forces (7).

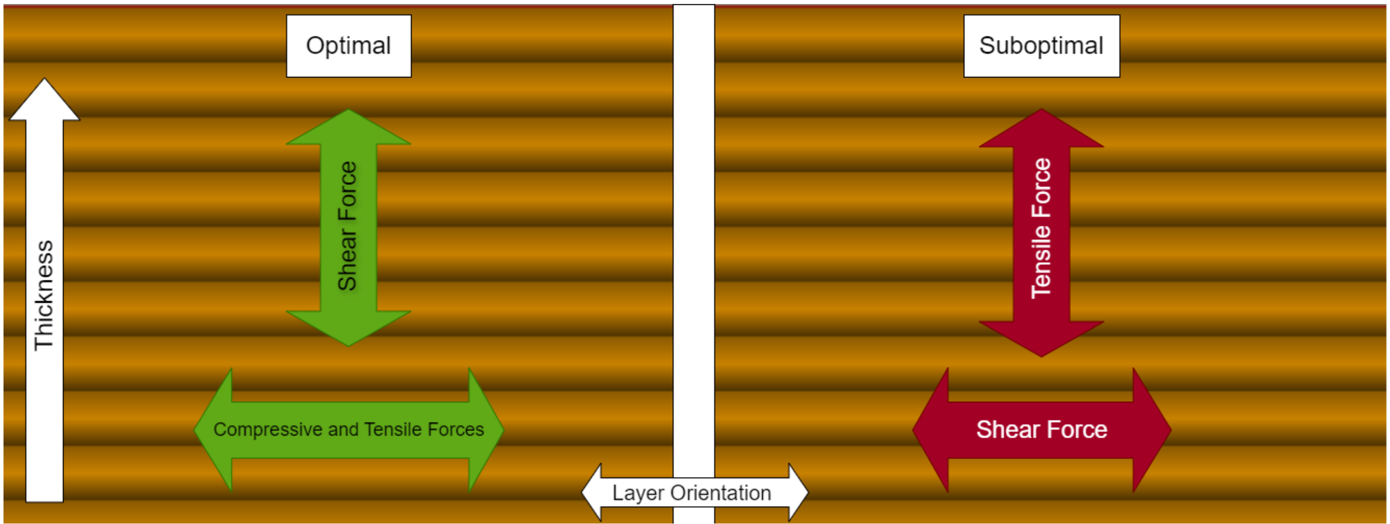

Figure 2: Visual representation of best practices when designing parts to be produced with additive manufacturing

What this means is that 3D-printed parts fail between layers as the force required to break the interlayer bonding is substantially lower than the force required to intralayer bonding.

Complicating the matter further is different features within a layer. The typical composure of a single layer is the perimeters and in fill. Conventional printing deposits the outer most perimeter first, followed by any other inner perimeter, before depositing the infill. Meaning that the individual features are also subject to the lower cohesive force joining them together.

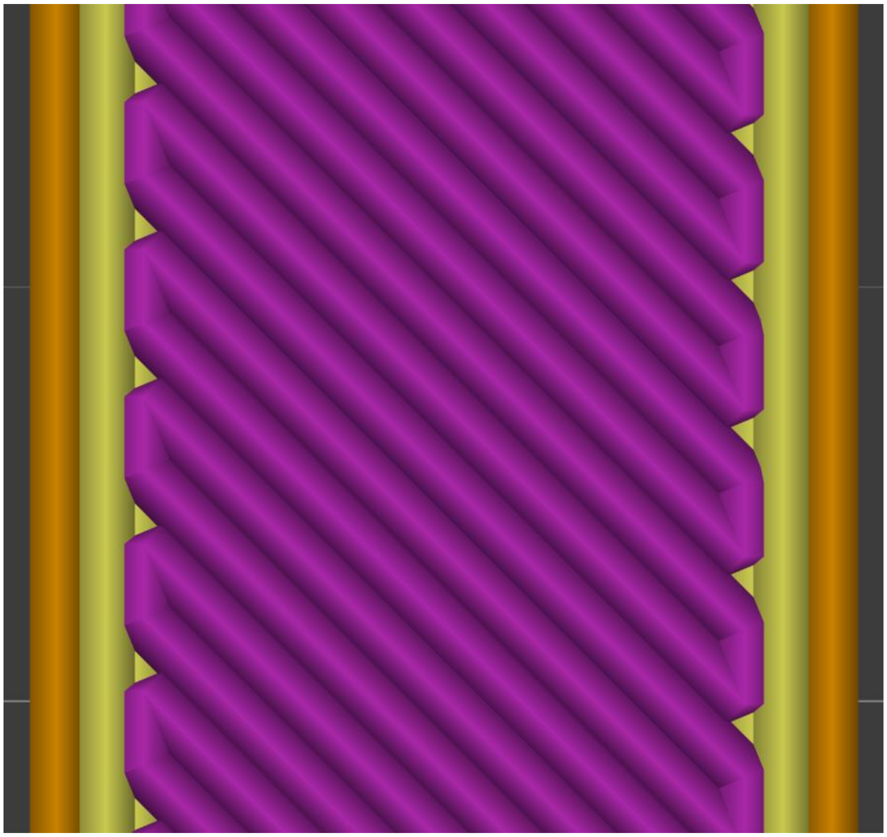

Figure 3: Different features within a single layer. The orange and yellow lines represent perimeters, and the purple represents the infill.

To maximize strength, two techniques are used: overlap and extrusion width. Overlap is a setting that moves the print head slightly into the adjacent feature so that new material is forced into contact with preexisting material. Extrusion width is the primary setting used to maximize strength, it does so by extruding more material than is necessary such that the extra material is forced into any gaps. Both overlap and extrusion width need to be tuned carefully as too much extra material will decrease the dimensional accuracy of the finished part. The following section describes specifically how the test samples were made for this investigation.

Print Parameters

Setting Print Parameters up correctly is the most important step, as these settings define every movement and action that the 3D printer makes. The only two issues that print parameters cannot fix are bad geometry in the design and failure to correctly set up the printer. While the impact of print parameters cannot be understated, changing and tuning is not a daunting task. The first step is exporting the design file as a mesh, usually an STL, and importing that file in a piece of software known as a slicer. The slicer is the bridge between the digital and the physical, it takes the mesh file and slices it into individual layers following the print parameters. Simplify3D was used because the printer used to make the parts utilities a proprietary, and frankly obnoxious, version of the industry standard g-code called x3g, which is used by MakerBot manufactured 3D printers. Simplify3D has a feature which automatically converts g-code into a .x3g file, which was uploaded to the 3D printer with an SD card.

There are four settings categories that are of concern for the vast majority of projects, they are: temperature, layer, infill, and speed.

Temperature settings include the extruder temperature, build plate temperature, and part cooling fans. Extruder temperature is dependent on the material being used; PLA is a common polymer which requires an extruder temperature anywhere from 150 – 180°C, whereas ABS requires 210 – 250°C. Filament manufactures will specify a temperature range on their product. 3D printers that include heated build plates allow for the bottom of the printed part to be heated to limit the temperature differences between layers, this aids in the prevention of warping or curling. Warping of the edges of a part while printing leads to the detachment of the part form the build plate, leading to failed prints. ABS is notorious for warping, which is one of the major reasons that ABS is less common than other materials for additive manufacturing. The last setting in this category is cooling fans, which rapidly cools the freshly deposited material so that it is firm enough to hold shape before material is deposited on top. For the production of test samples for this investigation, an extruder temperature of 235°C, build plate temperature of 110°C, and the cooling fan set to 60 percent of max speed. 3D printers that support build plate temperatures of 80°C or more are not common as electronics and building materials gets more expensive in order to support such a high temperature.

The layer settings group has four important settings: layer height, perimeters, and upper and lower solid layers.

Layer height sets how thick each layer is, usually this is no more than 80 percent of the nozzle diameter. Layer height is the most important setting as it affects the time to print, strength, and resolution stronger than any other slicer setting. More layers massively increases the time to print, increases the strength of the final part, and improves the accuracy of the final part. There are no hard and fast rules when it comes to layer height, knowledge of how to optimize layer height comes from years of experience, which is true of the other layer settings.

Perimeters describe the number of continuous outlines of the outer edge of the design are down. Perimeters are important because the continuous nature aids greatly in the strength of the part as the forces are directed away from the weak connections between layers and features. The requirement for strength determines the number of perimeters, with more perimeters greatly enhancing strength and rigidity but consequently increases the time to print and material used. Two perimeters was used for making the test samples to optimize the time to print. For normal applications, three or four perimeters for functional parts and two perimeters for nonfunctional parts is recommended.

The last two settings in the layers group are essentially the same, top, and bottom layer count defines how many layers of solid material encapsulate the less dense infill. The top and bottom layer counts slightly affects strength, but more so affects the aesthetics of the finished part. More solid layers yields a flatter surface at the expense of more time and material. There were no wrong choices for this investigation, so three solid layers for both the top and bottom was used. Depending on the slicer used, the layers category may contain width settings, used to fine tune part strength.

Infill settings define how the less dense innards of the part are created. The two important settings are the infill density and the infill pattern. Infill density is represented as a percent of the theoretical completely solid layer. A higher infill density creates a pattern which is more polymer than air, and the inverse is true. The effects of infill on strength are a strongly contested debate, experience says that a higher infill density is needed when a part contains layers which are printed across large gaps. The only other need for a high-density infill is to add strength to part with small cross sections. Infill pattern is also a contested subject, with no bad options. The most common, currently, are gyroid, rectilinear, and honeycomb. Due to the stiffness of most thermoplastics, like ABS, the infill pattern is inconsequential for the average project. This investigation utilized a 100 percent rectilinear infill with each layer being rotated 45° from the previous layer. These settings maximized the contact area between each layer and eliminated stress risers which would happen with an aligned infill.

Speed is the last settings group to discuss, it is fairly straightforward and dependent on the 3D printer itself and the material being used. More sophisticated slicers automatically adjust speed based on the geometry and type of features of the layer, but all slicers will have a default speed setting. The default speed is dependent on the motion system, rigidity, and electronics of the 3D printer. Default speed is also slightly dependent on the material being printed, with materials with high viscosities limits the speed, like TPU filaments. The manufacture of the 3D printer usually specifies operation speeds and filament manufactures might provide speeds optimal for that specific material. A default speed of 3600 mm/min was used with perimeters being printed at half speed and infill being printed at 80 percent speed.

The setting used to produce the test samples closely followed default settings from the filament manufacturer, Simplify3D, and common heuristics.

Part Production

All parts were made with a Flashforge Creator Pro, which is a MakerBot Replicator style printer which includes a top shroud to improve the printing performance of ABS and Nylon filaments.

Figure 4: Flashforge Creator Pro. https://www.flashforge.com/product-detail/flashforge-creator-pro-3d-printer (accessed 2023-09-26)

The important characteristics of the Creator Pro are the enclosed print volume and the ability to heat the aluminum build plate up to 110° C. These are vital to the successful production of the ABS parts because ABS warps due to temperature differences in the individual layers. As ABS cools, the polymer tries to contract in all three dimensions and is prevented from doing so by the adhesion of the part to the print bed. To aid with adhesion, a layer of painter's tape coated with PVA glue stick was used.

While seeming rudimentary, this technique has been used for nearly twenty years to great success. The painter's tape has a rough and porous surface which massively increases the contact area between the build plate and the part. The greater the adhesive force, the chance for contraction and failed parts decreases. Further adhesiveness can be achieved with basic PVA glue sticks. PVA glue sticks exhibits two favorable properties which explain its pervasiveness in 3D printing. Firstly, at high temperatures, like the 60°C build plate, the PVA glue melts and provides more adhesion than is possible with only the painter's tape. The second, lesser discussed property, of PVA glue is after being heated during the printing process and allow to cool back down to room temperature it will contract and unstick itself from the part. PVA glue being extra adhesive during the printing process and only slightly adhesive at room temperature, aiding in the removal of the part makes PVA glue indispensable. One layer of painter's tape is laid down on top of the aluminum build plate, minimizing the gaps between the adjacent pieces, and PVA glue stick is applied liberally while the build plate is set to 50°C. Applying the glue to the hot build plate speeds up the drying process as applying the glue to a cold build plate will pick up any particles and compromise the adhesiveness.

The combination of a heated build plate, heated build chamber, painter's tape, and PVA glue stick gives the best chance for success while printing with ABS. ABS is one of the most difficult materials to use without taking the proper steps to ensure the greatest level of adhesion between the part and the build plate and minimizing the temperature differences between the layers to prevent warping.

After the parts were printed, the chamber door was opened, and the top shroud was removed to hasten the cooling of the part back to room temperature. Allowing for the parts to cool to room temperature lets the PVA glue to unstick from the part and, more importantly, completely solidifies the ABS. Being impatient guarantees that the soft ABS will deform when removing the parts from the build plate, typically ruining the part.

To remove the part from the cooled build plate, a spackle knife with a sharpened edge can be carefully used to get under an edge of the part to lift and pry the part off the build plate. Often with a sharpened spackle knife the blade will cut and dig underneath the part and the painter's tape, removing sections of the tape. When this happens, because it happens a lot, the damage tape needs to be replaced following the same procedure as previously described. The finalized parts are labeled and bagged for use with the traction tester.

Tension Testing

Tension testing was the primary method for analyzing the changes in the mechanical properties of the recycled ABS, the properties of interest tested with the traction machine are the Young's Modulus, Ultimate Strength, Elongation Before Break, and Fracture Strain. The traction machine used was a Shimadzu AGS utilizing the ISO 527-1:2019 and ISO 527-2:2012 standards for the determination of tensile properties (4) (5). A strain gauge extensometer was used to accurately determine the elongation in the liner, elastic phase so the measurements for Young's Modulus and Ultimate Strength were as accurate as possible. As 3D-printed parts are not as strong or consistent as injection molded parts, the process used deviates from the recommend settings in the following significant ways: the max force was reduced from 10 kN to 3 kN and the separation speed was reduced from 50 mm/min to 5 mm/min (4) (5). Slower speed and lower force were necessary as the 3D-printed samples failed before the machine could begin to plot the force-displacement graph at the recommended settings. As discussed in the part production section, the bonding between individual layers in 3D-printed parts pales in comparison to the uniform bonding in all three dimensions possible with injection molding and other manufacturing techniques. Consequently, the number of sample runs required to confidently determine the tensile properties of the 3D-printed parts was increased from five to 15. The force-displacement curve was exported as a CSV and analyzed in Veusz. The values for Young's Modulus, Ultimate Strength, Elongation Before Break, and Fracture Strain was calculated using Shimadzu's Trapezium, which took the data directly from the traction tester.

Granulation

The first step in recycling the polymer back into usable filament is to grind the printed parts into small granules. The granules are fed into an extrusion machine in a later step. The extrusion machine works best with granules of less than 8 mm in any direction, but particles less than 3 mm can clog the extrusion machine and not melt correctly, leading to issues in the final product. The grinding was carried out with a low-speed grinder to limit the amount of heat buildup in the polymer. The dog bone testing samples were fed into the grinder and allowed to be crushed into small enough pieces to be pushed into a hopper to be vacuumed out. The first run of the parts through the grinder yielded inconsistently sized granules. Those first-run granules were fed back into the grinder and yielded consistent granules.

The granules then needed to be dried as attempts to extrude filament directly after grinding creates bubbles in the filament and rendered it unusable. The problems with moisture in the filament plagued the research for weeks, the process of chasing down the issues caused by the hygroscopicity of ABS is further discussed in the trials and tribulations section.

To dry the granules before extruding new filament, an oven was used to drive the water from the polymer. The granules were spread thinly on a baking sheet and placed into the oven for 4 hours at 80 degrees Celsius. The now dry granules were removed from the oven and placed into a bag before being brought to the extrusion machine.

The drying step is vital to the recycling process as any water trapped in the polymer can create steam bubbles when melted in the extrusion machine, creating an inconsistent extrusion of filament, or breaking the continuous strand required for 3D printing.

Extrusion

To produce new filament from the granules, a purpose-built extrusion machine built by Lucas Brunisholz was utilized. Lucas built the extrusion machine to process polyethylene and PLA plastics into 1.75 mm filament for use in most 3D printers for his master's thesis. Part of the research effort was to evaluate his machine with higher melting point polymers like the ABS used. The extrusion machine takes granules or pellets into a hopper and pushes the polymer through a heated tube with a specially designed extrusion screw driven by a stepper motor. The polymer is heated to the melting point as it reaches the extrusion nozzle. The newly extruded filament goes through a system of rollers and fans to cool the filament without completely solidifying before being fed through a winding system and fed onto a spool. The spool is driven by a motor to control the rate and tension that the filament is wound onto the spool. Lucas built an incredible machine that is on par with the performance of commercially available products of the same size. The extrusion machine performs best with polymers with a melting point around 150°C like polyethylene or PLA and struggled to produce reliable results with ABS, which had a functional melting point of 240°C.

Three important factors controlled the result of the filament: temperature, rate of cooling, and tension.

Temperature is controlled with two PID controlled heating elements set by the user. The rate of cooling is controlled by turning on five computer fans that the filament passes through. Commercial filament production uses heated water baths to precisely control the rate of cooling and the temperature of the filament. Cooling by fans is more of an art than a science to produce filament soft enough to be pulled into a consistent diameter and be wound on the spool without causing stress in the filament.

Tension is controlled by adjusting how quickly the filament is wound onto the spool at the end of the process. Tension is important to shape the filament down to 1.75mm and to pull the filament into a circular cross section. Commercial filament is typically within a dimensional accuracy of ±0.05 mm, filament too large is liable to get jammed while printing and any filament too small cannot be grabbed by the extruder on the 3D printer. Dimensional accuracy was the largest problem with using ABS in the extrusion machine, with the best filament produced having a dimensional accuracy of ±0.23 mm. This was due to the reliance on the speed of the winding spool to produce enough tension to pull the filament into shape. If more polymer was pushed out of the extruder suddenly, the filament would get thicker, and the system could not pull enough tension to compensate. The opposite was too if too little filament was extruded and the filament could be weakened and brake, which it did a number of times.

After two weeks of tuning the various parameters, A consistent result was achieved. Using a temperature of 238°C on the heated extruder, high speed spooling, and no active cooling yielded filament was mostly usable. Some sections of the filament could not be extruded with the 3D printer, which caused parts produced with the recycled filament to fail during production. In total, 15 testing samples were made from the recycled filament and tested.

Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) was used to assess the possibility of chemical change that could occur in the polymer when printing parts and when the polymer is re-extruded by means of a screw extruder. Infrared spectroscopy was chosen as the chemical bonds that make up the ABS filament have vibrational modes that can be detected by the technology. Specifically, FTIR Attenuated Total Reflectance (ATR) spectroscopy was used as solid samples would need to be dissolved for traditional FTIR technology. Dissolving the samples for traditional FTIR risked side reactions which would skew the results. A Bruker Alpha II with ATR spectrometer was used with the permission and supervision of the Chemistry department of the Haute école d’ingénierie et d’architecture de Fribourg. The samples were sections of virgin filament and recycled filament as well as sections of dog bone samples to record the difference between each step. These samples allowed for insight into the extent that the ABS polymer underwent thermal changes from virgin filament from the manufacture, the changes that occur when 3D printing, changes after being recycled back into filament, and the changes that the recycled filament undergoes after being printed into the dog bone samples. The results between the dog bone samples printed from virgin filament and recycled filament are emphasized as the spectra from the filament samples exhibited anomalous reading which arouse from the preparation of the samples owing to the cylindrical nature of the filament. Preparation of the samples involved using a hydraulic piston to squish the samples into the thinnest cross section possible. Ten metric tons of force deformed the samples into disks no thicker than 0.3 mm. The samples were loaded into the Bruker Alpha II and preloaded with a ram to ensure that the sample was pressed into the emitter and detector with no gap, which would cause aberrations in the measurement. The spectra was converted into a CSV file which was analyzed using Lab Cognition's irAnalyze-RAMalyze software using their AirPLS basline correction algorithm to align and correct the spectra from different measurement runs and to identify correspondent peaks to their representative molecules. The spectra was corrected based on the nitrile stretch. Nitrile is stable chemically and thermally, which caused the relative amount of nitrile between the virgin and recycled material to change by less than 0.1 percent. The corrected spectra was then analyzed using Veusz to plot the corrected spectra and calculate the differences in absorption peaks between the virgin material and the recycled material.

Melt Flow Index

Melt Flow Index (MFI) testing was used to compare the different flow rates of the virgin filament and the recycled filament using the ISO 1133-1:2022 standard for the determination of the melt mass-flow rate and melt volume-flow rate (6). MFI testing was conducted with a Göttfert mi 2.2. The filament manufacture has published the results of their MFI testing, so only the recycled filament was tested during this study. Per the ISO standard, a five-minute melt time at 220°C was used with a ten-minute test time using a full-sized die and 10 kg of weight applied to the piston. An automatic cutter, which cut the extruded material every five seconds, was used to limit the effects of gravity on the test. The Göttfert mi 2.2 then calculated the MFR value from the weight of polymer extruded after ten minutes.

Density

As part of the investigation into both the chemical changes and as quality assurance for the recycling process, the density was studied. The density of the virgin filament, recycled filament, and injection molding pellets were determined using Archimedes' Principles. Deionized water was poured in a small beaker and placed onto a weighing frame placed on a precision scale. An arm with two baskets was placed onto the weighing frame such that the lower basket was submerged. The lower arm had some bubbles attached to it, using a pair of tweezers, the basket was gently shaken until no more bubbles were present. The scale was tarred before a small section of filament was added to the top pan and the weight recorded. The samples was then placed into the submerged basket and the sample was weighed again and recorded. A thermometer measured the temperature of the water and air to accurately calculate the density of the water and of the air.

Results and Discussion

Following the methodology described above, this section presents the results, explanation of the results, and discussion into the implications. The testing laid out in the methodology aimed to demonstrate a clear change in the mechanical properties and associate the physical changes with changes to the chemistry. The results pertaining to tensile properties and chemical changes carry the greatest implications and are presented first.

Tension Testing

Tensile testing, following the ISO 527-1:2019 procedure, demonstrated a significant decrease in ultimate strength and Young's modulus when ABS material is recycled with a thermomechanical process. Inversely to the decrease in these elastic properties, the elongation at break and fracture strain increased with recycling. These results are evident that the ABS becomes less elastic and more plastic.

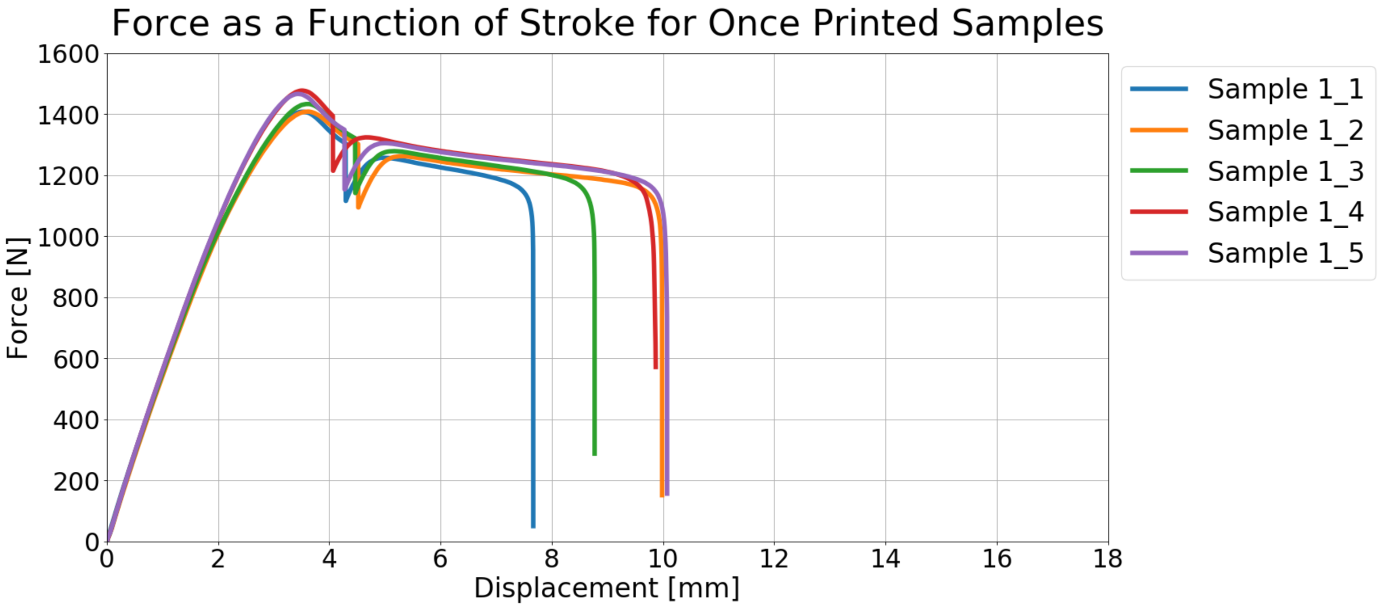

Figure 5: Force displacement curve for once printed samples.

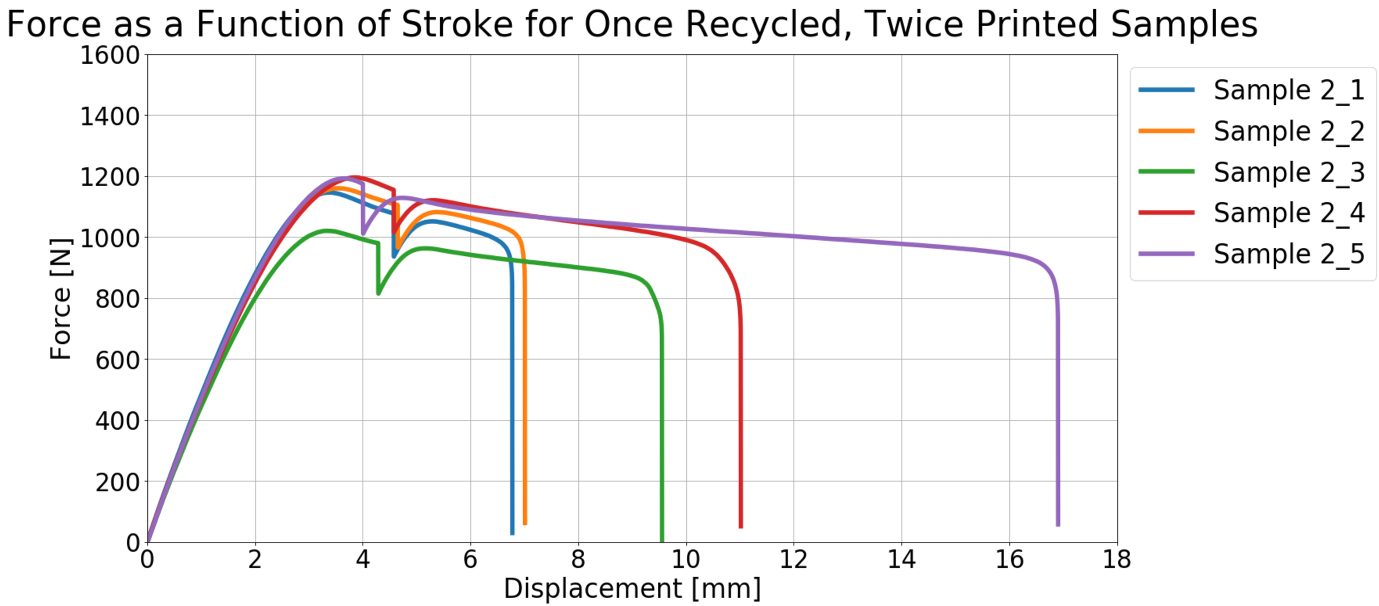

Figure 7: Force displacement curves for once recycled, twice printed samples.

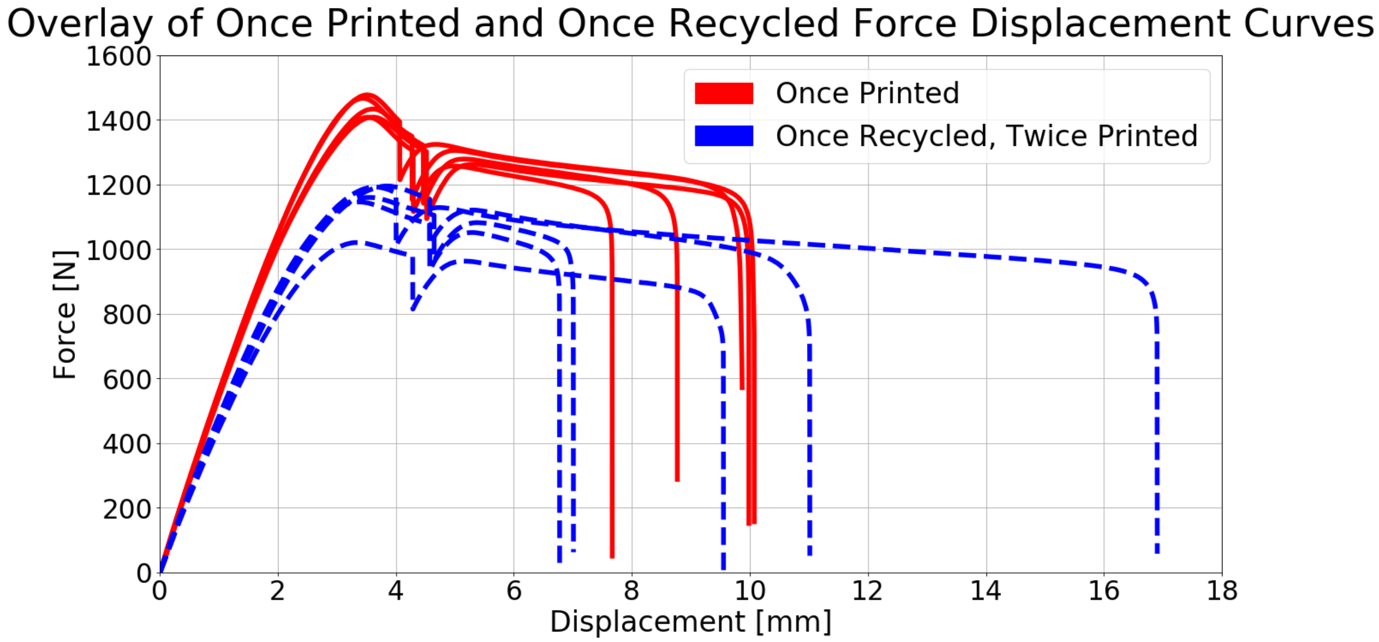

Figure 6: Overlay of force displacement curves for once printed and once recycled, twice printed samples.

The changes in the mechanical properties after recycling are evident from the plots of the force displacement curve. Of note is the sharp dip in the curve after surpassing ultimate strength, this is from the removal of the extensometer. The extensometer needs to be removed before failure of the material to prevent damage. While removing the extensometer, the traction machine only held its position and allowed the test samples to relax slightly before continuing the test. This has no impact on the results as once the test continued, the additional displacement from the traction tester brought the force back to the correct levels.

The force displacement curves graphed represent only a few samples tested. The data used for calculations of tensile properties was collected from 15 once printed samples and 15 once recycled and twice printed samples. The once printed samples exhibit little variance in ultimate strength and Young’s modulus whereas the once recycled, twice printed samples exhibited only slightly more variance in this regard. The variances in break elongation are significant in both the once printed and the once recycled, twice printed samples. What the invariance in the ultimate strength and Young’s modulus and variance in the elongation before break and fracture strain represent is a true test of the material and not the printed geometry being the limited factor. More variance was expected with a 3D printing process, but the lack of it is welcome.

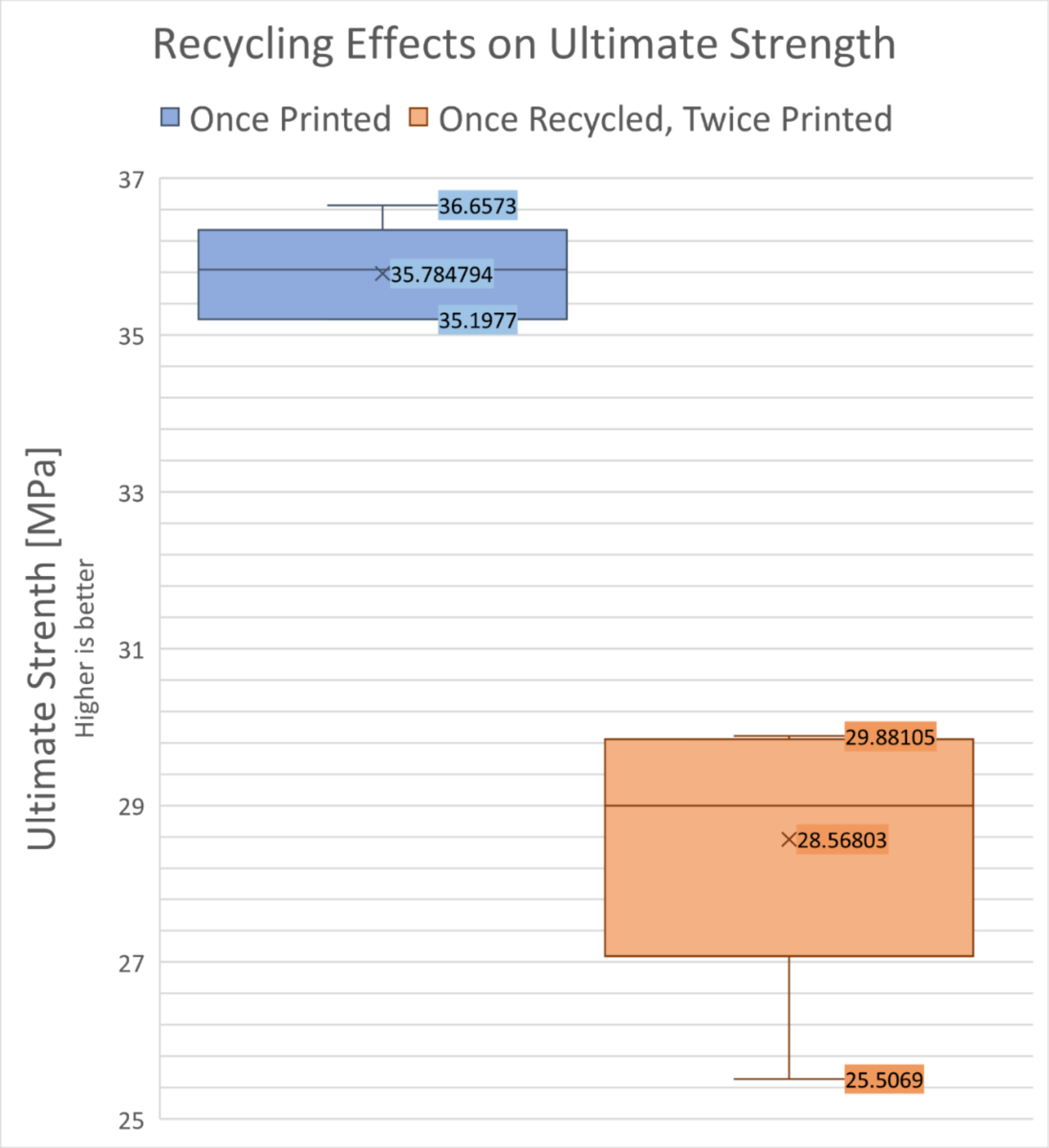

Figure 8: Ultimate Strength comparisons between the once printed and once recycled, twice printed samples.

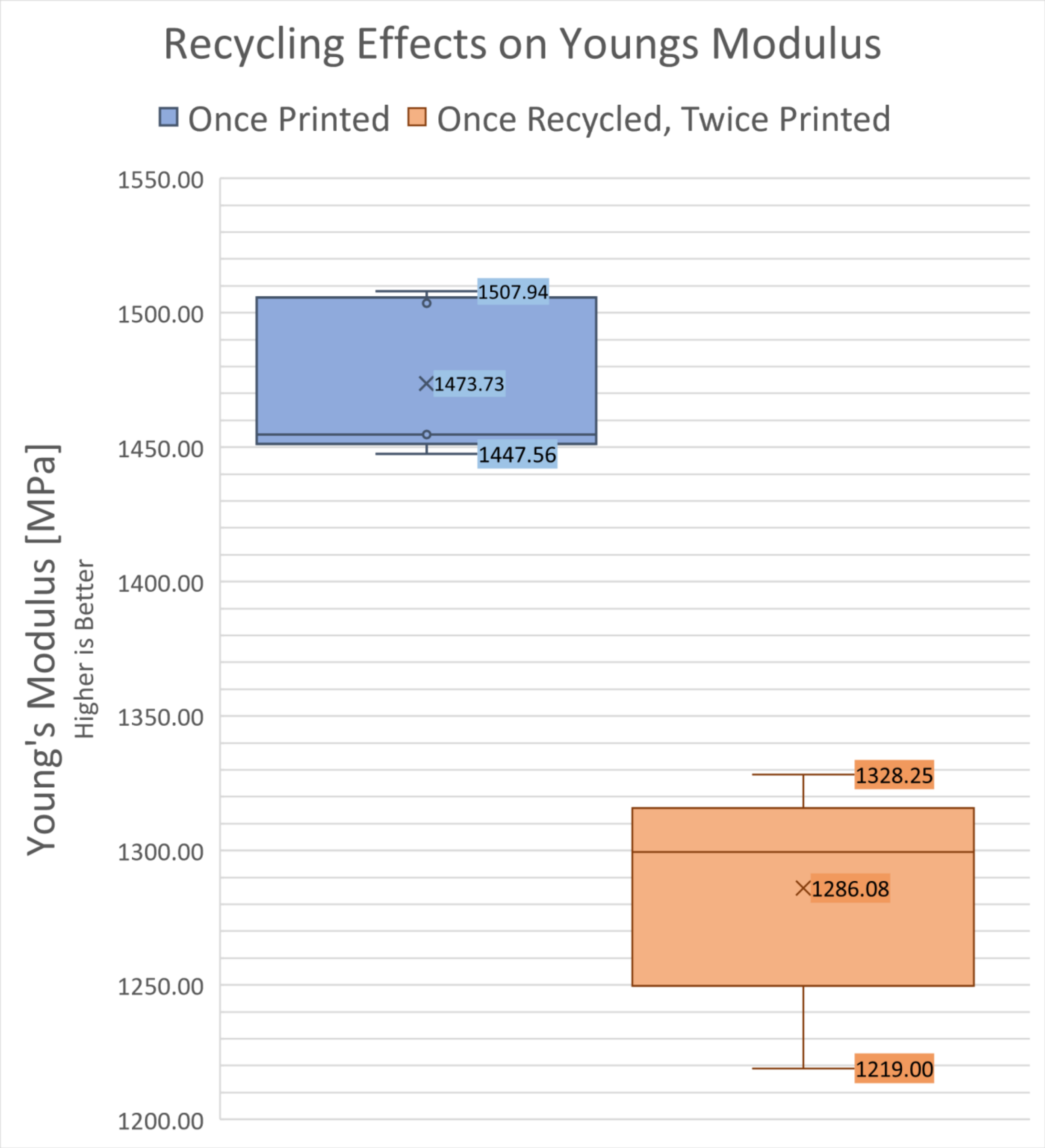

Figure 9: Young's Modulus comparisons between the once printed and once recycled, twice printed samples

A closer look into the effects of recycling on ultimate strength and Young's modulus reveals the extent to which recycling degrades the tensile properties. Ultimate strength decrease an average of 20.17 percent between the once printed samples and the once recycled and twice printed samples. Young's modulus decreased an average of 12.73 percent between the once printed samples and the once recycled, twice printed samples.

Of less importance to the possible use cases for recycled ABS is the elongation at break and fracture stress, these failure properties are still of interest for high stress applications where extra absorption of energy could be beneficial. The elongation at break increased by an average of 10.56 percent and the fracture strain increased by an average of 10.57 percent between the once printed samples and the once recycled, twice printed samples. This means that the recycled ABS absorbed more force before breaking by stretching further than the virgin material. This makes for an interesting application for the recycled material in force absorption where ABS that would otherwise go to waste could be used in packaging to protect products in transit by making a lower density ABS during the recycling process.

Despite the worse mechanical properties of recycled ABS, it can still be used in place of virgin material for applications where the maximum strength is not a requirement. The other consideration for the use of recycled ABS is color accuracy. Dyes are used to color ABS chemically bond to the polymer in way that stains the recycled material. This makes recycled ABS difficult to use for color accurate parts where variance between the color from one part to another is not tolerable. For parts that are to be painted or not visible, the recycled ABS provides an opportunity to reduce waste (8).

Fourier Transform Spectroscopy

The IR spectrum between the once printed samples and the once recycled, twice printed samples was surprising for two reasons: the presence of oxygen containing species and where absorption peaks changed.

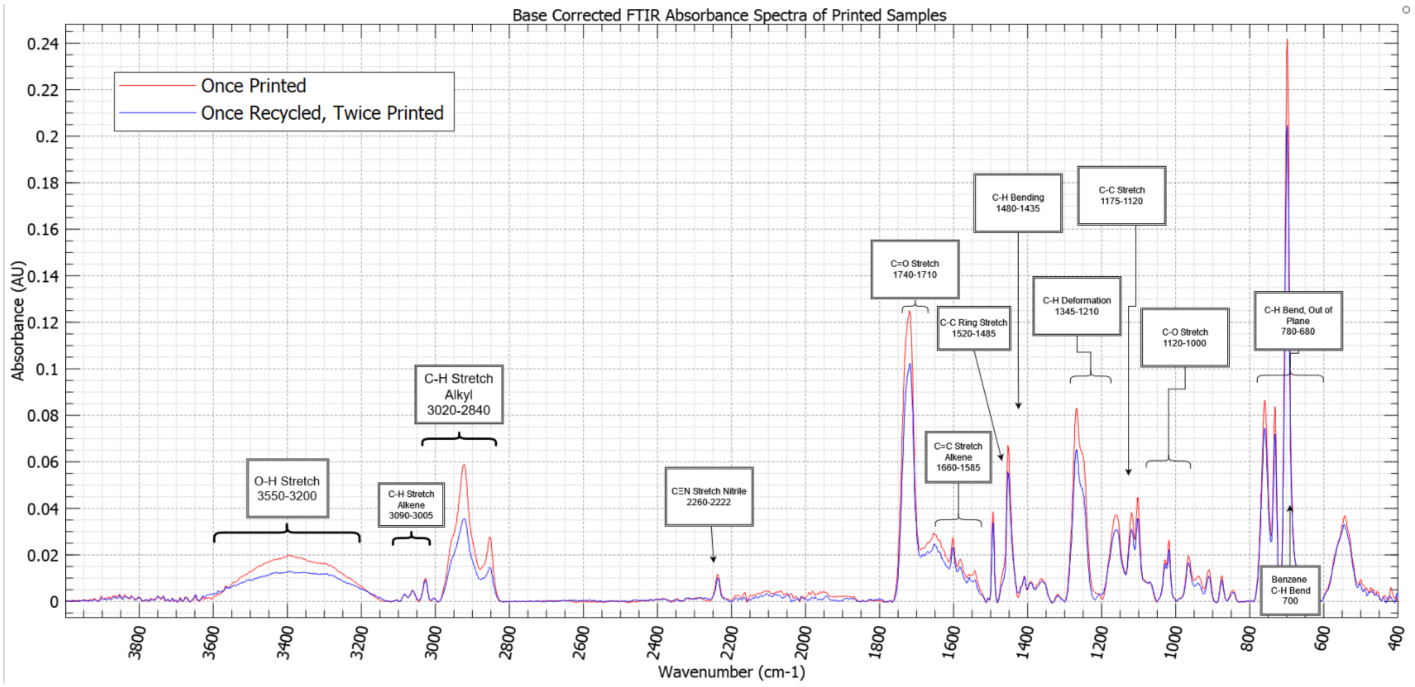

Figure 10: Full FTIR spectra of once printed and once recycled, twice printed samples.

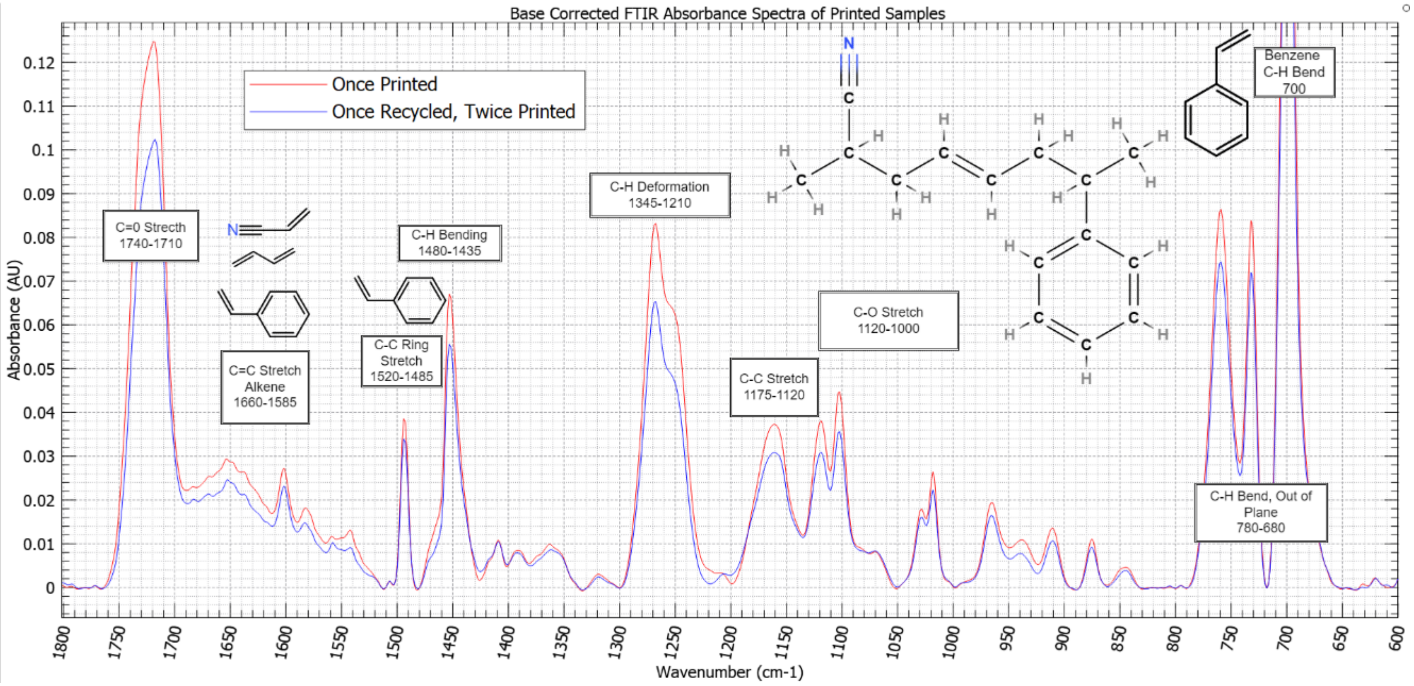

Figure 11: Narrow FTIR spectra of once printed and once recycled, twice printed samples.

The three oxygen containing species are interstitial water in the 3550 – 3200 cm^{-1} band, an additive only found in ABS for 3D printing in the 1740 – 1710 cm^{-1} band, and an alcohol in the 1120-1000 cm^{-1} band.

Benzene had the greatest decrease in absorbance between the once printed sample and the once recycled, twice printed sample. Likely caused by benzene volatilizing when heated by the 3D printer or during extrusion at the end of the recycling process.

The oxygen containing additives experienced the second greatest decrease in absorbance. The specific additive could not be determined by the spectra and the manufacturer was uncertain as well. From other literature, this peak appears to correspond to a plasticizer additive. This explains the decrease in the elastic properties measured from the tensile tests, as the plasticizer increases the flexibility of the ABS.

The last set of peaks to note correspond to carbon hydrogen bonds, specifically the peaks at 3020-2840 cm^{-1} and 1345-1210cm^{-1}. The polybutadiene rubber phase, styrene acrylonitrile matrix, and grafted ABS sections contain high levels of alkyls and alkenes owing to methyl and methylene groups. The spectra demonstrates that these alkyls alkenes are reacting to become IR inactive or volatilizing during printing or recycling (10).

The general decrease in the absorption peaks between the once printed and once recycled, twice printed suggests that IR active species are being ejected, usually as a vapor, or reacting to become IR inactive. These chemical changes, especially with the large decrease in the plasticizer peak, offer insight as to why the recycled ABS has worse mechanical properties than the virgin material. Other investigations found similar results in the FTIR spectroscopy but do not make the connection between the chemical changes and mechanical changes as this investigation does.

Melt Flow Index

The results from the melt flow index testing does not have same obvious implications as the tensile testing result do. Melt flow index, or melt flow rate as preferred now, is important to consider when designing a manufacturing process, whether additive manufacturing or injection molding. The melt flow index describes the amount of material that can be extruded at a given temperature and force application over a period of time. Melt flow index is important for 3D printing as materials with lower indexes require more force to extrude and informs the print speed setting previously discussed. MFI also informs the injection molding process as higher MFI materials behavior better than low MFI polymers. Ideally the melt flow index would not change after the polymer is recycled so that the recycled material can be used in the same process as the virgin material. The ABS used with this study went from 55 g/10 mins to 76 g/10 min after being recycled. For 3D printing, this means more material is being extruded than accounted for and the additional material could reduce the dimensional accuracy of the finished part. A changed melt flow rate is only a problem because it complicates the use of the recycled material in the same process stream as the virgin material. By blending the recycled material with virgin material, additives, or other polymer to negate the effects of a different MFI within a process stream intended for virgin material.

Density

Density testing served to attempt to quantify the amount of material lost when recycling ABS, as many of the degradation products of ABS are volatile. Density affects the viscosity, which affects MFI, and the energy transfer rate, affecting warp. In addition to the 3D printing filament, the density of ABS injection molding pellets was tested as a comparison. The density of the virgin filament was 1.13 g/cm^3, the recycled filament had a density of 1.12 g/cm^3, and the injection molding pellets had a density of 1.05 g/cm^3. The lower density of the recycled filament is plausibly caused by the chemical species that were identified to be volatile. The low density of the injection molding pellet was unexpected and upon further investigation, the pellets contained more air pockets than the 3D printing filament did.

Light Microscopy

Curiosity into the quality of the filament produced from the recycling and extrusion and the failure modes of the test samples led to some microscopy to answer those curiosities. Comparisons between the virgin filament and the recycled filaments looked at the surface roughness and inclusion of impurities.

Figure 12: High magnification image of commercially manufactured filament.

The manufactured filament has a smooth, consistent texture with few inclusions of impurities. This section of filament appeared to have a minor carbon contamination, no greater than 50 µm.

Figure 13: High magnification image of filament extruded from recycled material.

The filament the was produced with the extrusion machine had an irregular surface with no consistent texture, consistent with the formation of air bubbles during extrusion. This section of filament contained a large metal impurity, about 80 µm across.

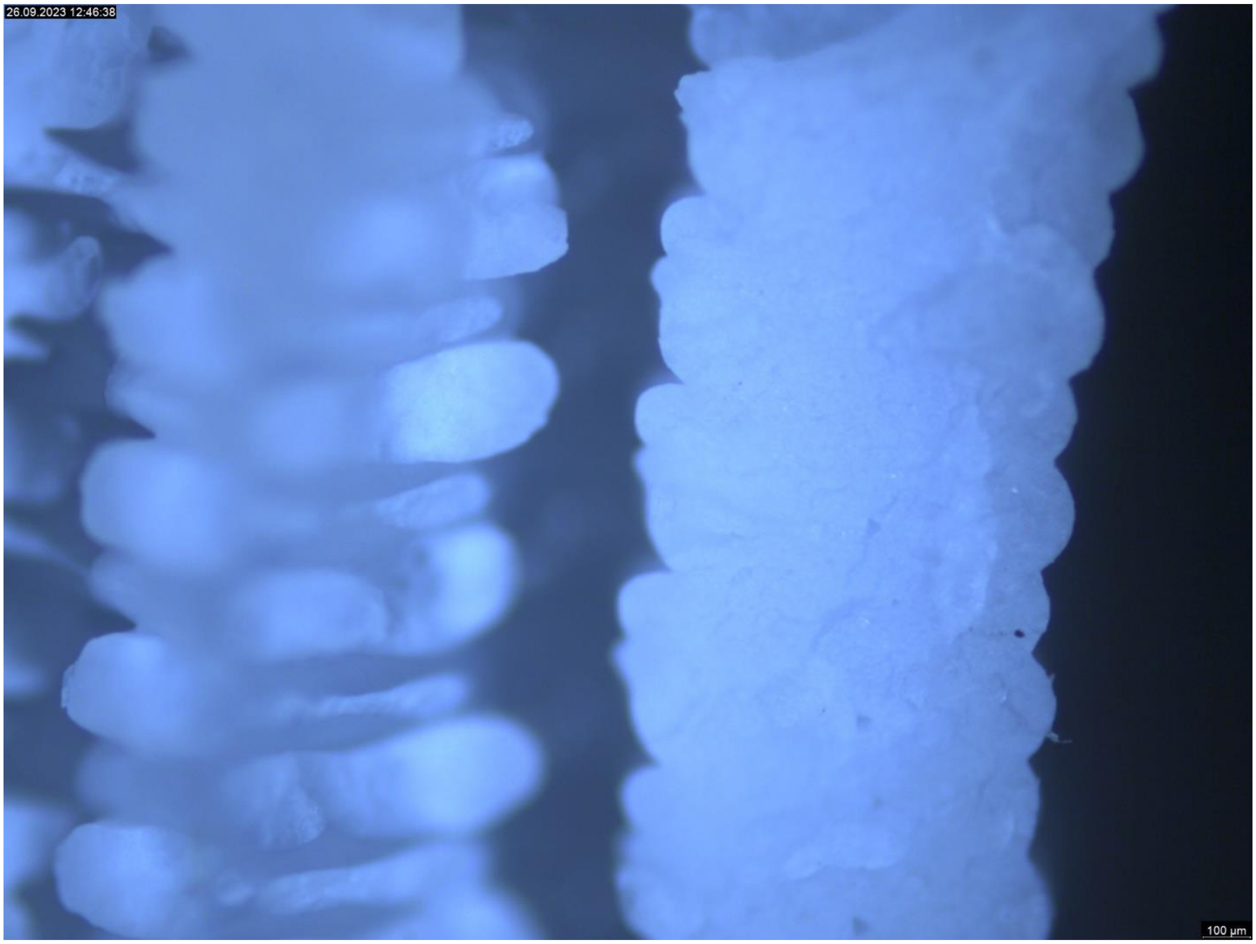

Figure 14: High magnification image of the cross section of a failed test sample.

The cross-section of a test sample after failure reveals exactly what was expected, which was the failure would be between layers and features. This is specifically the section between the two perimeters, demonstrating that the continuous material deformed after the features had separated. The material itself failed in a ductile manner once the force overcame the interlayer cohesion.

Recommendations and Next Steps

This investigation is only a preliminary study into the effects of recycling on polymers. Only one type of polymer was studied and only one recycling process was completed. Only post-industrial waste was investigated, where post-consumer waste could impact the material differently. More diverse tests would deepen the understanding into the extent that recycling changes a polymer.

To this end, further investigations could include additional polymers, blends of polymers, or polymers with additives, such as carbon fiber. Repeated recycling procedure would determine the extent to which ABS or other polymers can be recycled before the material properties degrade too far.

Additional test types would corroborate the findings from the tests performed during this investigation. Tests of immediate interest would be impact tests, rheological testing, differential scanning calorimetry, thermos-mechanical analysis, and scanning electron microscopy with energy-dispersive X-ray spectroscopy.

Recycling from post-consumer waste would investigate degradation that the polymer experiences between production and recycling. An example of degradation the post-consumer waste would experience is photooxidation, which could cause the recycled polymer to be worse than material that is only recycled from post-industrial wastes.

Conclusions

This investigation into the effects of recycling on the mechanical and chemical properties of ABS used in additive manufacturing demonstrated the degradation of tensile properties and explained the possible cause of those changes by looking at the change to the chemical structure. Additional testing into the density and melt flow index of the recycled ABS produced results with process design implications.

While recycling does cause a degradation to the desired qualities of ABS, the recycled material has myriad applications where requirements for strength and color are not of upmost concern. Including recycled ABS into the process stream represents not only a reduction in environmental impact but also material and energy savings. Whether recycled ABS is used with virgin material in the original process stream or used in a different process, the less than perfect recycled material still meets the requirements for a multitude of different products (12).

As the chemical structure of the ABS is damaged during the recycling process, further recycling of already recycled ABS will further degrade the material to the point in which it cannot meet design requirements.

Until more environmentally friendly alternatives to ABS and other oil derived polymers satisfy the same roles, all those polymers will continue to end up in landfills and the oceans without measures taken to utilize recycled polymers in manufacturing. We are stuck with these polymers for the foreseeable future, either it will end up recycled and used productively or it will continue to plague our planet and its inhabitants.

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