

Designing Polymer Materials for Improved Additive Manufacturing

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DEDICATION

This thesis is dedicated to my parents, Jian Guan and Yanguang Dong, and all the people who helped me during my time in the graduate school.

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ABSTRACT

Currently, two of the most used additive manufacturing methods for polymers are selective laser sintering (SLS) and fused filament fabrication (FFF). Although at high market size, they both have imperfections. The materials for SLS are limited and the objects manufactured by FFF existing anisotropic behavior. Targeting on these drawbacks, this thesis has proposed a novel method to prepare polypropylene (PP) microsphere which is suitable for SLS with low cost and scalable potential; and a novel material with polycarbonate as matrix that has shown a decrease in anisotropy after FFF printing.

The PP microsphere in this thesis was prepared via liquid-liquid phase separation, by changing the processing condition such as temperature, solution concentration and molecular weight, we have the capability to control the size of microsphere. The size of resulting particles was characterized by scanning electron microscopy and analyzed by ImageJ. The relationship between processing condition and particle size has been correlated to phase diagram, in which a higher equilibrium polymer-rich phase concentration will result in a larger particle size. We have also shown the versatility of this method by successfully prepared SLS suitable PP powders from a recycled pill bottle.

The polycarbonate matrix has been blended with photoinitiator and crosslinker by a single screw extruder. We have applied a customized UV-LED functionalized 3D printer to print our blend. Tensile strength has been used as an indicator of anisotropy. Although decrease in anisotropy for some samples, the result indicates a competition between interlayer crosslink and in-bulk crosslink. For interlayer crosslink, it will decrease anisotropy by the crosslink on the interface with adjacent layers of the oxidation product of polycarbonate. The in-bulk crosslink, on the other hand, will increase anisotropy by crosslink in the filament and constraint the flow of polymer melts during FFF.

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CHAPTER ONE

INTRODUCTION

Additive Manufacturing and the 3D Printing Concept

Additive manufacturing (AM) or 3-dimensional printing (3D printing) was first introduced in the 1980s with a goal of providing a process for rapid prototyping^{1,2}. Since then, it has expanded to being used in different technologies and applications including manufacturing³, medicine⁴⁻⁸, construction⁹⁻¹², food^{13,14}, and the automobile industry¹⁵. Moreover, AM technologies have been developed for a variety of materials, including polymer¹⁶, ceramic¹⁷ and metal¹⁸. The principal advantage of AM is that it is “complexity free”^{19,20}, which gives the user ultimate control on the structure of the final products, free from many limitations that exist in traditional machining.

As shown in Figure 1.1¹⁶, an additive manufacturing process can be divided into three steps:

1. Creating a digital file containing the structure of the objects of interest.
This digital file may come from a 3-dimensional scan of a real-world object or a virtual file generated by computer-aid-design (CAD). The format file generated in this process is “.stl”, which refers to “stereolithography”.
2. Horizontally slice this digital file with a given thickness (layer height), including the generation of support structures for any portion of the object that may overhang. These slices represent two-dimensional contours that the printer will follow to print each layer of the object. Each layer is stacked upon one another to form the final 3-dimensional targeted structure.

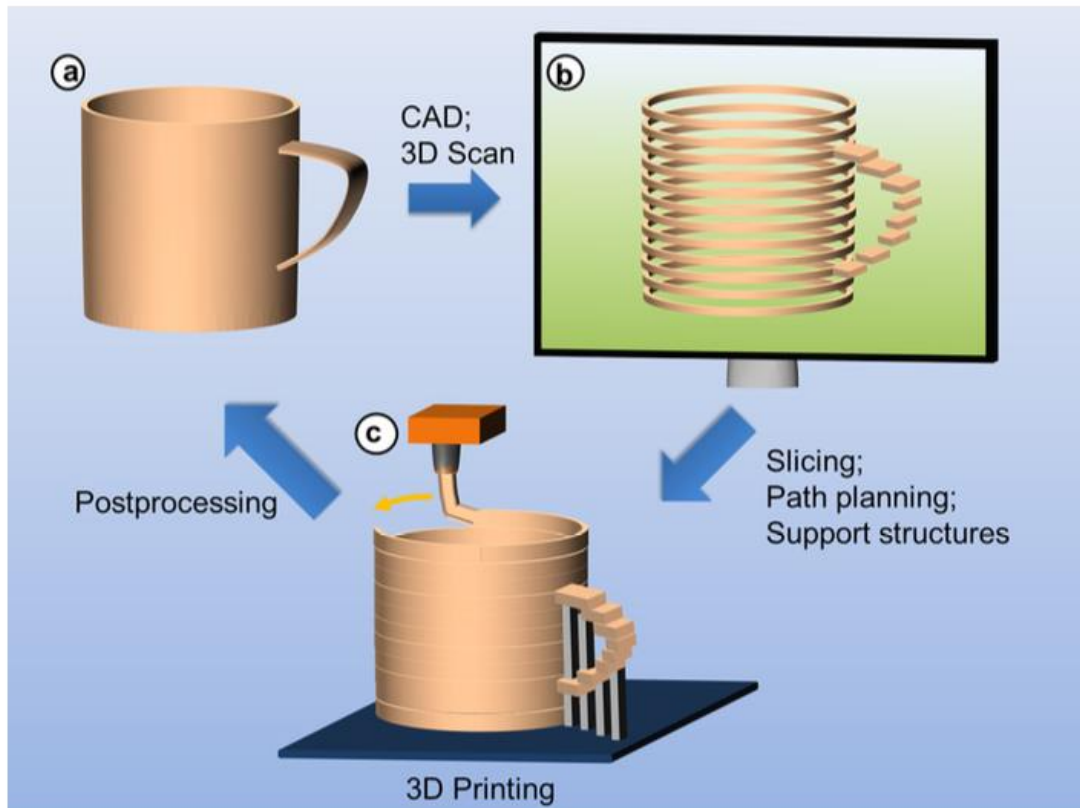


Figure 1.1 General representation of an additive manufacturing process¹⁶.

3. Printing the digital slices in a layer-by-layer pattern. The code generated by the computer guides the operation of the printer to fabricate the targeted structure.

The typical height of each layer is about 10-300 μ m for practical purposes. The human eye cannot differentiate objects below $\sim$ 10 μ m, and a post-printing process is needed to improve surface quality if required and the layer is too thick. The choice of layer thickness is also case-dependent, as for some applications, such as mechanical interlocking or tissue growth in medical applications, a smooth surface is not required. In this case, a thicker layer thickness can be used and the time to fabricate the object is shorter.

The definition of AM from the American Society for Testing and Materials (ASTM) is “Additive manufacturing (AM) – Processes of joining materials to make objects from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing fabrication methodologies^{21,22}.” AM differs from the traditional subtractive method in manufacturing, where the material is removed. In AM, materials are deposited in a layer-by-layer pattern, which is cost- and material-efficient and gives the operator the ability to produce sophisticated and complex structures such as “stair wall in a castle²³” (Figure 1.2), which is impossible to fabricate by the traditional subtractive method.

In additive manufacturing, the materials used are only added to the pre-deposited object, resulting very little loss of material. For example, recent research²⁴ shows that by adjusting the surface of the printing bed, an artificial tooth for a dental clinic can be fabricated by AM from a single resin drop. In this case, the utilization efficiency of the material is 99.6%. Using AM, the cost in product development and design may be reduced by 50%, and time to market can be reduced by 90%²⁵.

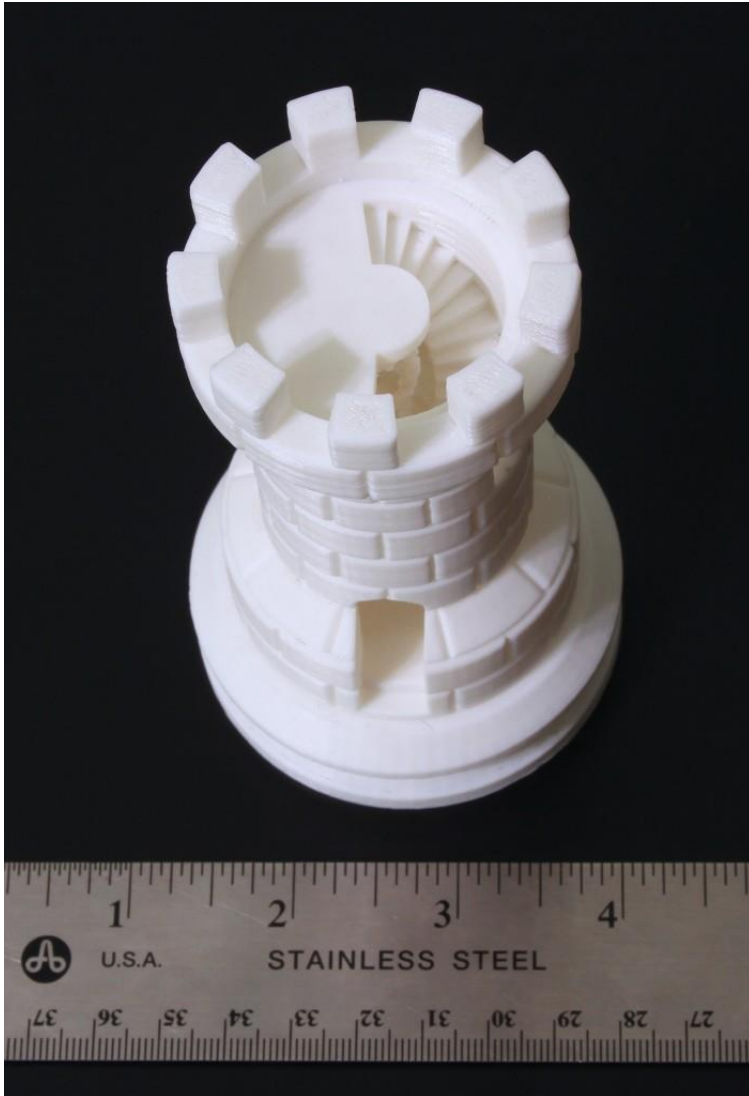


Figure 1.2. Stair wall in a castle²³.

A long-term goal of additive manufacturing is to compete with or surpass traditional manufacturing methods. However, besides the low production speed that results from the layer-by-layer nature of the process, other challenges also exist in attaining this goal. One particular barrier is that the number of materials available for 3D printing is limited. Although AM has been shown to be suitable for a variety of material categories, the availability of materials within many categories is limited. For example, polyamide 12 takes up more than 95% of the current selective laser sintering market²⁵. The printing process will also generate unavoidable porosity^{26,27} in printed objects. Figure 1.3 shows an example of these voids at the intersection of filaments in a 3D printed object between each layer.

Other than limited materials and voids in the object, another significant drawback that limits the expansion of 3D printing toward manufacturing is the anisotropy of mechanical properties. As shown in Figure 1.4, because objects in AM are manufactured in a layer-by-layer fashion, the mechanical properties of the printed object will vary with the direction probed. The mechanical properties of an object that is produced by AM approaches that of objects created by traditional manufacturing methods, such as injection molding^{28,29}, when measured parallel to the layers, but are significantly weaker in the perpendicular Z-direction. This anisotropic performance^{30,31} varies with specific additive manufacturing technology, and is most prominent in laminated object manufacturing where sheets of plastic are fused by heat and pressure, and least evident in selective laser sintering where material powders are sintered together by a laser to form each layer. Research in reducing anisotropic performance is an active area, and the development of new materials³² to mitigate this anisotropy has shown potential in overcoming this limitation.

Among various types of 3D printing, two of the most widely used³³ are fused filament fabrication (FFF) and selective laser sintering (SLS).

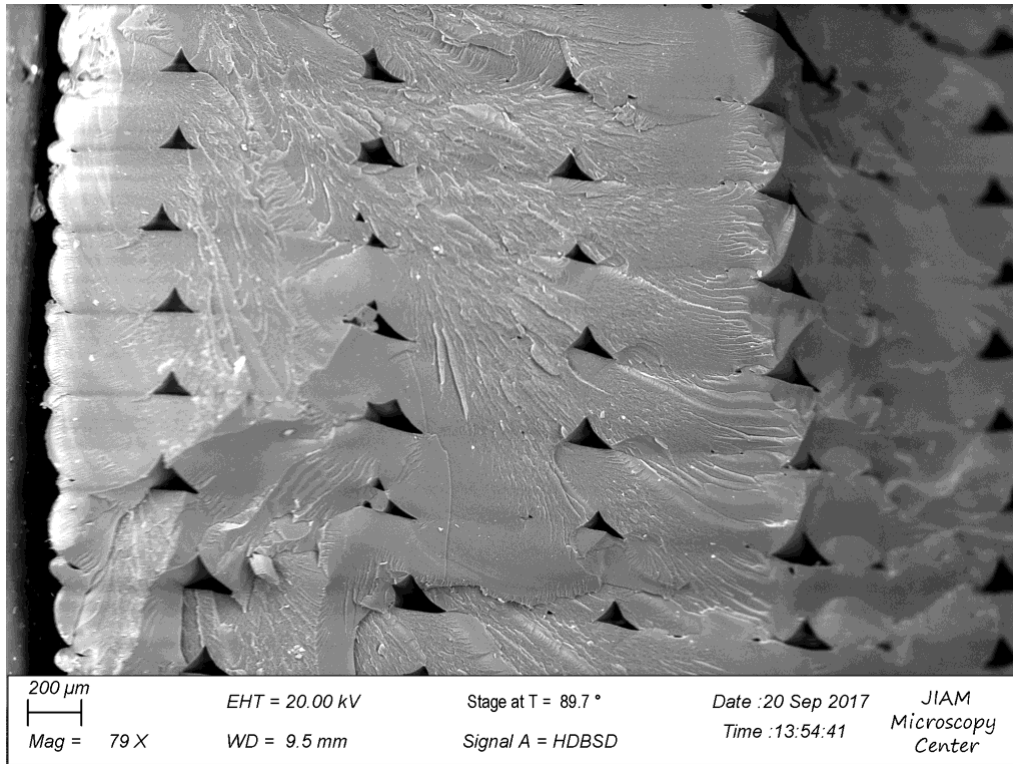


Figure 1.3. Voids at the interlayer interface in 3D printing objects.

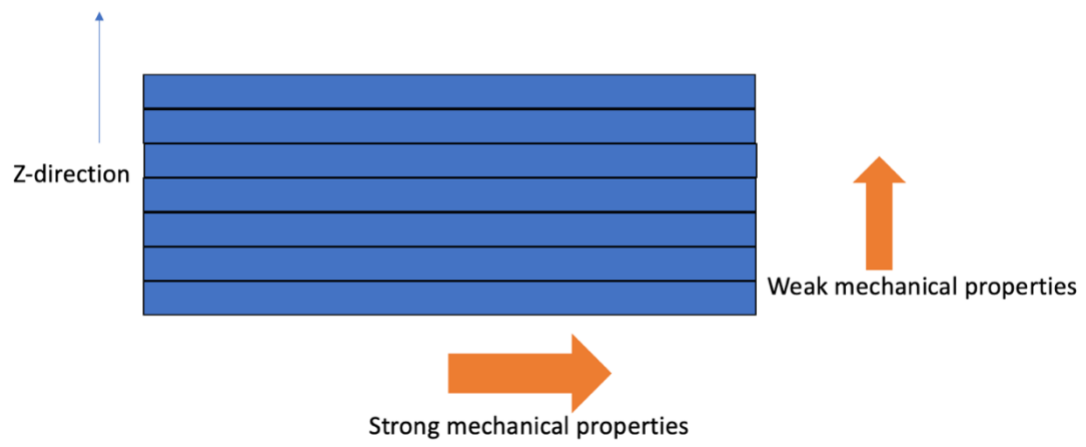


Figure 1.4. Anisotropy in 3D printed objects.

Selective Laser Sintering (SLS)

Principle of SLS

First developed in 1986 by Carl Deckard³⁴, SLS grants its users a choice of ceramic, metal or thermoplastic powders. SLS is now widely used in not only prototyping but also as a supplement to traditional manufacturing. For example, Boeing³⁵ has used SLS to produce low-volume parts for cost reduction. By using SLS, Saab Avitronics³⁶ has successfully reduced the mass of some products by almost 50% and have successfully fabricated objects with complex features that are impossible or difficult to produce traditionally.

Figure 1.5 shows the general structure of an SLS printer³⁷. The printing process follows these steps in a typical SLS printing process:

1. The printer chamber is heated up to a temperature close to the material's melting point, followed by the deposition of a thin layer of powder to the deposition bed from the powder supply bed.
2. A laser spot guided by the scanning mirror scans over this powder layer to heat up and consolidate the pre-deposited powder layer. The pattern of the laser beam is specified by the cross-sectional slice of the ".stl" (CAD) file. Due to the high energy that comes with the laser beam, the solidification is often finished in milliseconds.
3. After the consolidation, the bed is lowered by a predetermined distance, typically one layer height (10-300 μ m), and a new layer of powder is spread over the pre-sintered object by a roller from the powder reservoir next to the printing bed.
4. The process then repeats until all the layers have been successfully sintered to create the targeted object. The unsintered powder acts as support material, which makes the generation of excess support structures unnecessary.

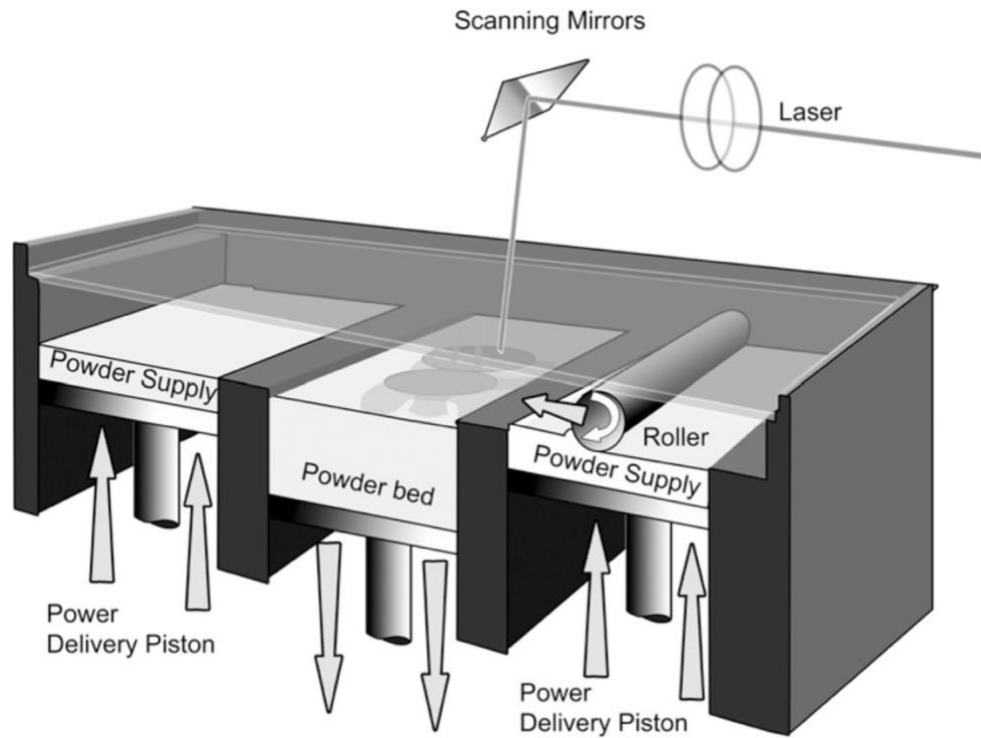


Figure 1.5. A diagrammatic representation of an SLS 3D printer³⁷.

Beyond the aircraft industry, SLS has been used extensively in other fields. For example, in the medical field³⁸⁻⁴¹, internal implants or external prosthetics that accurately match the anatomical requirements for each individual patient can be fabricated by SLS.

Current Challenge in Polymer Powder Preparation for SLS

Although SLS has many advantages, a major drawback is the limited number of materials⁴² available for SLS, especially in polymers. While there are tens of thousands of polymers available for traditional manufacturing, only about 30 are available for SLS.

Theoretically, a broad range of polymers should be suitable in SLS; however, options available for industry are very limited. For instance, 95% of materials used in SLS is polyamide 12²⁵. The reason for this is partially due to the history of SLS, where it was one of the first polymers used in SLS. Additionally, polyamide-12 powder is relatively easy to fabricate for SLS and is low-cost relative to other SLS-grade materials. The materials that are used in SLS are also more expensive²⁵ than non SLS-grade polymers.

There are several aspects of the SLS printing process and structural features in polymer powders that are important in determining their suitability for use in SLS. These factors include, but are not limited to bed shape, printer bed temperature, powder morphology and size, and traveling pattern of the laser beam. Among these factors, the structural properties of polymer powder are the most critical since they will affect not only the ability to print an object with SLS and sinterability, but also impacts the properties of the final objects such as surface roughness and porosity.

The shape and size of the of polymer powder will affect its flowability, which impacts the coating process between layers. In the literature, Prescott et al.,

defines flowability as “the ability of the powder to flow in a desired manner in a specific piece of equipment”⁴³. Flowability will affects the powder deposition⁴⁴⁻⁴⁶ step when a thin, smooth and compact powder layer is desired for better printing quality.

The shape of polymer powder is also crucial, and highly depends on how it has been prepared. General powder preparation methods are cryogenic milling, solution precipitation, and emulsion polymerization (Figure 1.6, from left to right, respectively). During the coating of the powder layer to the previously sinter objects after each layer deposition, the particle prepared from emulsion polymerization with a perfect spherical shape exhibits the best flowability, followed by potato-shaped particles that are formed from solution precipitation, while the irregular shaped particle created from cryogenic milling has the worst flowability⁴⁷. Several approaches have been attempted to increase flowability. However, due to the high cost of emulsion polymerization, the most widely used method commercially to increase the flowability of polymer powder is blending with an inorganic compound like silica, alumina, mica, and kaolin.

Other than particle shape, particle size is also an essential factor in SLS, where particles with 20-100 μm diameter perform well in SLS^{48,49}. Larger Particles will not flow easily and often require post-processing to create a smooth surface; particles that are too small “evaporate” when exposed to the high energy beam during the print process, limiting their cost effectiveness. Notably, multimodal powders containing particles with a range of sizes have shown better performance in SLS printing, where particles with smaller sizes can improve flow properties, and larger particles increase overall density of the printed object.

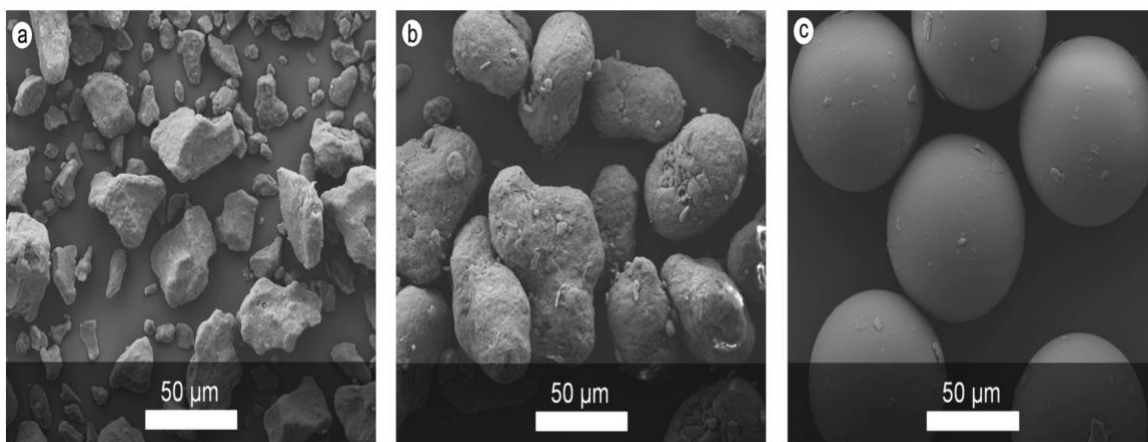


Figure 1.6. Polymer particles prepared from different methods¹⁶.

Current Needs for Polymeric Materials in SLS

In summary, there is a need to expand the polymeric materials available for SLS printing, where identifying cost effective, broadly applicable and scalable processes that can create powders with the required size range and flowability is of paramount importance. As a result, one goal of the research in this thesis will be to provide a more thorough understanding of the opportunities, limitations, and fundamental physical processes that drive the use of liquid-liquid phase separation in the fabrication of polymer powder for SLS, with a focus on polypropylene. A particular focus will be on developing a foundation to fabricate appropriate SLS powder from polypropylene regardless of molecular weight. Additional studies will examine the ability of liquid-liquid phase separation to create suitable powder for SLS by upcycling polypropylene in the waste stream.

The liquid-liquid phase separation method used in these studies will be thermally induced phase separation (TIPS). Traditional powder preparation methods, such as cryogenic grinding, solution precipitation, and emulsion polymerization, are expensive, time consuming, sensitive to material properties, and often result in powders with low sphericity. However, TIPS is scalable and can be cost effective. Moreover, a more complete understanding of the fundamental physical processes that guide powder production in TIPS will open opportunities to create suitable powders for SLS for a broad range of polymers.

One shortcoming of previously reported polymer powders fabricated by TIPS is that it has been limited to formation of powders from solutions with very low concentration (0.1wt%) and studies have focused on a single polymer molecular weight. In this thesis, we report the results of studies that use the TIPS method to create polypropylene powders from solutions with higher concentrations using polypropylene with a broad range of molecular weights. Scaling up this process makes it possible to prepare PP microsphere powders for SLS in an energy and solvent efficient way. Moreover, the study of TIPS on solutions consisting of

polypropylene with various molecular weights provides insight into the mechanism of powder formation, and affords rational control of powder particle size with easily controllable processing conditions. In parallel studies, TIPS has been used to successfully produce polypropylene powder from a used pill bottle, with suitable size, sphericity, and flowability for use in SLS. The powder prepared by this method has also been successfully SLS printed by Professor Christopher Williams group in Virginia Tech. This demonstrates the potential of this application in the upcycling of plastics in the waste stream.

Fused Filament Fabrication (FFF)

Principle of FFF

While FFF or fused deposition modeling (FDM) was first presented in the 1980s and commercialized in 1990 by Stratasys, FFF is now widely used for its low purchase, use and maintenance cost. Different from most other AM methods, where the size of the fabricated object is often limited by energy transfer requirements or build chamber limitations, FFF is capable of manufacturing large objects, such as a full-size car⁵⁰ or even a house⁵¹.

As shown in Figure 1.7⁵², the polymer FFF printing process consists of the following steps:

1. The printer head is heated up to a temperature near the molten temperature (T_m) of the polymer, and the printer bed is heated to a temperature near the glass transition temperature (T_g) of the thermoplastic.
2. The plastic filament is fed into the heated head by a drive, where it becomes semi-molten. The softened filament is pushed through the heated head exiting the nozzle and deposited on the pre-deposited

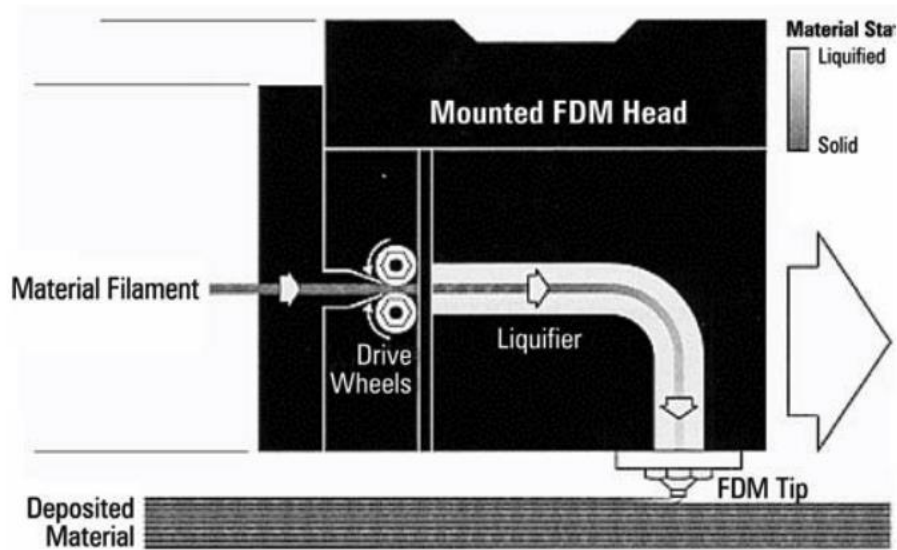


Figure 1.7. The Hardware of the FFF (FDM) printer⁵².

material. As the polymer is semi-molten, the new layer will fuse with the previously deposited layer.

3. The FFF head moves in the X-Y plane along the two-dimensional pattern generated during slicing of the CAD file.
4. After the successful deposition of one layer, either the printer bed is lowered, or the printer head is raised by a certain distance and a new layer is deposited.

A crucial limitation of objects fabricated by FFF is the anisotropy in material properties. The “building unit” in SLS is a polymer sphere with μm dimension, where this small size allows for a reasonably uniform distribution of applied energy, resulting in significant interdigitation of spheres within and between adjacent layers. Consequently, an object with more isotropic performance is often produced in SLS ³¹. However, in FFF the interdigitation of polymer between larger filaments at the interlayer interface are more limited, resulting in a weak filament-filament interlayer adhesion.

Anisotropic Material Properties in Objects Fabricated by FFF

On a molecular level, the transience of extruding semi-molten filament limits the diffusion of polymer chains between the building layer and adjacent previous layers⁵³. This results in weak interlayer interfaces, where the mechanical properties of the 3D printed objects across this interlayer interface are weaker than those tested along the printing direction. This is demonstrated by the results of Figure 1.8, where the subscript represents for number of layers deposited, from work by Ahn et al. These results show that the injection molded ABS sample failed at 26 MPa, while four specimens fabricated by FFF failed at much lower stresses⁵². Moreover, the tensile strength of the 3D printed samples, decrease with an increase in raster angle with the transverse sample showing the weakest

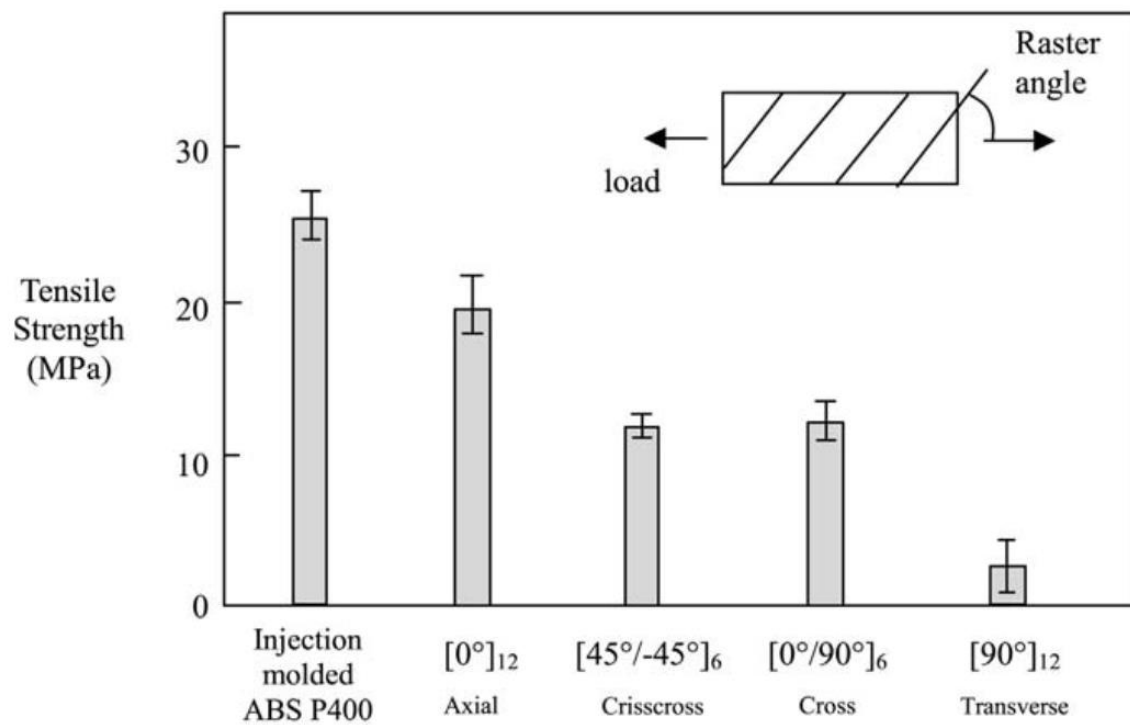


Figure 1.8. Tensile strength of ABS samples prepared with varying raster directions⁵².

performance. Figure 1.9⁵² provides some insight into these results; in that they show the magnified views of the fracture surface of the axial and crisscross samples after break.

These data lead to the conclusion that in the transverse or 45° samples, the load is distributed between the fiber and the interface between each layer. The weak interfaces between layers thus drive the lower tensile strength of these printed geometries.

Therefore, developing materials or processes that can improve interlayer adhesion is needed to rationally and predictably reduce anisotropic mechanical behavior in structures that are fabricated by FFF.

Previous studies have shown that two crucial factors that impact structural anisotropy in printed objects are material design and printing parameter optimization⁵⁴. Optimizing printing parameters can mitigate, but does not eliminate anisotropy, and therefore we will focus on material design and use a consistent set of printing parameters throughout. Some of the most commonly used materials in FFF include polyacrylonitrile-butadiene-styrene (ABS), polylactic acid (PLA), and polycarbonate (PC). ABS is a complicated multi-component system with a crosslinked polybutadiene (PB) core combined with an acrylonitrile-styrene copolymer, making it difficult to rationally control molecular structure and morphology. Similarly, PLA is a semi-crystalline polymer, where variation in crystallinity during the complex thermal history of the printing process may complicate further analysis of material design studies. Finally, PC is an amorphous, tough, transparent engineering thermoplastic with excellent thermal properties. Thus, it is a suitable and interesting material to focus on in the design of new materials that can mitigate the anisotropy of structures fabricated by FFF.

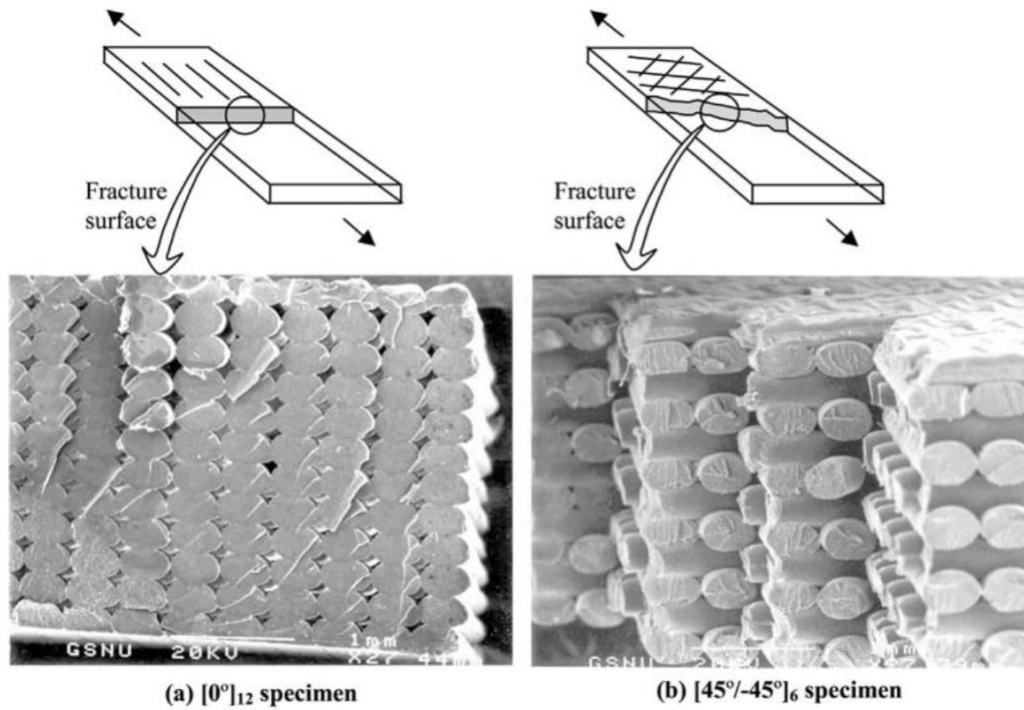


Figure 1.9. Scanning electron microscope (SEM) pictures of the fracture surfaces of the same samples reported in Figure 1.8⁵².

Material Design to Address Anisotropy in Structures Fabricated by FFF

Even though FFF has been used for more than 30 years, the anisotropy in mechanical properties of structures formed by FFF remains a limitation in the growth of FFF into the manufacturing realm. The desire to expand FFF as a manufacturing method makes the study of methods to mitigate mechanical anisotropy an active research area. In this thesis, we will present work that elucidates the benefits and limitation of a reactive processing approach to mitigate anisotropy in polycarbonate structures created by FFF. The results offer insight into the success of interlayer reactions, and their competition with reactions that may occur away from the filament-filament interface.

These studies build off of previous studies in our group that focus on material design and reactive processing protocols to improve interlayer adhesion. These studies have examined two of the most commonly used polymers in FFF, ABS^{55,56} and PLA^{57,58}. In one study, Levenhagen et al. reported the benefit of incorporating surface-segregating materials to the polymer filament, where the surface segregating polymer hastens polymeric diffusion between filaments and improves the isotropic performance of fabricated FFF objects^{57,58}. This research program exemplifies the potential of material design to enhance interfilament interfaces as a rational path to reduce anisotropic performance. In parallel studies, Perryman et al. showed that the addition of a crosslinker between layer deposition will decrease the anisotropic performance in ABS structures⁵⁵. This improvement is driven by the reaction of multi-amines with the oxidation products on the filament that emerge during the printing process to form covalent crosslinks between layers.

Building off of previous studies, Levenhagen et al. examined a reactive processing approach to reinforce the interfilament interface with covalent bonds⁵⁶. In this process, an FFF printer is coupled to UV initiated reactions to form covalent bonds. In these studies, the filament consists of a ternary mixture

of crosslinker, photoinitiator, and polymer. The results are promising as the interlayer strength increases by 200%, nearly eliminating anisotropy. This thesis expands on this research to examine methods to simplify the material design and reaction processing protocol, using polycarbonate as the polymer matrix.

These studies are presented in Chapter 3, where the reactive behavior of ternary filament systems (crosslinker-photoinitiator-polymer) is compared to that of a binary component filament (photoinitiator-polymer). Surprisingly, the binary system appears to exhibit better performance in terms of decreasing structural anisotropy. As presented in Chapter 3, this is interpreted to be the result of the competition between the crosslink reaction that occurs at the interface and the crosslink reactions that may occur in the center/bulk of the filament, the surface segregating properties of additives, and potential for thermally induced oxidation of the polymer.

Organization of This Thesis

The remainder of this thesis is organized as follows. First the research on the preparation of polypropylene powders that can be used in SLS is presented. In this chapter, the results of PP microsphere preparation through TIPS are presented, including a discussion of the fundamental physical processes that drive powder formation. We have successfully prepared PP microspheres of various controllable sizes from polymers with a range of molecular weights. Interpretation of these data offers insight into the physiochemical mechanisms that drive the powder formation and correlate the resultant particle size to the polymer molecular characteristics and processing conditions.

This is followed by a chapter that discusses the use of reactive processing to reduce structural anisotropy in FFF printed structures. In this chapter, a customized 3D printer together with a functionalized PC filament will be introduced. The tensile test results, which monitor the extent of structural

anisotropy in these studies, are presented followed by analysis and interpretation of these data. The variations in mechanical properties are correlated to crosslinking reactions that occur in the filament. Finally, the work is summarized in a chapter that gathers the conclusions of this study and outline potential future studies.

CHAPTER TWO

POLYPROPYLENE POWDER FORMATION BY THERMALLY INDUCED PHASE SEPARATION

Introduction

As mentioned above, the size and shape of the polymer powder is crucial in the success of the selective laser sintering (SLS) printing process. The exact size and shape of the powder will affect the quality and properties of the printed structure, such as its strength, definition, or accuracy to the design. Consequently, producing polymer powder with the proper size and sphericity is crucial in fabricating SLS powder from new polymers. Current methods that produce microspheres with proper shape can be divided into two major categories: dispersion of preformed polymer and the polymerization of monomers in confined geometries.

Solution Based Methods for Polymer Powder Preparation

The dissolution of polymer into a solvent followed by its precipitation from solution is a common approach to forming polymer powders for SLS. Among these processes, the most popular methods include solvent evaporation⁵⁹, nanoprecipitation⁶⁰⁻⁶³, dialysis^{64,65}, and supercritical fluid⁶⁶⁻⁶⁸ technology. In the solvent evaporation process, polymers are dissolved in a volatile solvent such as dichloromethane or ethyl acetate with a lipophilic surfactant to form an emulsion. The solvent is then evaporated to form polymer powder. This method has shown success in preparing polymer particles with various sizes for different polymers and is the most widely used approach in polymer particle formation⁵⁹.

In the nanoprecipitation method, also known as the solvent displacement method, the polymers are dissolved in a "good solvent" and subsequently rapidly mixed with a "bad solvent" (non-solvent). During the rapid mixing of solvents,

small polymer rich droplets are formed, and upon drying, polymer particles are formed. Dialysis can also be considered a special solvent displacement method, where a dialysis tube is required. In this process, the polymer solution is sealed in a tube within a dialysis or semipermeable membrane and placed into non-solvent. This allows the osmosis of bad solvent into the solution, where the solubility of the polymer in the new mixed solvent decreases, which in turn will lead to an aggregation of polymers. In this process, the dialysis is cut off when the particles reached a desired particle size.

In the previous three methods, one shortcoming is that they all require a large amount of solvent and are time consuming. Moreover, control of particle size is non-trivial, as during the removal of solvent or decrease in solvent quality, the polymer particle may undergo coalescence.

To handle these problems, supercritical fluid technology is an emerging approach to produce polymer particles. In this process, the polymers are dissolved in a supercritical fluid such as carbon dioxide. This solution is then either expanded to ambient air or, in some cases⁶⁸, into a "bad solvent" like water. Both processes result in a rapid drop in polymer solubility, forming polymer particles. A major disadvantage of this method is the limited solubility of most polymers in many supercritical fluids.

Another category that results in polymer particles is the polymerization of monomers in a confined geometry, which is represented by emulsion polymerization⁶⁹⁻⁷². In an emulsion polymerization, monomers are polymerized in micelles that are stabilized by surfactant, which gives round polymer particles upon polymerization. The size of resultant particles from this method is mainly controlled by the concentration of monomer and emulsifier, which offers improved controllability over that of the dispersion of preformed polymers. Based on the size of micelles, emulsion polymerization can be subdivided into subgroups; mini- and micro-emulsion. In mini-emulsions⁷³⁻⁷⁷, high-shear devices

like ultrasound probes are combined with a co-stabilizer to break and stabilize micelles into a smaller volume. In micro-emulsions⁷⁸, an excess amount of emulsifier is used. This differs from traditional emulsion polymerization, in that each micelle does have monomers inside, rather there are many empty micelles which has increased cost from excess emulsifier.

Another disadvantage is the potential residue of surfactant that may remain with the final polymer particle and is difficult to remove. A standard method to remove the surfactant uses chromatography, but this also dissolves the polymer particle, destroying the targeted round particle shape. The dilute concentration of the emulsion also limits its potential for scale-up preparation. Moreover, any residue surfactant will significantly affect the properties of the polymer sphere when sintered.

From the summary in Table 2.1, it is clear that these methods are all limited by a large amount of solvent that is required during the particle formation process. In the solvent removal and supercritical fluid approaches, excess amounts of solvent and non-solvent are needed, while in the emulsion polymerization, a large amount of solvent is required to form an emulsion with proper monomer concentration. Another disadvantage is the number of components needed that do not form polymer powder, including surfactant, solvent, and monomers.

All of these drawbacks limit the potential for economic and technological scale-up of these processes for polymer powder preparation for the SLS industry. As these methods are often too expensive, commercial SLS polymer powders are often fabricated by cryogenic milling, which most often creates eccentric shaped particles with limited flowability.

Table 2.1 Summary of current polymer particle preparation methods

Methods		Disadvantages
Dispersion of polymers	Solvent removal	Time-consuming Polymer coalescence during the solvent removal process large amount of solvent required
	Supercritical fluid technology	Solubility of polymer in SCF is limited
Polymerization of monomers	Emulsion polymerization	Residual surfactant Dilute emulsion limits scale up

Thermo Induced Phase Separation (TIPS) to Prepare Spherical Polymer Powders

As an alternative, fast procedure to prepare spherical polymer powders, physical manipulation of polymer solutions such as quenching to enable thermally induced phase separation (TIPS) is a good choice. Figure 2.1⁷⁹ below shows the concept of a TIPS process, where this figure shows the binodal line for liquid-liquid phase separation (LLPS), the spinodal line, and crystallization temperature of a typical solution of a crystalline polymer.

In a typical TIPS process, the polymer is dissolved in a solvent and homogenized at high temperature. After complete dissolution, the thermal energy is removed by quenching the solution to the temperature below the upper critical solution temperature (UCST). Liquid-liquid phase separation (LLPS) will take place when the solution penetrates the binodal line. It has been reported that when the polymer concentration is lower than the critical point, the polymer-rich phase will become the dispersed phase, and the polymer-poor phase will be the matrix after LLPS⁸⁰. This dispersion of polymer-rich phase in polymer-poor phase is the foundation that results in polymer particles by TIPS. Thus, the concentration of the solution must be lower than the critical point in TIPS, otherwise the polymer-rich phase will be the matrix, and a porous membrane will form instead.

During the quenching process, phase separation proceeds by nucleation of the polymer-rich phase, followed by droplet coalescence. This results in the formation of polymer particles after the removal of solvent. Varying the concentration of polymer solution and the quench temperature provides pathways to control the size of the final particles.

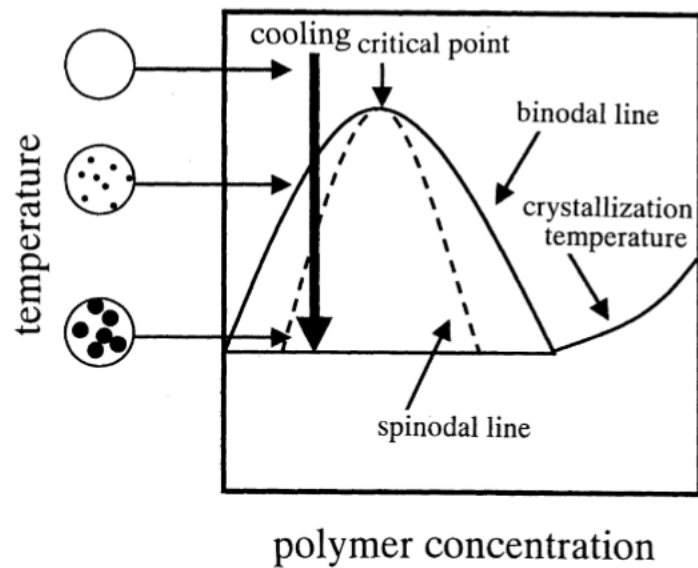


Figure 2.1 Scheme for spherical polymer powder formation by TIPS. In the thermal quenching process, the polymer precipitates by nucleation⁷⁹.

Polymer Choice for TIPS Microsphere Preparation

Although widely used in industry, polypropylene (PP) is not a common material in SLS, where the reproducible formation of suitable powder for SLS is one barrier. Therefore, providing an economically viable and scalable process to form PP polymer powders for SLS may broaden the range of materials available for SLS. Previously reported research on PP powder formation has focused on low solution concentration or specific molecular weight, limiting the potential of this previous processes to enable the application of PP as a suitable SLS material.

Previous research has shown the potential for this process. Research studies have examined the formation of polymer powder for SLS via the TIPS process with various polymers including polyethylene⁸¹ (PE) and nylon⁸². For example, in the preparation of nylon SLS powder by Hou, nylon was dissolved in a theta solvent at 1wt% concentration, heated above the theta temperature and quenched rapidly⁸². The polymer powder acquired by this method formed highly spherical particles.

Previous reports in the TIPS preparation of PP particles resulted in particles with a maximum diameter of 10 μ m⁷⁹. This size is too small for SLS because it might "evaporate out" during the high intensity laser exposure during sintering⁸³. Consequently, the PP sphere prepared in this previous study is not suitable for SLS printing. Rather it is blended with larger particles. Such a multimodal powder is beneficial to print quality because the small powder increases flowability and can fill gaps between larger powder particles. This combination of particle sizes maintains suitable flowability and increases the density of the printed object.

In this chapter, the use of the TIPS method will be examined to produce PP powder with a range of sizes, with the goal of providing feedback that can be used to create designed multimodal polymer particles. Concurrently, studies will be completed to expand the use of TIPS by developing an understanding of the

relationship between polymer molecular weight and polymer powder diameter. This knowledge will provide a foundation to form SLS powder of the required diameter from any PP molecular weight. Finally, the formation of PP polymer powder from pill bottles in the waste stream will be studied to open opportunities to use TIPS to create SLS powder from recycled materials.

Instrumentation and Experimental Procedure

Polypropylene Microsphere Preparation

The general preparation process of the PP powder consists of dissolving the PP in xylene at elevated temperature, quenching to a targeted temperature below the binodal, vacuum filtration of the formed polymer powder and subsequent drying. The following protocol is an example procedure to form PP spheres with a diameter at ~40 nm. All chemicals were purchased from Sigma-Aldrich and used as received. Important thermodynamic and dynamic properties of entangled PP are summarized in Table 2.2. These data were collected from the vendor's website⁸⁴.

91.0g xylene, 9.0g PP beads and a stir bar are added to a 250ml round bottom flask. The system is placed in a 190°C oil bath, homogenized and refluxed for 1hr (stir rate=200rpm). A cold trap is set up using a Fischer Isotemp with 50/50-water/ethylene glycol mixture as the refrigerant. Once the reflux has finished after 1hr, the flask is placed directly into the cold trap. The transfer of hot solution to the cold trap is completed as quickly as possible so the temperature change to the target temperature is rapid. The sample is then quenched for 1 hour. After the quench time is reached, the mixture is vacuum filtered for five minutes. The PP powder is then washed with cold ethanol three times to remove any residue xylene. Recovered polymer powder is then transferred into vials for future study. Each vial is then placed into a vacuum oven at 40°C until a constant weight is

Table 2.2 Properties of polypropylene

Property	Unit	Value
Glass Transition Temperature (T_g)	K	ca. 273
Melt Temperature (T_m)	K	ca. 430 for 12k PP ca. 433 for 250k and 340k PP
Melt index	g/10 min	12k PP: No record 250k PP: 12 340k PP: 4
Density ρ	g/cm ³	ca. 0.9
Entanglement Molecular Weight (M_e)	g/mol	ca. $4.50 \cdot 10^3$

reached, sealed with Parafilm and stored in a desiccator. To study the formation of PP powder from the waste stream, the preparation of microspheres from recycled materials was examined. In these studies, standard prescription pill bottles were cut into small pieces, dissolved in xylene and powder formation followed the processes described above. The distribution for PP particle size was characterized by scanning electron microscopy, where quench temperature, molecular weight, and concentration are targeted parameters studied.

Scanning Electron Microscope (SEM)

SEM was used to determine the size and shape of PP powder produced. The PP powder was first dispersed in ethanol and dropped on the sample stage. Before visualizing in the SEM, a thin gold layer was sputtered on the sample surface to eliminate surface charging. The SEM used in this study is a ZEISS-EVO with electron high tension (EHT) is set as 20.00kV.

High Temperature Gel-Permeation Chromatography (Hi-Temp GPC)

The molecular weight and dispersity of the polypropylene samples studied was determined by a high temperature gel permeation chromatograph using 1,2,4-trichlorobenzene (TCB) as the eluent (1.0-1.5mg/mL in concentration) and a Malvern High Temperature OMNISEC system equipped with one TSK gel column thermally stabilized at 150 °C. Viscometry, refractive index (RI), low angle light scattering, and right-angle light scattering were used as detectors to acquire molecular weight and polydispersity information.

Particle Size Analysis

The particle size was determined by using Image J to analyze the SEM images of the powder. In this process, each pixel is correlated to a length scale, where the size of each pixel was calibrated by the scale bar on the SEM image. Each

particle of interest was manually labeled, and their maximum length tabulated. At least ten particles were measured for each sample.

Results

Polypropylene microsphere powders were fabricated using the TIPS process for three molecular weights, with number average molecular weight (M_n)/ weight average molecular weight (M_w) of 5k/12k (12k), 67k/250k (250k) and 97k/340k (340k). For each PP sample, the impact of xylene solution concentration and quench temperature on the size and shape of the resultant nanoparticles are studied. The ability to use TIPS to create suitable PP powder for SLS from waste polymers was also examined by utilizing PP from a used pill bottle in the TIPS process. Figure 2.2 shows the SEM image for the polymer powder that is formed by TIPS of the pill bottle, where this is formed from a 9wt% PP-Xylene solution that is quenched to 40°C. The highly spherical and relatively uniform particle size indicate the universality of this approach.

Tables 2.3 to 2.6 present the average size (in microns) of the PP powder particles formed as a function of xylene solution concentration and quench temperature. In these studies, the quench temperature varies from -20°C to 40°C (253.15K to 313.15K), while the xylene solution concentration varies from 4% to 20% polypropylene. Table 2.3 shows the results for the 12K PP sample, while Tables 2.4 and 2.5 show the results for the 250K and 340K PP samples, respectively. Table 2.6 shows the results for the formation of PP powder from the recycled pill bottle. All these results characterize samples that are formed from identical dissolution, quench and filtering procedures, thus the only variables that impact these results are PP molecular weight, quench temperature and xylene solution concentration. The data in Tables 2.3 to 2.6 clearly show that the polymer particle size increases with increasing quench temperature and increasing solution concentration.

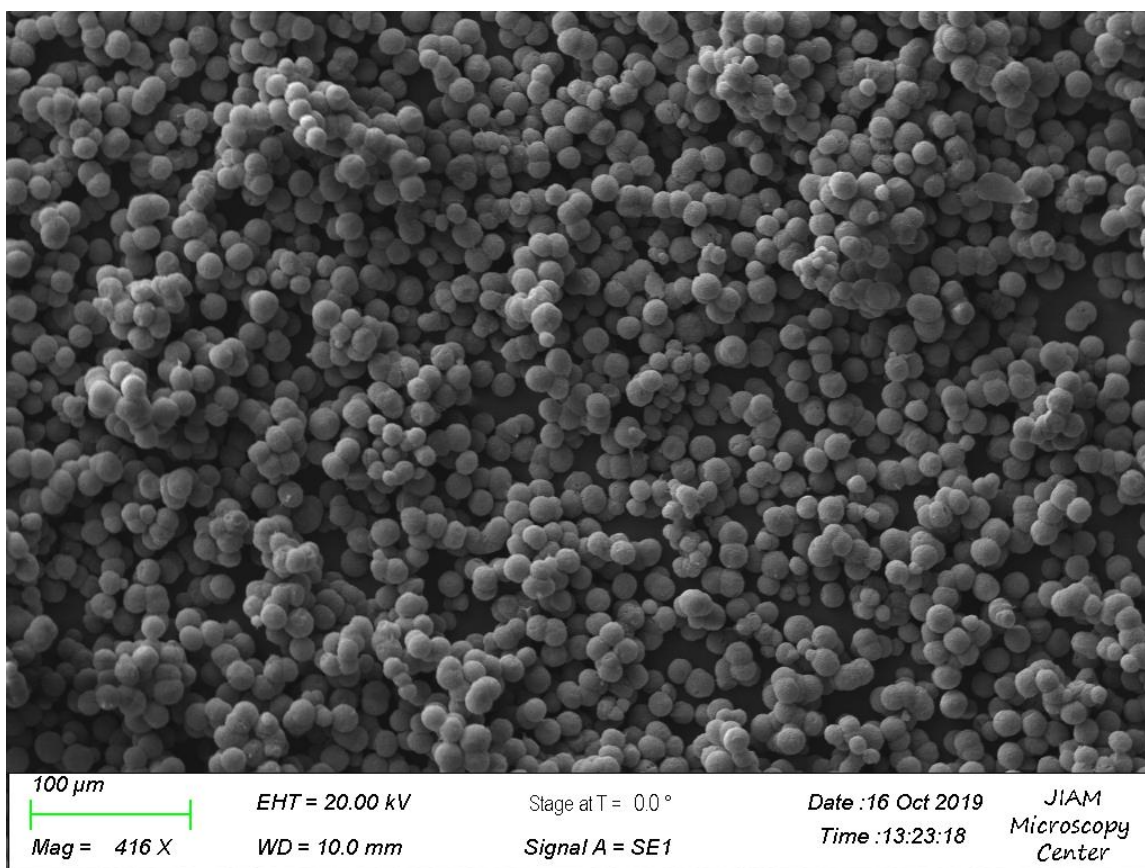


Figure 2.2 SEM image of polymer powder prepared by TIPS from a recycled pill bottle.

Table 2.3 Particle size in μm of 12k polypropylene powder formed with the TIPS process.

Quench temp	253.15K	273.15K	293.15K
Concentration			
4wt%	$0.284 \pm 0.068 \mu\text{m}$	$0.330 \pm 0.110 \mu\text{m}$	$0.469 \pm 0.079 \mu\text{m}$

Table 2.4 Particle size in μm of 250k polypropylene powder formed with TIPS process, - means no experiment was performed at that condition.

Quench temp Concentration	253.15K	273.15K	293.15K	313.15K
4wt%	$6.18 \pm 1.72 \mu\text{m}$	$7.33 \pm 1.82 \mu\text{m}$	$9.26 \pm 2.68 \mu\text{m}$	-
10wt%	-	$63.1 \pm 13.0 \mu\text{m}$	-	$70.2 \pm 12.8 \mu\text{m}$
15wt%	-	-	-	$92.1 \pm 11.8 \mu\text{m}$
20wt%	-	-	-	$107 \pm 11 \mu\text{m}$

Table 2.5 Particle size in μm of 340k polypropylene powder formed with the TIPS process, - means no experiment was performed at that condition.

Quench temp Concentration	253.15K	273.15K	283.15K	293.15K
4wt%	15.4 $\pm$ 3.2 μm	19.3 $\pm$ 2.2 μm	-	22.5 $\pm$ 3.9 μm
6wt%	-	-	31.5 $\pm$ 5.8 μm	-
9wt%	-	54.8 $\pm$ 5.5 μm	-	-
12wt%	-	-	76.7 $\pm$ 19.6 μm	-

Table 2.6 Particle size in μm of recycled polypropylene powder formed with the TIPS process, - means no experiment was performed at that condition.

Quench temp Concentration	273.15K	313.15K
9wt%	10.3 $\pm$ 1.1 μm	16.3 $\pm$ 2.0 μm
12wt%	-	23.0 $\pm$ 1.8 μm
20wt%	-	35.0 $\pm$ 4.8 μm

Table 2.7 shows the molecular weight characteristics of the recycled pill bottle, as determined by high temperature GPC. These results show that the number average molecular weight (M_n) and weight average molecular weight (M_w) of the recycled sample are 14,000 and 220,000, respectively. This sample therefore has a lower M_w , and a broader dispersity than the 250K isotactic sample. These results provide additional detail that can aid in understanding the relationship between molecular weight and particle size in the TIPS process, where an increase in molecular weight correlates to an increase in particle size.

Discussion

In this thesis, the impact of three variables on the size of polypropylene powder formed by TIPS are studied, namely, concentration, quench temperature and polymer molecular weight. Particle size increases with the increase of each of these variables. The following discussion focuses on the fundamental mechanisms behind these trends and relates these processes to the polypropylene-xylene phase diagram.

Effect of Solution Concentration on Particle Size

To elucidate the effect of solution concentration on the particle size, the diameter and volume (characterized by d^3) of the particles formed are summarized in Tables 2.8 and 2.9 for a fixed quench temperature and polymer molecular weight. These data are extracted from Tables 2.4 and 2.6, respectively. Standard deviations for each particle size have been omitted for simplicity. In these analyses, the data has been isolated for only those samples where powder has been formed from three concentrations at a given temperature. The only data sets that meet this requirement are the powder formed from the 250k PP when quenched at 40°C (313.15K) and the powder that is formed from the recycled pill bottle when quenched at 40 °C.

Table 2.7 Molecular weight of PP recycled from pill bottle as determined by high temperature GPC.

Recycled PP from the pill bottle	
Peak RV - (ml)	16.6
M _n - (Daltons)	1.40*10 ⁴
M _w - (Daltons)	2.20*10 ⁵
M _z - (Daltons)	1.52*10 ⁶
M _p - (Daltons)	1.22*10 ⁵
M _w / M _n	15.8

Table 2.8 Particle size of powder formed from 250k polypropylene quenched at 313.15K as a function of xylene solution concentration.

Concentration of Solution	Diameter in μm (d)	d^3 (μm^3)
10wt%	70.2	3.46×10^5
15wt%	92.1	7.81×10^5
20wt%	107	1.22×10^6

Table 2.9 Particle size of powder formed from recycled PP quenched at 313.15K as a function of xylene solution concentration

Concentration of Solution	Diameter in μm (d)	d^3 (μm^3)
9wt%	16.3	4.33×10^3
12wt%	23.0	1.22×10^4
20wt%	35.0	4.29×10^4

Figure 2.3 illustrates the role of solution concentration on the phase separation process in an ideal polymer solution, offering a thermodynamic understanding of the variation in particle sizes with concentration. In this figure, two quenching processes are depicted, where process 1 describes the process from a solution with a lower concentration while process 2 describes the process from a solution with a higher concentration.

In the phase separated mixture, two phases coexist with fixed polymer concentration. The concentration of the polymer-rich and polymer-poor phases are denoted C_{Rich} and C_{Poor} , respectively. These concentrations are independent to the initial concentration, and only depended on the quench temperature. The initial solution concentration will only affect the *amount* of each phase that coexists, which can be determined by the “lever rule” ($C_{\text{Rich}} \cdot R_1 = C_{\text{Poor}} \cdot P_1$).

The amount of the polymer-rich phase correlates to the size of the polymer particles, where more polymer rich phase corresponds to larger particles. Moreover, the equilibrium fraction of the polymer-rich (f_{Rich}) phase is proportional to the length of the tie line to the left of the initial concentration (R_1 or R_2) by $f_{\text{Rich}} = R_i / (R_i + P_i)$. As shown in the phase diagram, a higher solution concentration corresponds to a larger R_i tie line, which corresponds to larger particles. Thus, this aspect of the phase separation process offers a thermodynamic explanation that qualitatively correlates polymer particle size to solution concentration.

It has also been reported that during the TIPS process, the volume of the particle, which is proportional to the cube of the particle diameter, increases proportionally with the solution concentration⁷⁹. To test this prediction for our samples, the cube of the particle diameter is plotted as a function of xylene solution concentration in Figures 2.4 and 2.5 for the 250k PP and the recycled pill

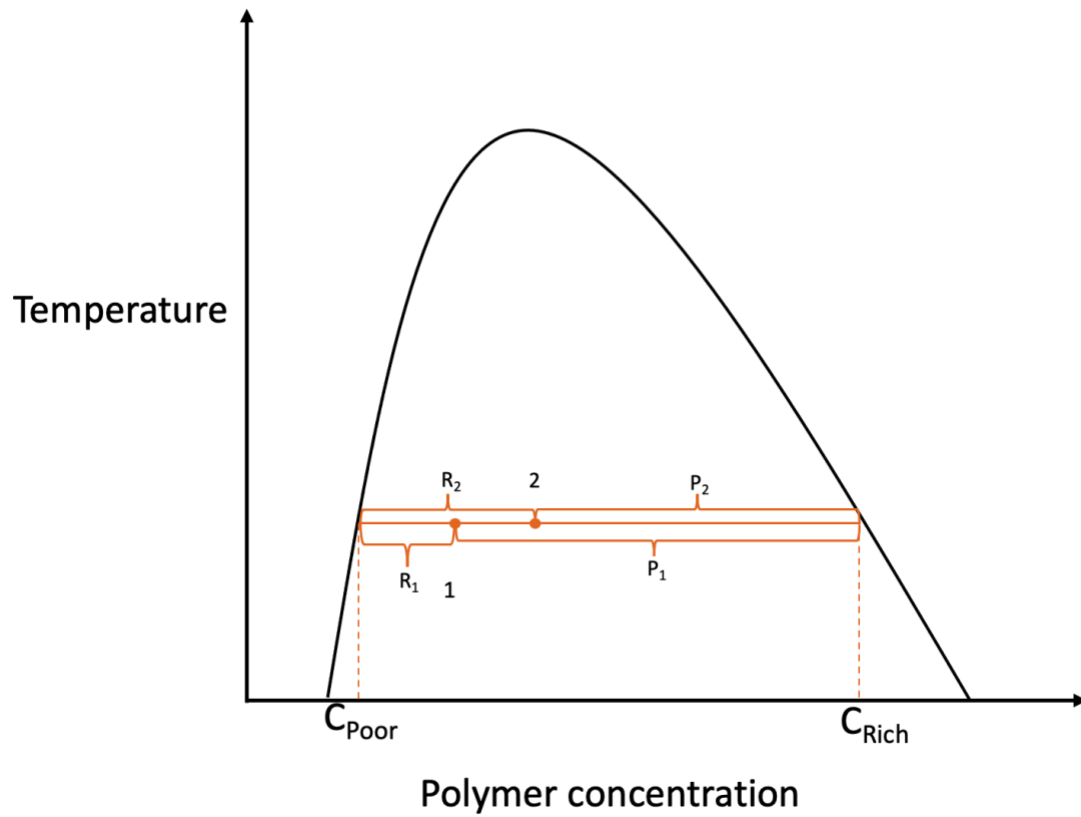


Figure 2.3 Scheme of two quench processes of two solutions with varying concentration in an ideal solution phase diagram.

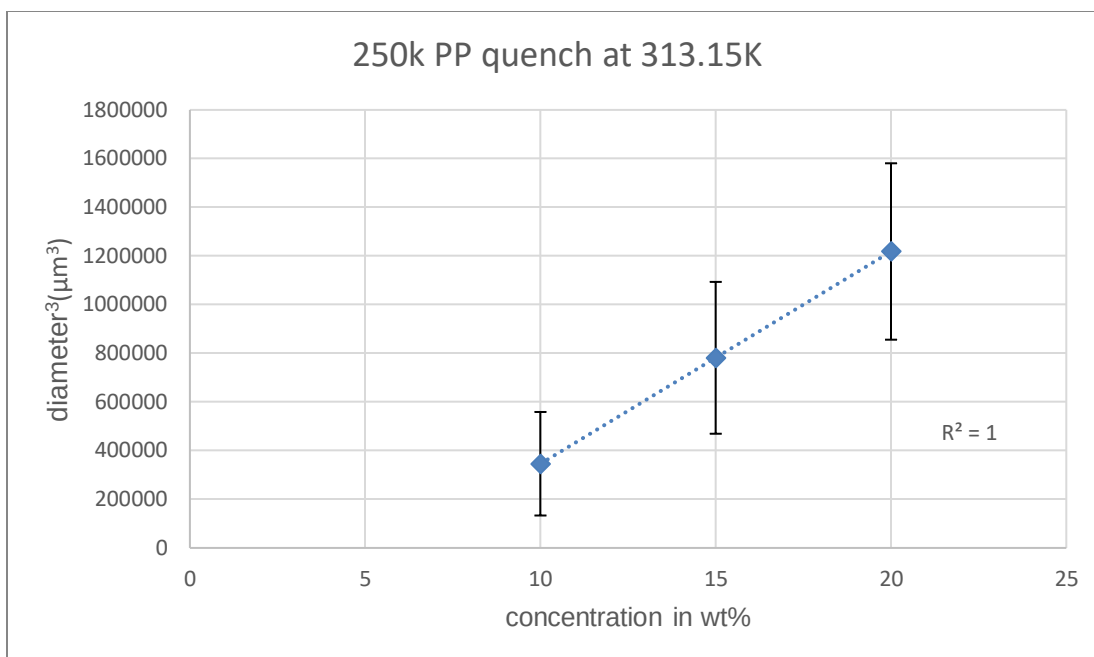


Figure 2.4 Plot of particle volume ($\sim d^3$) as a function of solution concentration for the powder formed from 250k PP when quenched at 313.15K.

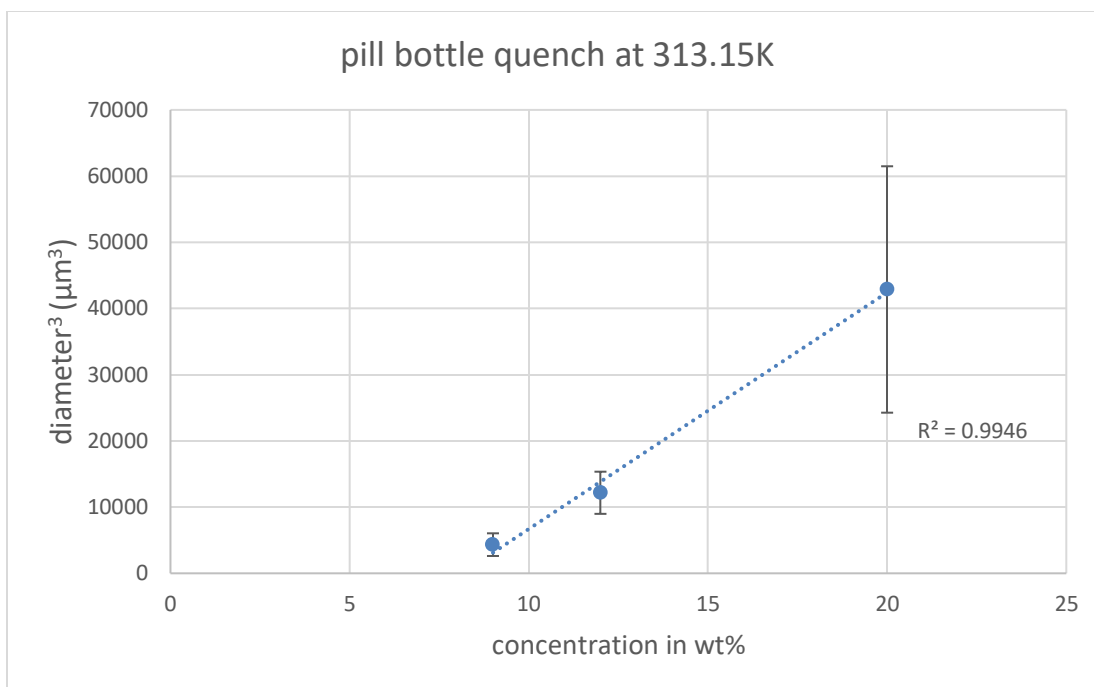


Figure 2.5 Plot of particle volume ($\sim d^3$) as a function of solution concentration for the powder formed from the recycled PP when quenched at 313.15K.

bottle, respectively. Both data sets show strong linear correlation of particle volume with solution concentration.

This relationship can be correlated to the fact that particle formation occurs by the Ostwald ripening or coalescence mechanism⁸⁵. In this process, the volume of the particle formed ($\sim d^3$) is proportional to the volume fraction of particles (ν), temperature (T) and the coalescence time (t), and inversely proportional to the viscosity of the solution (η), as shown in Equation (1). In Equation (1), k is Boltzmann's constant, and d is the diameter of the droplet or particle. As the volume fraction of particles (ν) is proportional to the solution concentration, this equation provides a foundation to understand the correlation of particle size to solution concentration in TIPS.

$$d^3 = [8kT\nu/(\pi \eta)]^*t \quad (1)$$

Effect of Polymer Molecular Weight on the Powder Particle Size

In order to study the influence of molecular weight on the final particle size, Table 2.10 presents the particle size formed from PP with various molecular weights using TIPS. These data were extracted from Tables 2.3-2.5. Each column in Table 2.10 can be used to monitor the influence of molecular weight on the particle size with all other parameters being constant. The standard deviation for each particle size have been omitted for simplicity.

Inspection of the data in Table 2.10 indicates that the polymer particle size increases with polymer molecular weight. This dependence of powder particle size with molecular weight can also be explained by invoking the phase diagram of the polymer solution. Figure 2.6 illustrates the change in the phase diagram of a polymer solution with polymer molecular weight, where a higher MW polymer is less soluble than a smaller polymer chain, as is predicted by Flory-Huggins theory. For example, Matsuyama et al., reported that the cloud point in the TIPS

Table 2.10 Particle diameter of PP powder for various polymer molecular weights at different temperatures. Solution concentration is constant at 4wt%.

MW \ Quench Temp	253.15K	273.15K	293.15K
12k	0.280μm	0.330μm	0.470μm
250k	6.18μm	7.33μm	9.26μm
340k	15.4μm	19.3μm	22.5μm

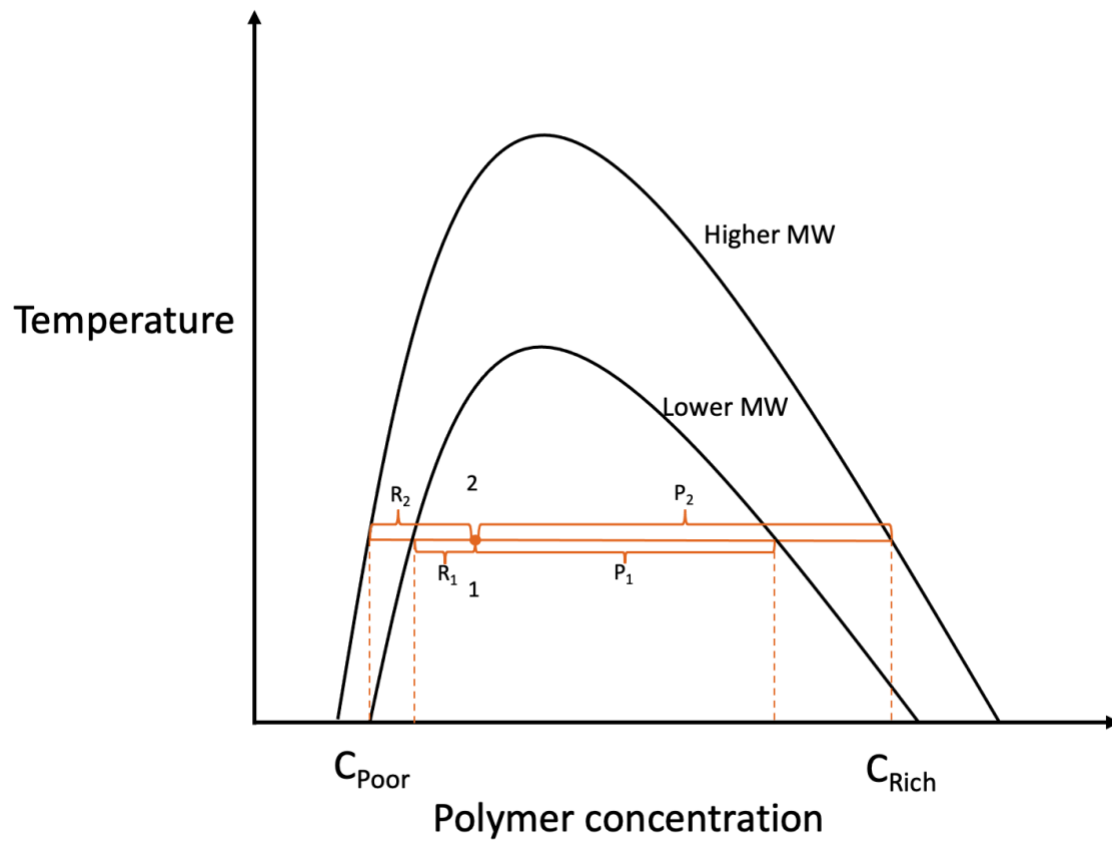


Figure 2.6 Scheme of two quench processes in polymer solutions with different molecular weight polymers. This scheme has been simplified.

process of PP in diphenyl ether (DPE) shifts to lower temperature with a decrease in polymer molecular weight⁸⁶.

Figure 2.6 further illustrates the impact of polymer molecular weight on the amount of coexisting phases in a phase separated polymer solution. If both solutions are brought to the same quench temperature and concentration, the tie line for the solution with the higher molecular weight is longer ($R_2 > R_1$), corresponding to a higher fraction of polymer-rich phase. This then corresponds to a larger particle size formed from a solution that contains higher molecular weight, with all other parameters being equal. Further quantitative studies are planned that will more precisely document the phase diagram of the PP solutions with varying molecular weights.

Effect of Quench Temperature on the Particle Size

Each row in Table 2.10 provides insight into the correlation of quench temperature to the particle size. Equation 1 shows that d^3 is proportional to the quench temperature, so Table 2.11 presents the cube of the particle diameter for the same powder formation conditions as Table 2.10. The quench temperatures studied are 253.15, 273.15 and 293.15K, with the concentration constant at 4wt%. Standard deviation for each particle size have been omitted for simplicity.

If droplet coalescence is controlling particle size as indicated by the solution concentration dependence of particle size, then the temperature dependence of Equation 1 should quantitatively account for the experimentally observed temperature dependence. Inspection of Equation 1 shows that the particle volume is proportional to temperature, but in Equation 1, the viscosity is also temperature dependent. Therefore, the temperature dependence of the particle size will deviate from linearity by a factor that is dependent on the temperature dependence of the viscosity. The temperature dependence of the viscosity of

Table 2.11 Cube of particle diameter (μm^3) of PP powder formed from PP with various molecular weights and at a variety of quench temperatures. Solution concentration is constant at 4wt%.

Quench Temp M _w	253.15 K	273.15 K	293.15 K
12k	0.0220 μm^3	0.0360 μm^3	0.104 μm^3
250k	238 μm^3	389 μm^3	804 μm^3
340k	3.38*10 ³ μm^3	6.86*10 ³ μm^3	1.14*10 ⁴ μm^3

polymer solutions follow Arrhenius behavior⁸⁷, as shown in Equation 2. In Equation 2, A and Q are constants for a fixed system.

$$\eta = A * e^{Q/(RT)} \quad (2)$$

The temperature dependence of the particle size is therefore a convolution of the linear temperature factor and the temperature dependence of the viscosity. Moreover, an increase in quench temperature lowers the viscosity of the polymer solution, thus both the temperature and viscosity factors in Equation 1 drive the formation of a larger particle at higher quench temperatures.

To examine the quench temperature dependence of particle size more quantitatively, Equation 1 can be rewritten as

$$d^3(T) = T / \eta(T) * (8k_u / \pi) * t$$

where $8k_u / \pi * t$ is independent of temperature. Rearranging this equation shows that $\eta(T) \sim T / d^3(T)$ with a proportionality constant of $8k_u / \pi * t$. Taking into account the Arrhenius dependence of the solution viscosity leads to the prediction that $A * e^{Q/(RT)} \sim T / d^3(T)$ if droplet coalescence is controlling the particle size.

Taking the natural log of both sides leads to the proportionality of $1/T$ with $\ln(T/d^3(T))$. Thus, a plot of $\ln(T/d^3(T))$ as a function of $1/T$ should be linear if Equation 1 describes the temperature dependence of the particle size formed in the TIPS process. Figure 2.7 shows the plot of $\ln(T/d^3(T))$ as a function of $1/T$, including linear fits. This plot clearly shows that $\ln(T/d^3(T))$ varies linearly with $1/T$ for all PP molecular weights studied. This strongly suggests that droplet coalescence is the dominant process that controls polymer particle size in the TIPS process of polymer powder fabrication.

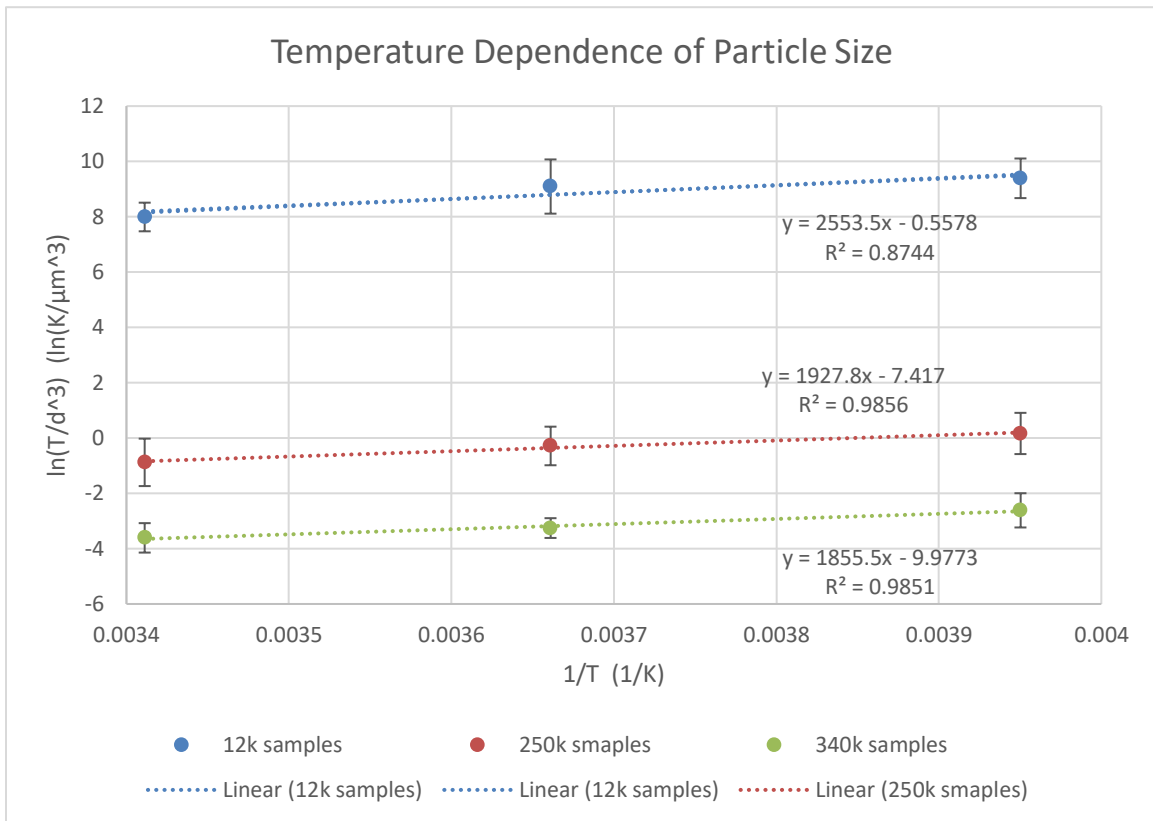


Figure 2.7 Plot of $\ln(T/d^3)$ as a function of $1/T$ to verify droplet coalescence controls particle size.

This interpretation is consistent with the analysis of the concentration dependence of the particle size. In this previous discussion, concentration is the only variable that changes in Equation 1, providing a straightforward (and linear) correlation between d^3 of the final polymer powder and solution concentration. By accounting for the temperature dependence of all variables in Equation 1, Figure 2.7 clearly shows that the temperature dependence of the particle size formation can be accounted for by the factors included in the droplet coalescence process.

Conclusion

In this chapter, we have successfully prepared PP powders by applying the TIPS process to polypropylene-xylene solutions. The simple physicochemical mechanism of TIPS provides a process by which a researcher can prepare polymer microspheres based on thermodynamic solubility. The process requires information on the binodal line of the polymer solution, which guides homogenization at higher temperature, which is then quenched at a lower temperature to form particles that can be isolated.

The particle size is also tunable by control of the TIPS conditions. The particle size increases with an increase in solution concentration, quench temperature and molecular weight. The solution concentration dependence can be qualitatively explained by considering the fraction of the polymer-rich phase at the quench temperature in the phase diagram. Similarly, the molecular weight dependence of the particle size can be qualitatively explained by invoking the shift in polymer solubility with molecular weight.

The Ostwald coalescence mechanism provides a more quantitative correlation between the specific conditions of the TIPS process and the resultant particle size. Solution concentration and molecular weight both affect the particle size by their relation to the volume fraction of particles (ν) in Equation 1.

When studying the effect of temperature to particle size, the temperature dependence of the coalescence process and the viscosity of the solution must be accounted for. Considering a convolution of both temperature and viscosity leads to an expected dependence of particle size (d) and Temperature (T) of $1/T \sim \ln(T/d^3)$, which is verified for the samples studied.

Thus, the analysis of concentration dependence and temperature of the resultant polymer particle size indicates the dominant process that controls the particle size is droplet coalescence during phase separation process. Consequently, Equation 1 can be used as a guide in any polymer solution that undergoes the TIPS process to prepare polymer powder. Tuning the parameters in Equation 1, offers a quantitative mechanism to produce polymer microspheres with controllable diameter.

CHAPTER THREE

REDUCING THE ANISOTROPY IN 3D PRINTED POLYCARBONATE SAMPLES WITH REACTIVE PROCESSING

Introduction

Anisotropy in mechanical properties is an ongoing challenge in samples fabricated by fused filament fabrication (FFF)^{52,88-91} or fused deposition modeling (FDM). The strength perpendicular to the deposition layer (z-direction) is much lower (30-70%) than the strength along the deposition direction. This anisotropic performance relegates objects manufactured by FFF to applications that do not require load bearing, which limits its utility as a manufacturing technology in industry. The structural foundation for this mechanical anisotropy is poor interlayer adhesion in the final printed structure.

In order to alleviate this drawback, researchers have focused on methods to enhance the strength of the interlayer interface in different ways. Figure 3.1 from Zhang et al. illustrates the molecular level processes that are important in the development of this interface during the 3D printing process⁹². From left to right, these are deposition, interfilament contact, polymer diffusion and formation of entanglements between filaments. In this figure, “d” denotes the depth or height of entanglement between layers.

Methods to enhance the strength of the interlayer interface can be divided into a few different categories, including interface modification during printing or via post printing treatments, printing parameter optimization, and chemical or physiochemical modification of the interface. Our discussion will focus on developing methods to chemically modify the interface in this introduction.

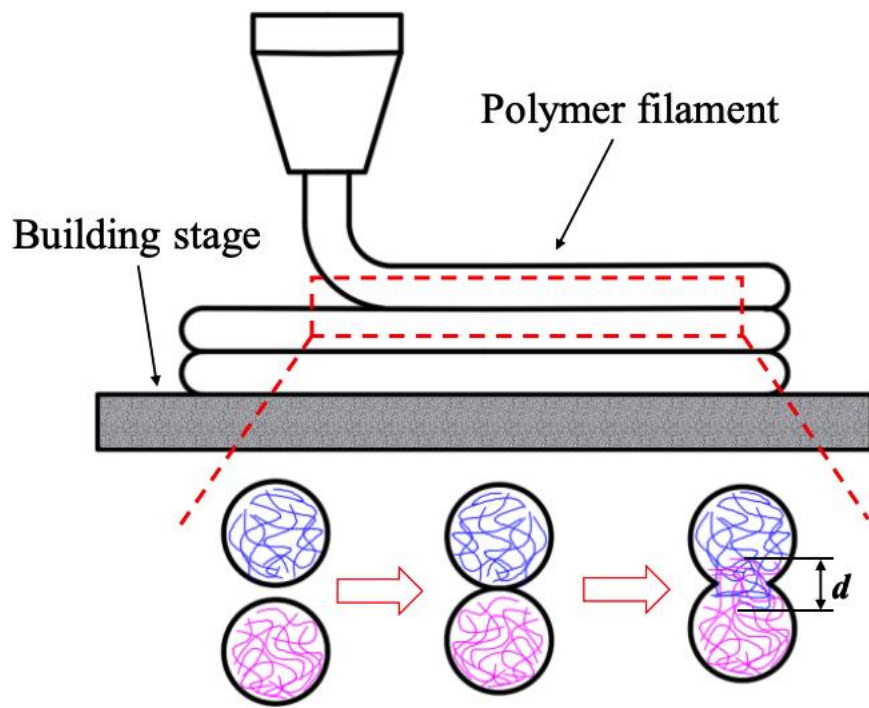


Figure 3.1 Scheme for the interlayer entanglement formation during FFF⁹².

Chemical Modification of Materials

The most straight forward approach to increase interlayer strength is by the formation of covalent bonds (crosslinks) between layers. Previous studies have demonstrated the potential of this approach, which may enhance the interlayer strength significantly. A critical factor in this approach is to find a molecule that will react to form a crosslink at the interlayer interface during or after printing, yet still allow the polymers in the neighboring filaments to diffuse during the printing process, as well as extrude from the print head.

These competing effects makes the use of reversible crosslinks, such as in a Diels-Alder (D-A) reaction, an interesting candidate to strengthen the interlayer interface. When a polymer filament contains functionalities that can undergo a D-A reaction are printed, the D-A linkage will break at the high temperature of the print head, allowing extrusion of the filament to form a deposited layer. After the deposition and potential diffusion of polymer between layers, the D-A reaction will form bonds between molecules, and thus layers, at the lower temperature. This process, therefore, potentially bonds two layers more strongly through the formation of crosslinks at the interlayer interface. Davidson et al. have tested this concept, by synthesizing a partially crosslinked D-A adduct as a mending agent for samples printed using polylactic (PLA) as the matrix⁹³. The addition of 10% and 25% mending agent to the PLA filament showed an increase in the interlayer strength by 88% and 130%, respectively. This D-A adduct thermally de-crosslinks during deposition but reforms the crosslink in the printed object after deposition and cooling. Rather than using D-A adducts as additives, Yang et al. prepared three different kinds of D-A crosslinked polymers as feedstock materials⁹⁴. Objects printed with these materials show strongly isotropic mechanical properties, where the transverse strength approaches 95% of the longitudinal strength.

Another approach to strengthen the interfilament interface is to blend the polymer filament with crosslinkers that won't react during printing, but their reaction can be initiated after deposition. An example of this is work by Shaffer et al., that prepared functionalized PLA by blending it with 10wt% of a radiation sensitizer⁹⁵. After this functionalized PLA was printed, the objects were annealed at 60°C while exposed to ionizing radiation (gamma rays). Both annealing at high temperature and exposure to ionizing radiation are required, to allow for both interlayer diffusion and crosslink reaction to occur to strengthen the interlayer interface. By applying this process, the ultimate strength of the reacted sample reached 35.9MPa, which is an increase from 23.5MPa for the control sample.

Previous research in our group by Perryman et al. has also reported that by applying multi-amine crosslinkers between layers of FFF printed objects immediately before filament deposition in the printing process, the interlayer strength will also increase⁵⁵. In this study, the researchers apply the multi-amine crosslinker on the interface between adjacent layers. The oxidation products from the butadiene segment in the ABS matrix reacts with these crosslinkers and form a stronger crosslinked interlayer interface.

Physiochemical Modification of Materials

Relative to chemical modification of interlayer interfaces, the physiochemical modification of interlayer interfaces is more straight-forward and may be more cost-effective. A primary goal in the physiochemical modification of interlayer interfaces in 3D printed objects focuses on improving the rate of polymer diffusion and lowering the polymer viscosity to form more robust interlayer interfaces during the print process. Materials that can be blended into the polymer filament that are effective modifiers can be divided into two major categories, inorganic and organic.

By addition of inorganic nanofillers, such as calcium carbonate, multiwall carbon nanotube and silica, Meng et al. showed increased interlayer strength of acrylonitrile-butadiene-styrene (ABS) structures printed by FFF by 18-60%⁹⁶. Gao et al. doubled the interlayer strength of PLA structures printed by FFF by the addition of talc⁹⁷. More specifically, structures printed from PLA/talc filament exhibited an interlayer strength of 52.6MPa whereas structures printed from neat PLA filament exhibited an interlayer strength of 25.7MPa. This improvement is attributed to the decrease in filament viscosity, which correlates to more interlayer polymer diffusion during the print process and stronger interfaces. It is worth noting that not all inorganic fillers reduce anisotropy in 3D printed structures. It is crucial that the proposed additive lowers the viscosity and increases interlayer polymer diffusion during the printing process. An increase in filament melt viscosity increases anisotropic performance since it limits the polymeric diffusion between layers during the printing process⁹⁸⁻¹⁰¹.

Previous research from our group by Levenhagen et al. has shown that the addition of linear or branched low molecular weight polymers is effective in reducing anisotropy in structures fabricated by FFF using PLA^{57,58}. The addition of a linear low molecular weight additive leads to a 66% increase in interlayer bond strength, while the addition of three-arm star low molecular weight additives leads to a 100% increase. Levenhagen et al. have also reported that the addition of low molecular weight surface segregating additives materials such as PLA and polymethylmethacrylate (PMMA) to ABS filaments increases the transverse interlayer strength in printed objects by 40% and 25%, respectively⁵⁶. Interestingly, the miscibility of the additive with the filament polymer is not critical. These experiments clearly demonstrate the importance of improving molecular level entanglement between layers, and an effective additive should not only lower the viscosity but also increase the diffusion of the polymer across the interlayer interface.

Examined Methods to Reduce Anisotropy with Reactive Processing

In this thesis, reducing anisotropic properties in 3D printed structures will focus on the chemical modification of the interlayer interface through reactive processing. This work builds from previously work in our group by Levenhagen et al¹⁰². In these previous studies, it was shown that the UV initiated in-situ reaction of crosslinkers at the interlayer interface during printing is an effective method to significantly strengthen the interlayer interface. The crosslinkers examined in this study include linear and three-arm star low molecular weight PLA that are terminated with reactive methacrylate groups. This in-situ reactive processing protocol forms interlayer interfaces with strengths that increased up to 140% and 200% over that of the neat 3D printed structures for linear and three-arm star additives, respectively. Figure 3.2 shows a picture of the UV-LED optical source that is coupled to the 3D printer, which enables in-situ UV exposure during the deposition process.

Polycarbonate (PC) is an attractive material for 3D printing for its superior properties, including transparency and high impact resistance. Figure 3.3 shows the chemical structure of PC. The absence of clearly reactive functional groups in PC, such as a carbon-carbon double bond, suggests that the decreasing the anisotropy of PC objects printed by FFF through chemical modification is non-trivial. In this thesis, we examine the ability of UV-initiated in-situ crosslinking of PC to improve the anisotropy of PC objects fabricated by FFF.

In these studies, filament that includes PC blended with crosslinker and photoinitiator are examined as targeted feedstocks for the reactive processing protocols. The most popular method to prepare such solid-solid mixtures is through melt mixing, where crosslinker, photoinitiator and neat polymer pellets were dry blended together followed by co-extrusion. However, in order to minimize unnecessary high temperature exposure before the final printing, a solution-based homogenization method was also studied.

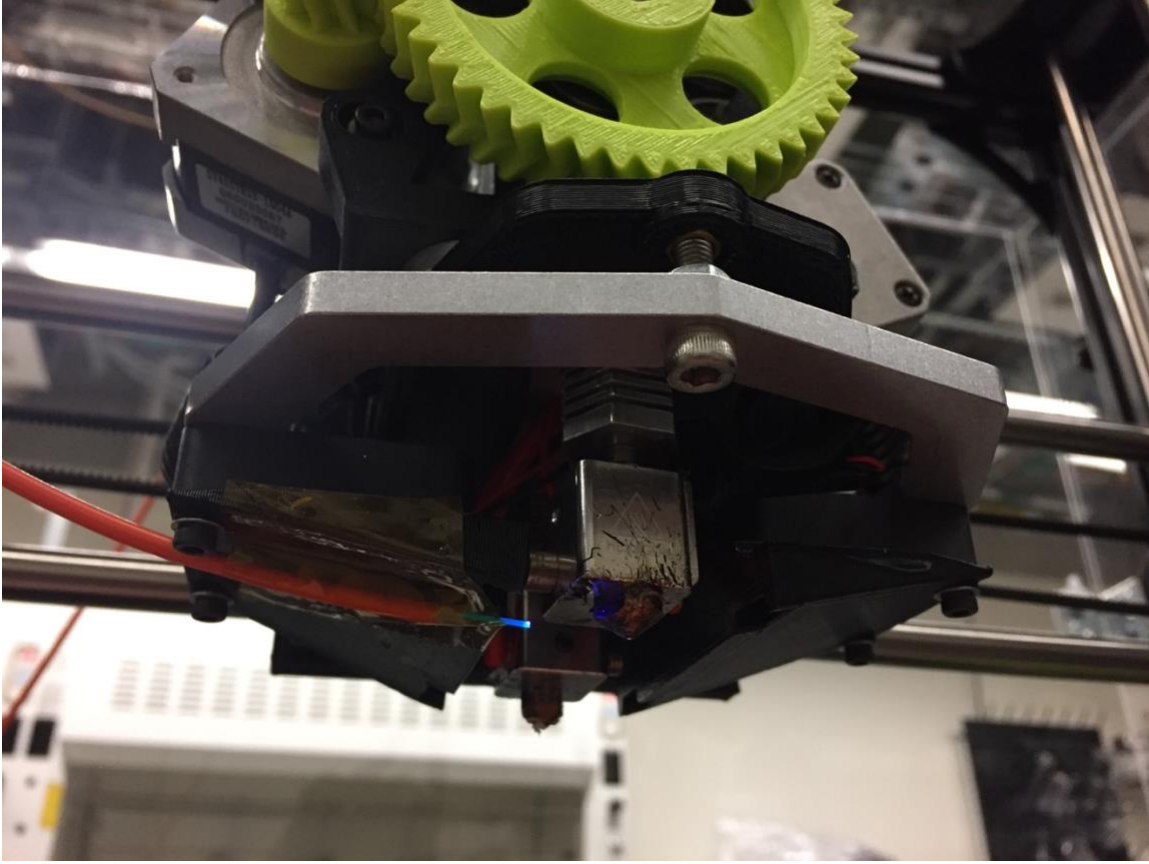


Figure 3.2 Photo of a UV-LED mounted on the FFF printer, the angle of the optical fiber has been modified to focus the UV light spot on the nozzle.

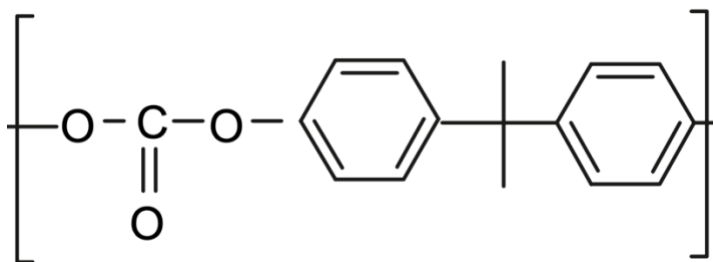


Figure 3.3 Chemical structure of polycarbonate (PC).

Tris[2-(acryloyloxy) ethyl] isocyanurate and 4,4'-bis(diethylamino)benzophenone are chosen as suitable crosslinker and photoinitiator, respectively, where their structures are presented in Figures 3.4 and 3.5, respectively. In this chapter, tris[2-(acryloyloxy) ethyl] isocyanurate will be termed the “crosslinker”, while the 4,4'-bis(diethylamino)benzophenone will be called the “photoinitiator”. This crosslinker is chosen for its similarity to the three-arm functionalized PLA previously used as a crosslinker in FFF reactive processing protocols¹⁰². The photoinitiator was chosen as its absorption peak (340-370nm) is located near the emission wavelength of our UV-LED (365nm).

Instrumentation and Experimental Procedure

The Homogenization of PC Pellets, Crosslinker and Photoinitiator

Polycarbonate pellets were purchased from 3DXTECH as a 5lb bag, while the crosslinker and photoinitiator was purchased from Sigma-Aldrich, and toluene was purchased from Fischer Scientific. All chemicals were used as received. To prepare PC blended with crosslinker and photoinitiator, all components were co-dissolved in solution and then precipitated by solvent evaporation.

For example, to make the filament with 3 wt% crosslinker and 0.5 wt% photoinitiator (a sample that is abbreviated as PC 0.5B3X), the subsequent procedure was followed. 96.5g polycarbonate pellets, 3g crosslinker and 0.5g photoinitiator are dissolved in ~400ml toluene, stirring 12hrs (overnight) to obtain a homogenous solution. The solvent was then removed in a rotary evaporator at 30°C. Once all the solvent has been evaporated, the white solid was removed to a vacuum oven at 30°C until a constant weight is reached. The solid chunk was shattered into small pieces by a dry blender to create pieces that are approximate 5mm. It was found that targeting this size was optimal for the filament fabrication process described below.

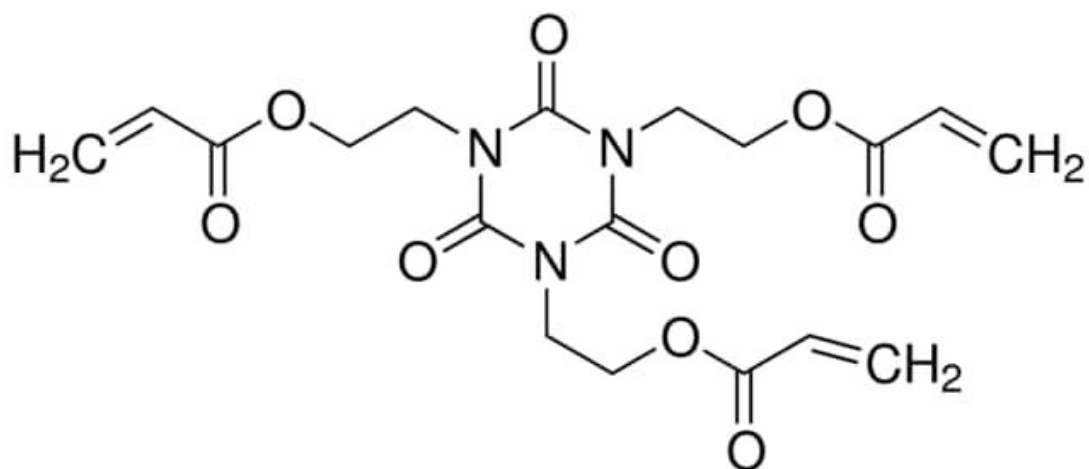


Figure 3.4 Structure of the crosslinker, tris[2-(acryloyloxy)ethyl] isocyanurate examined in these studies.

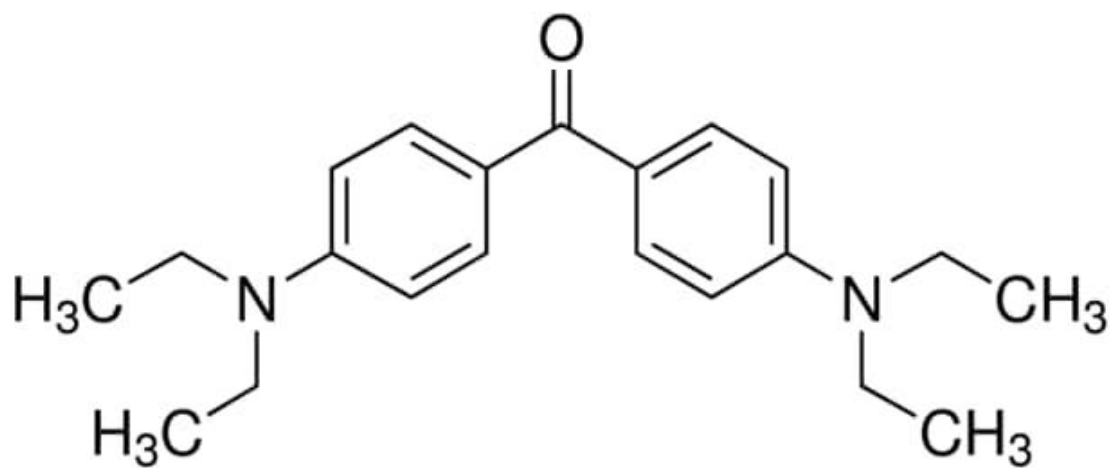


Figure 3.5 Structure of a suitable photoinitiator, 4,4'-bis(diethylamino)benzophenone.

These small pieces were further vacuum dried at 30°C to a constant weight, where these samples are ready for extrusion. All PC formulations studied in this thesis contain 0.5wt% photoinitiator, with variation in the concentration of crosslinker from 0wt% (PC 0.5B), to 1wt% (PC 0.5B1X), and 3wt% (PC 0.5B3X).

Filament Extrusion

A Filabot Extruder 2™ was used to extrude filament suitable for 3D printing. In the extrusion process, the screw rotating speed is kept constant at 1 s⁻¹ with an extrusion temperature of 232°C. The diameter of the resultant filament fluctuated since the size of feed materials varies significantly. Thus, this initial filament is pelletized and re-extruded to form filament suitable for 3D printing. Upon extruding the re-pelletized material, the uniform pellets provide filament with a consistent diameter of 2.70mm. In order to ensure all samples undergo the same thermal history, filament prepared from the neat PC also underwent the same homogenization, drying, extrusion, pelletizing and re-extrusion processes.

3D Printing and Tensile Sample Formation

Both neat PC and functionalized PC filament are printed using the same printing parameters, nozzle temperature (290°C) and bed temperature (135°C). The printed object is a cube with edge length 70mm x 70mm and a 3mm wall thickness. The total number of layers in each sample is 233 with a layer thickness of 0.3mm. Traveling speed of the printing head during printing is 60mm/min in the X-Y plane. The samples are all printed on a TAZ6 by Lulzbot™ with a 0.5mm nozzle.

After the printing is finished, the cube is removed from the print bed and ASTM-D638 type V (“dogbone”) tensile bars are outlined on the wall of the objects as shown in Figure 3.6, to provide both transverse and longitudinal dogbones. The detailed dimension of this tensile bar is shown in Figure 3.7. The tensile bars

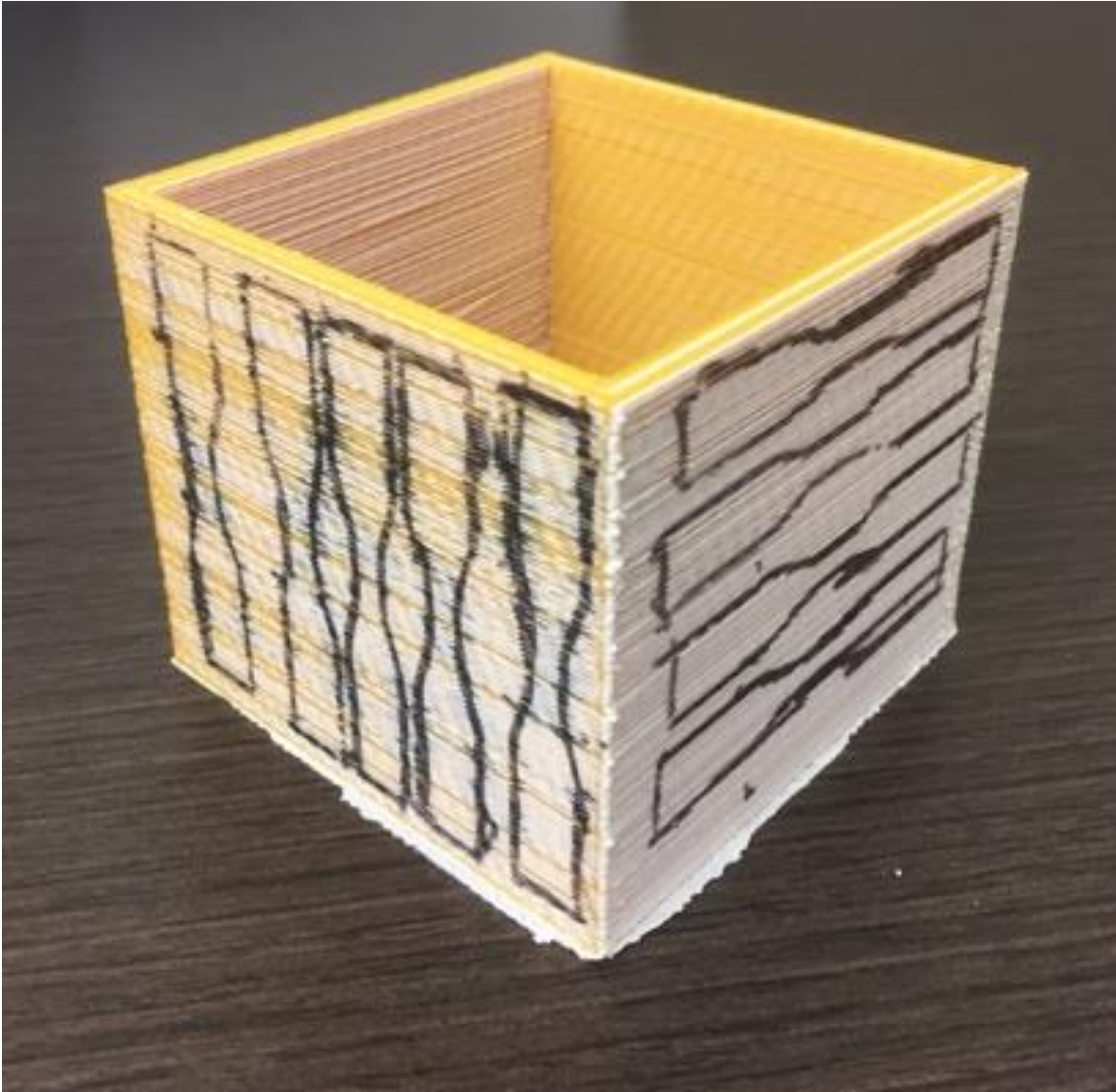


Figure 3.6 Picture of printed cube with the outline of the ASTM-D638 Type V dogbone outlined on the wall of the printed cube.

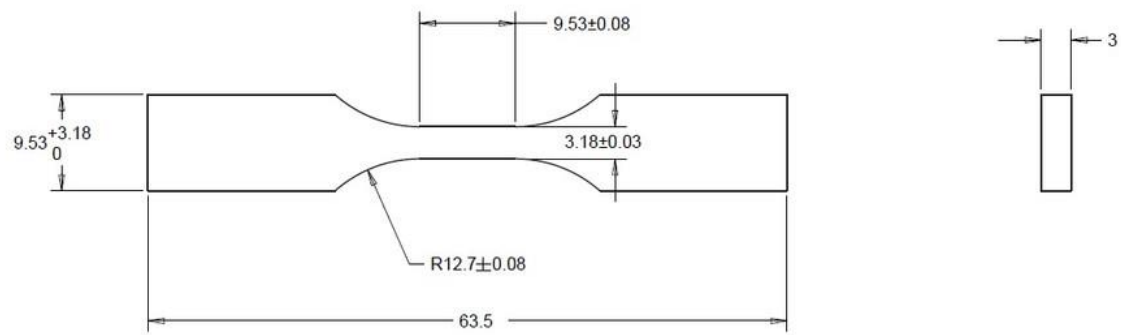


Figure 3.7 The detailed dimension of ASTM-D638 Type V tensile bar.

were then cut out of the cube along the outline by a Dremel™ saw. By applying this method, we ensured that each sample has the same thermal history and the raster in the specimen is along the desired direction.

For each component and each direction, at least 6 samples are prepared and tested for statistical purposes. The scheme of the raster orientation in the longitudinal and transverse tensile specimen are also shown in Figure 3.8.

Tensile Property Determination

The interlayer strength is characterized by determining the tensile properties of the dogbones, where the stress at failure of the transverse specimen is considered as the interlayer strength. The tensile properties of each dogbone were determined using an Instron™ universal testing machine equipped with a 100kN load cell. The extension rate is 1mm/min.

Results

The maximum tensile strength of each dogbone in both the longitudinal and transverse direction are presented in Figure 3.9, where the red bars denote the longitudinal strength and blue bars denote the transverse properties of the sample. The moduli of each these samples are also presented in Figure 3.10. In these experiments the composition and processing protocol are systematically varied to identify the important characteristics of the reactive processing protocols that impact the ultimate properties of the printed sample.

The simplest system examined is the pure polycarbonate filament, which is printed both in the presence and absence of UV. Comparison of the tensile strength of these two samples in Figure 3.9 shows little change in the transverse strength and a slight decrease in the longitudinal strength with exposure to UV. This decrease may be due to the slight oxidation or degradation of the PC with the exposure to UV. Inspection of the properties of the samples with added



Figure 3.8 The orientation of raster in the two tensile test specimens (top: longitudinal, bottom: transverse) using the ASTM-D638 Type V geometry⁵⁸.

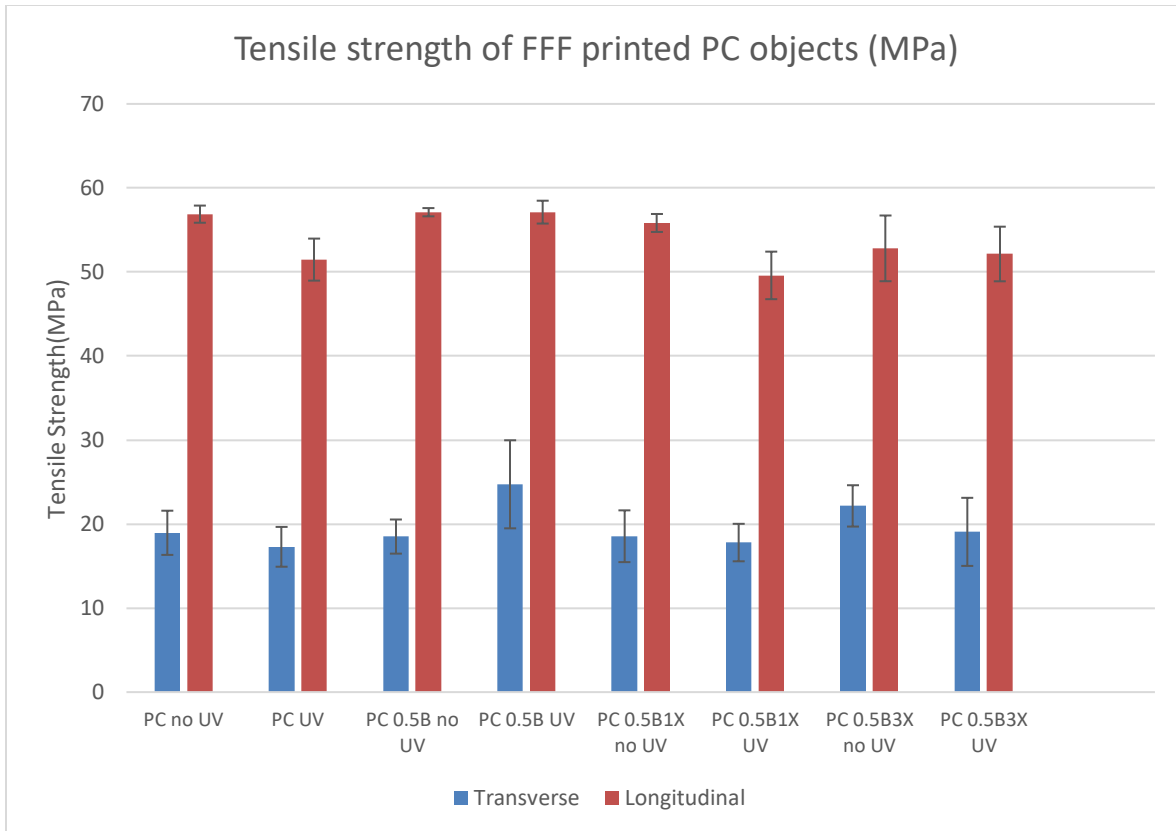


Figure 3.9. Maximum tensile stress of each sample studied in both the longitudinal and transverse directions.

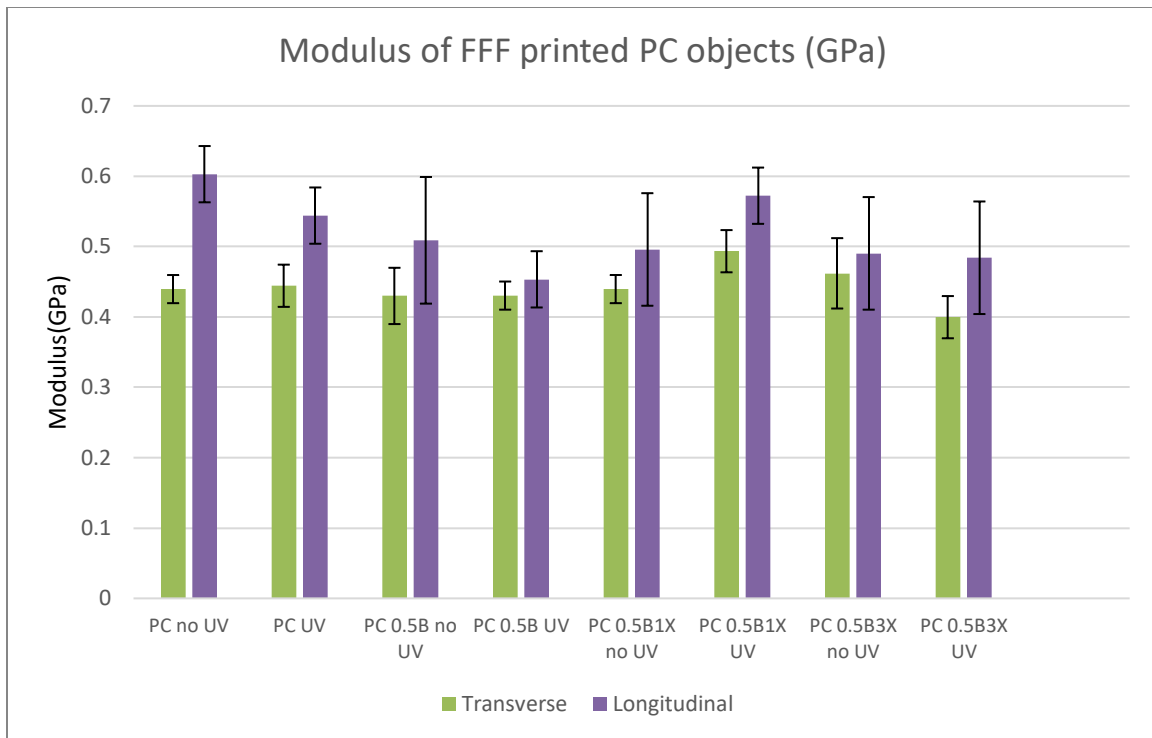


Figure 3.10. The modulus of each sample studied in both the longitudinal and transverse directions.

photoinitiator (but no crosslinker) [PC 0.5B] shows little change in the tensile strength in either direction for the sample that is not exposed to UV when compared to the cubes printed from the neat PC filament. However, exposure of this sample to UV creates a significantly stronger interface, as defined by the increased transverse tensile strength (43% increase). This sample also exhibits nearly isotropic behavior in terms of its modulus. Interestingly, incorporation of the crosslinker to this sample at either 1% or 3% does not show a further increase in transverse tensile strength, rather these samples exhibit tensile properties that are similar to (or slightly less than) those of the sample printed from the neat PC, regardless of exposure to UV.

Discussion

Thus, the sample with the most enhanced interlayer adhesion is the sample with 0.5% photoinitiator that is printed in the presence of UV, which exhibits a transverse tensile strength that is increased by 43% relative to that of the neat PC. Interestingly, the incorporation of the crosslinker to this sample does not further increase the interlayer adhesion. Our interpretation of these results is that in these PC samples, there is a competition between interlayer crosslinks that occur at the interface between layers and a bulk crosslink reaction that occurs throughout the filament, away from the interlayer interface. This interpretation revolves around the idea that an interlayer crosslink will increase interlayer strength, while crosslinks in the bulk will increase polymer molecular weight, increase viscosity, and decrease polymer diffusion. Each of these factors will decrease the ability for polymers to diffuse across the interlayer interface during the print process and will increase anisotropy⁹⁸⁻¹⁰¹.

Moreover, there exist additional processes that impact the success of these crosslinking reactions. One is the oxidation of polycarbonate that can result in the formation of free radicals and oxygen containing functional groups or degradation of the polymer chain. For instance, Lee et al. reported that the oxidative

degradation of PC can occur at ca. 300°C, which is close to the nozzle temperature in our printing process, 290°C¹⁰³. This oxidative degradation is identified as free radical cleavage or rearrangement of the polymer backbone or side group of PC. More specifically, Kuroda et al. has proposed potential intermolecular crosslink reactions that will increase polymer molecular weight ¹⁰⁴. Possible mechanisms for these crosslinks are illustrated in Figure 3.11, taken from the work of Kuroda et al¹⁰⁴.

Additionally, infrared spectroscopy provides supporting evidence of the oxidation of PC in some of our printed samples. Figure 3.12 shows the IR spectra of polycarbonate samples used in this study, as well as that of the benzophenone photoinitiator. The blue and light green curves show the IR spectra of the commercial PC pellets and the filament before printing.

Similarly, the dark blue and purple curves are the IR spectra for the printed polycarbonate polymer in the presence and absence of UV, respectively. Inspection of all these four curves, shows that there is no significant change in the IR spectra, indicating there is no significant oxidation of the neat PC during extrusion into filament or printing by FFF.

The red curve shows the IR spectra of the benzophenone based photoinitiator, while the dark green curve and golden curve are the IR spectra of the printed PC-photoinitiator mixtures in the presence and absence of UV, respectively. Both PC-photoinitiator samples show the introduction of a new peak at ca. 1700 cm⁻¹, which is not present in the neat photoinitiator. This peak is consistent with the presence of the product of PC oxidation, such as phenylsalicylate¹⁰⁵. The structure of this oxidation product is shown next to the designated peak in Figure 3.12. This clearly shows that the printed PC-photoinitiator mixture, especially when exposed to UV, forms new functional groups that are consistent with PC oxidation and may participate in further crosslinking reactions.

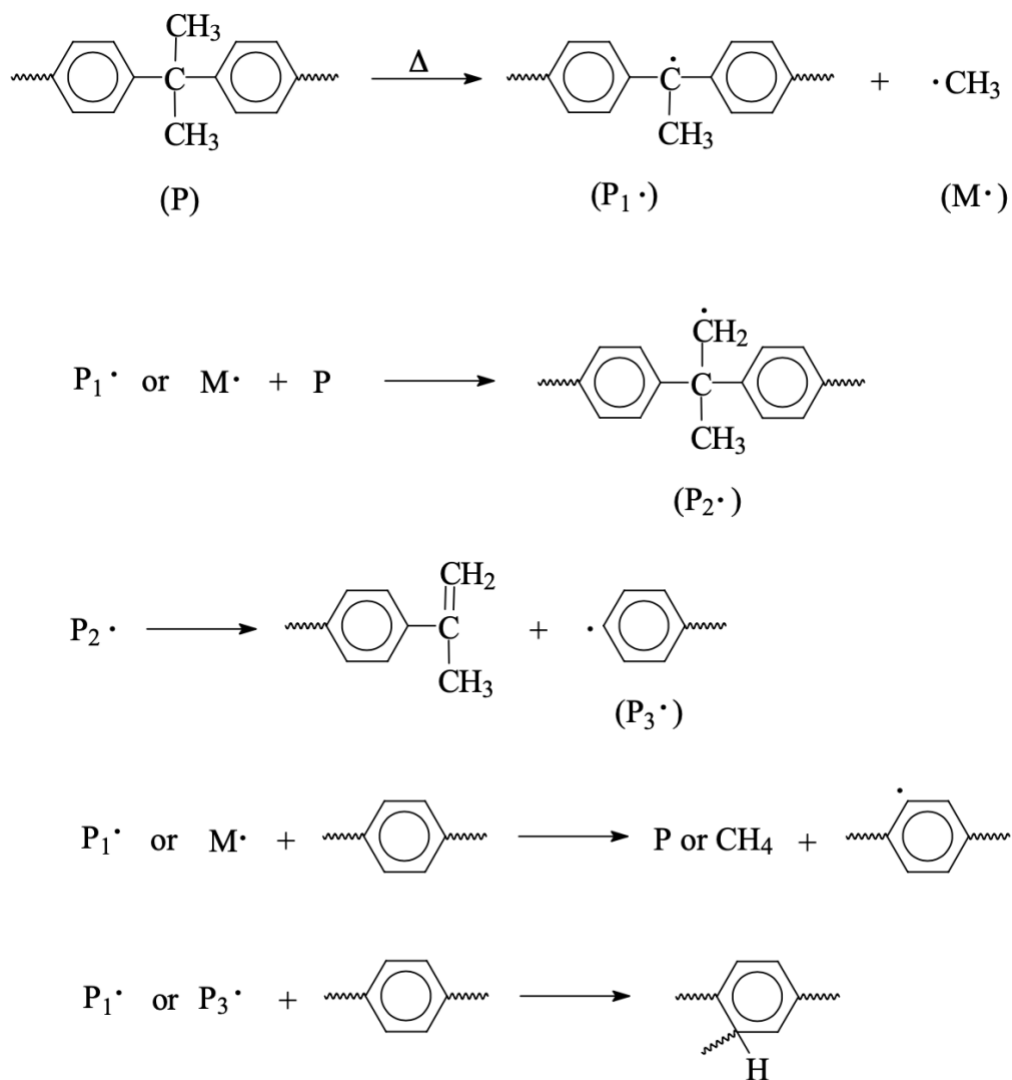


Figure 3.11 . Potential intermolecular crosslink mechanism for PC at elevated temperature¹⁰⁴.

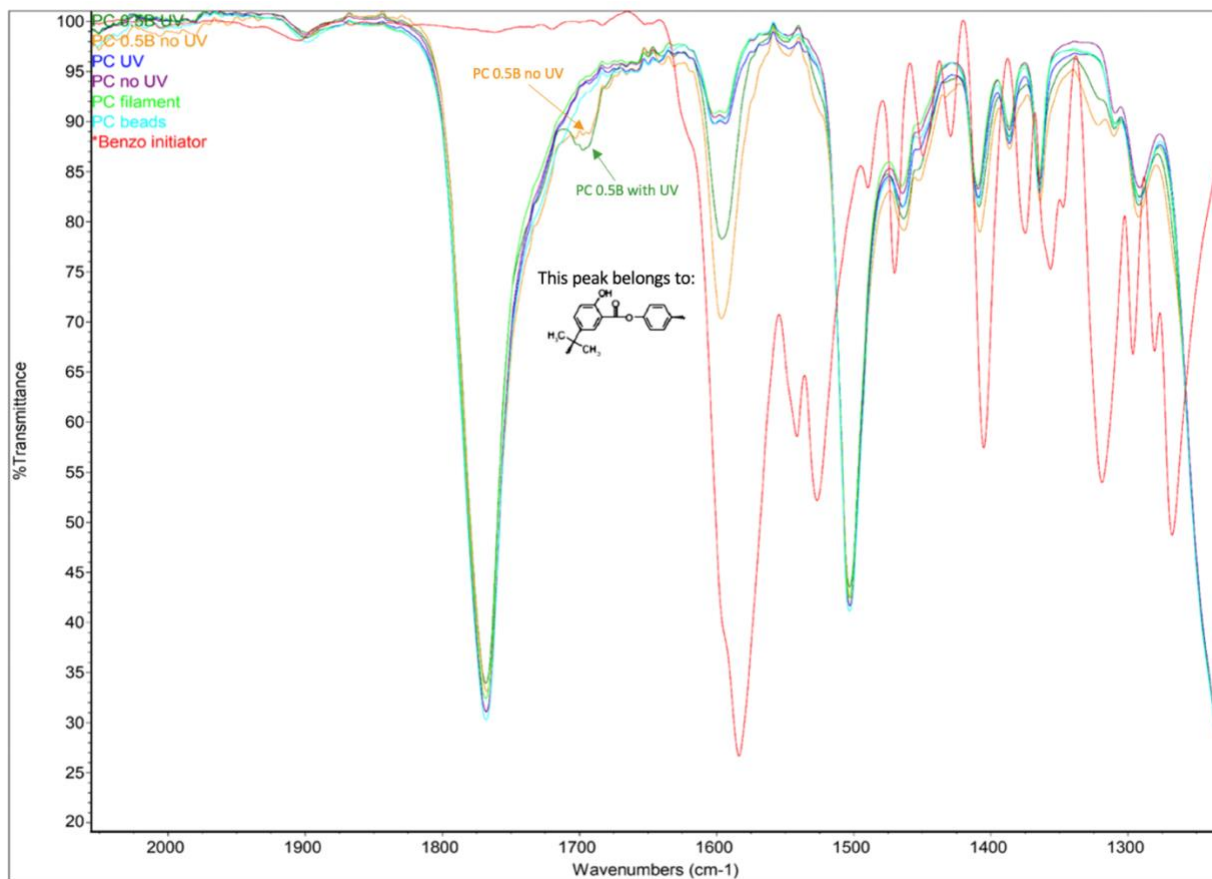


Figure 3.12 IR of various samples examined in this study. Dark blue and purple curves are [PC with UV] and [PC without UV]; Dark green and Golden curves are: [PC 0.5B with UV] and [PC 0.5B without UV]; Light blue and Light green curves are: PC filament and PC beads; Red curve is the photoinitiator used in this experiment. The arrow denotes a new peak corresponding to the oxidation of the printed polycarbonate with photoinitiator samples at $\sim 1700\text{cm}^{-1}$.

From previous reports, neat PC does not show a change in the 1600cm^{-1} doublet peak after exposure to UV¹⁰⁵. However, in Fig. 3.12 a strong singlet peak replaces the doublet peak at ca. 1600cm^{-1} for the samples that contain the photoinitiator. This change may either come from the carbonyl group in the photoinitiator (Figure 3.5), an increase in the carbonyl containing oxidation products that form with exposure to UV of the samples that contain photoinitiator, or a combination of the two.

However, the success of the crosslinking reactions relies on the polymer being at elevated temperature. The thermal history of a deposited bead in the FFF process is quite complex. For instance, as shown by our group and others^{55,106}, the temperature of the deposited bead cools after it is extruded from the nozzle. However, as new hot filament is deposited on the previous layer, heat transfers onto the supporting layer, heating it up. This continues for multiple layers, as shown in Figure 3.13. Consequently, there is continued potential for the PC to crosslink at elevated temperatures at the interface as multiple layers are deposited, potentially enhancing interlayer strength.

On the other hand, if the crosslink reaction occurs in the bulk of the filament during the deposition, e.g., when the polymer melts coming out of the nozzle, this will limit the diffusion of the polymer between layers and inhibit interlayer strength. Thus, there exist two potential crosslink reactions in our systems, one that relies on the oxidation of the PC at elevated temperature near the filament surface, while the other involves the reaction of the added crosslinker with the polymer. As the oxidation of the PC requires elevated temperature and exposure to oxygen, it would seem that this reaction is more likely to occur on the filament of the surface. However, as the crosslinker may be distributed throughout the filament, these crosslink reactions may occur throughout the filament.

Moreover, the temperature profile of the filament as it passes through the nozzle may impact these reactions as well. For instance, Wang et al. determined the

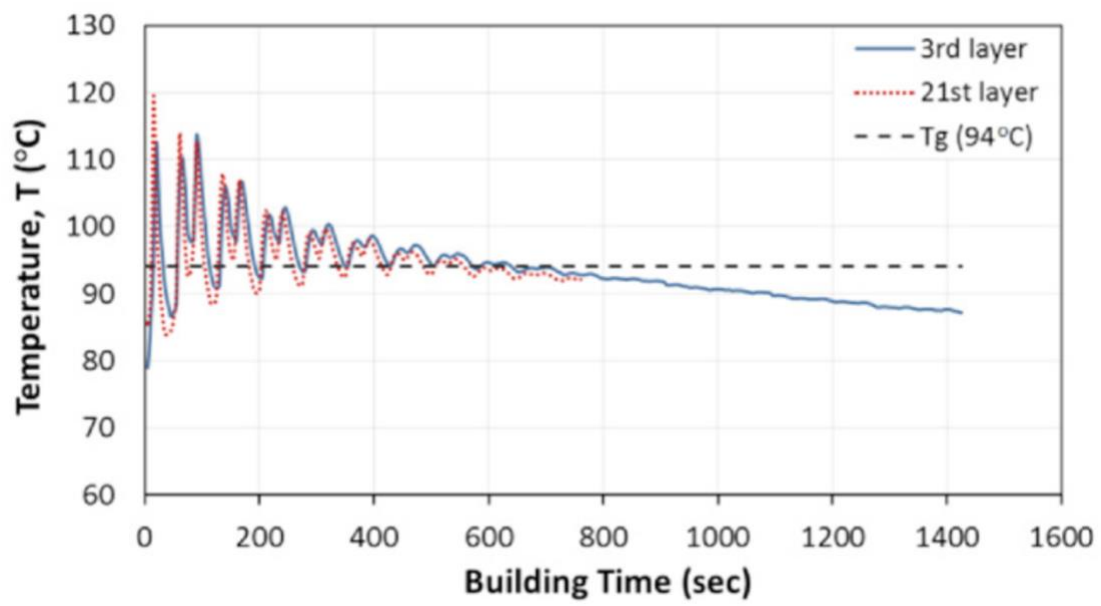


Figure 3.13 Layer's post-deposition temperature oscillation with the deposition of further layers¹⁰⁶.

temperature distribution of a filament as it passes through an FFF nozzle¹⁰⁷. As is shown in Figure 3.14, the temperature profile of the filament in the nozzle is uneven, consisting of a peripheral outer cylinder with an elevated temperature that surrounds an inner core that is slightly cooler¹⁰⁷. Thus, the outer portion of the filament is heated, and exposed to ambient oxygen during the print process, provide an environment that is conducive to oxidation and the formation of interlayer crosslinks when a new layer is deposited. The core, due to its lower temperature and lack of oxygen, is less conducive to oxidation and to generate crosslinks.

Thus, the IR spectra suggests that the addition of the photo initiator and UV exposure appears to initiate more oxidation of the PC and the potential for crosslinking reactions. Furthermore, the photo initiator may also initiate more crosslinks on the surface due to its elevated temperatures, more free radicals and ambient oxygen. The absence of a photoinitiator appears to limit the crosslink reaction, as in the neat PC (exposed to UV or not) as well as the polycarbonate-photoinitiator sample that is not exposed to UV, the interlayer interfaces are similar in structure and tensile strength. However, inclusion of the photoinitiator that is activated by exposure to UV exposure generates an environment that creates the strongest interlayer strength.

However, with the addition of the crosslinker to the blend, the strength of the interlayer interface is not improved over that of the samples printed from the pure polymer. In samples with photoinitiator and crosslinker, it appears that there exist processes that limit the improvement of interlayer adhesion, which that compete with the potential crosslinking between filaments that will strengthen the interlayer interface.

Our previous work shows that the presence of crosslinks can also inhibit polymer diffusion across the interfilament interface⁵⁸ and similar processes may occur in these samples. The crosslinking of the polycarbonate throughout the filament can

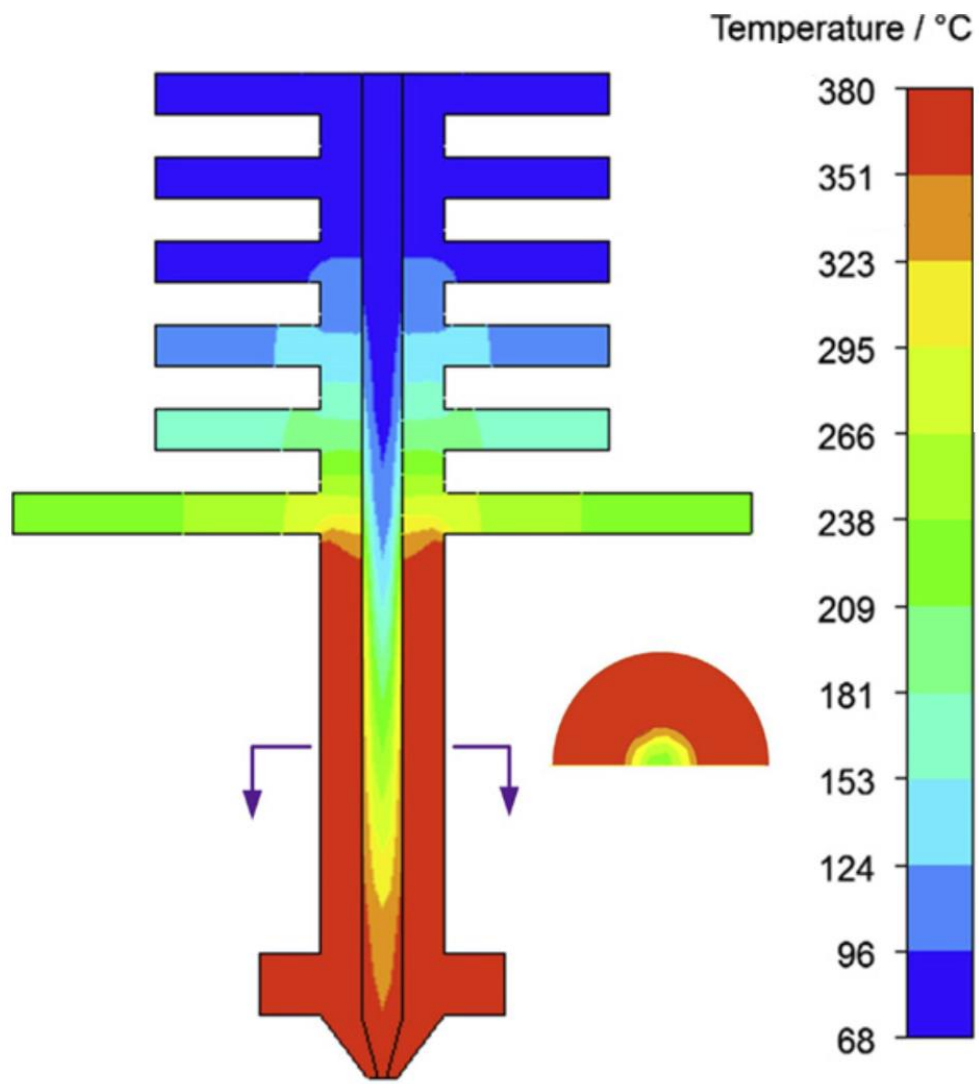


Figure 3.14 Temperature distribution inside the nozzle where the filament inside has a hot peripheral and a cooler core¹⁰⁷.

occur due to the presence of both photoinitiator and crosslinker, which create larger molecules that diffuse more slowly. This increase in polymer molecular weight increases viscosity and decreases polymer diffusion, which will limit the formation of interlayer adhesion between the interfaces. It does appear that the increase in crosslinker concentration from 1 to 3% results in excess crosslinker at the filament interfaces, which results in a slight increase in interlayer strength.

Conclusion

This chapter examines potential reactive processing protocols to strengthen the interlayer adhesion in objects created from polycarbonate with FFF. These results show that the incorporation of a photoinitiator to the polycarbonate combined with in-situ exposure to UV during printing creates the strongest interlayer adhesion. The addition of a separate crosslinking agent or the absence of the UV light or photoinitiator result in weaker interfacial adhesion between layers.

These observations are interpreted to indicate that there exist two potential crosslink reactions in these reactive processing protocols, one that relies on the oxidation of the PC at the filament surface, while the other involves homogeneous crosslinking of the polymer throughout the filament. The oxidation of the PC at the filament appears to require elevated temperature and exposure to oxygen, and benefits from the UV activation of the photoinitiator. On the other hand, the reaction of the crosslinker throughout the filament appears to occur during the elevated temperatures of the printing process. Moreover, the UV initiated reactions at the filament interface serve to strengthen the filament-filament interface, while the homogeneous crosslink reactions increase polymer

molecular weight, slow polymer diffusion and limit the formation of entanglements between filaments.

The competition of these two reaction pathways is consistent with the mechanical property data presented in this chapter. The improved performance of the photoinitiator-PC filament printed in the presence of UV can be attributed to the dominant formation of interlayer crosslinks with minimal bulk crosslinks. On the other hand, the poorer interfacial adhesion of the samples with the crosslinker can be attributed to the increased reaction of the crosslinker throughout the sample, which will decrease the interlayer diffusion and mitigate the strengthening that may occur in the formation of interlayer crosslinks in this system.

These results thus provide insight into the competing molecular level processes that occur in UV assisted reactive processing protocols to reduce the anisotropy in 3D printed objects. In designing further protocols, the competition between beneficial and adverse reaction must be considered. For instance, the incorporation of surface segregating crosslinkers and increasing the peripheral temperature of filament during the printing process should maximize the formation of interlayer crosslinks providing improved transverse tensile strength and reducing structural anisotropy.

CHAPTER FOUR

CONCLUSIONS AND FUTURE PLANS

Polypropylene Powder Formation by TIPS Summary

We have successfully produced polypropylene powders with appropriate size for selective layer sintering using thermally induced phase separation (TIPS) of polypropylene-xylene solutions. These studies elucidate the relationship between the processing conditions and resultant particle size in the TIPS process, where control of processing conditions directs the size of the ultimate polypropylene powder. More specifically, the relationship between particle size and solution concentration, molecular weight and quench temperature has been qualitatively explained in terms of the phase diagram of the polypropylene-xylene solution, and quantitatively correlated to the Ostwald ripening or coalescence mechanism.

Qualitatively, the particle size increases with solution concentration, which can be ascribed to the composition dependence of the amount of the polymer rich phase that emerges from the phase separation process. Quantitatively, the volume of the formed particle increases linearly with concentration, which is consistent with the known relationship between volume fraction of droplets and droplet size in the Ostwald ripening mechanism⁸⁵.

The increase in the particle size with polymer molecular weight can be qualitatively connected by the phase diagram as well. In this case, an increase in polymer molecular weight shifts the binodal line to higher temperature, which increases the amount of polymer rich phase that forms the particle. This results in larger particles formed from solutions that contain higher molecular weight polymers for a given temperature and solution concentration.

The dependence of resultant particle size on quench temperature appears to be well described by the understanding of the droplet coalescence mechanism,

where the temperature dependence of the coalescence process must be convoluted with the temperature dependence of the viscosity. Accounting for both factors leads to the prediction that the temperature dependence of the particle size is $\ln(T/d^3(T)) \sim 1/T$. All of the samples examined in this work show robust agreement with this temperature dependence. This agreement and the observed relationship between solution concentration and powder particle size indicate that coalescence mechanism is dominant in the TIPS process. This insight offers pathways to controllably target the particle size for any polymer particle that is prepared by the TIPS process.

Future Plan for PP Powder Formation

Particle Size Distribution with Laser Diffraction Analysis (LDA)

The particle sizes in this thesis were measured by SEM and analyzed by ImageJ. This method is time consuming and limits the sample pool to about 50 particles for each TIPS condition. This limits the statistics of the analysis, but this limitation can be overcome by the use of laser diffraction analysis (LDA) to determine the average particle size and size distribution of the fabricated polymer particles. Horiba has commercialized an LDA instrument that has successfully measured the size of polyvinylchloride powder that are in the micron range^{108, 109}. LDA has also been used in the work reported by Kloos et al. to analyze the size of PC microsphere prepared by the TIPS process¹¹⁰. The data acquired from LDA will be a normal distribution which will readily provide the mean and standard deviation of the particles size distribution.

Phase Diagram of the PP-Xylene Solution with Various Molecular Weight

When we studied the effect of molecular weight, the shift of binodal line is the reason for the particle size change. To determine the binodal line of each solution as a function of polymer molecular weight, we will use a melting point

device to determine the cloud point of the solutions¹¹¹. For the PP-xylene system a series of solutions will be prepared for each molecular weight with different concentrations. These solutions will be sealed in a capillary tube and heated. Rather than looking for the melting of a solid, in these experiments, the temperature where the solutions become cloudy will be identified as the cloud point and binodal of that solution⁸⁶. The shift in the binodal line with temperature will then be directly correlated to the change in particle size to provide quantitatively data.

Viscosity Measurement of PP-Xylene Solutions

To study the relationship between viscosity and temperature, the viscosity of the PP-Xylene solutions as a function of temperature will be determined by a high temperature viscometer. These viscosity data will explicitly account for the change in viscosity with temperature of Equation 1. Thus, a plot of $d^3 \times \eta$ (T) should vary linearly with temperature according to Equation 1. This analysis will provide a self-consistent check on the analysis of the temperature dependence of the particles size described above.

SLS Printing for Resultant Polymer Microsphere

The printability of resultant powders will be examined by incorporating them into an SLS printers. Collaborations with the Williams group at Virginia Tech, verify the printability of the PP powder that forms from the recycled pill bottles. Examination of the mechanical properties of the printed objects will also be completed to correlate how powder sphericity, size and flowability as formed from TIPS impacts mechanical properties of the printed parts.

Fabricating Polymer Powders for Other polymer Systems Using TIPS

To verify the versatility for the TIPS method to create polymer particles from a broad range of polymers, we will create polymer particles for SLS using the TIPS

with various polymer-solvent systems. Example systems include polyamide 11/ethanol system¹¹², PC/cyclohexanol system¹¹³ and poly(L-lactide)/triacetin system¹¹⁴. For each system, the polymer will be dissolved in the solvent at high temperature and quenched to a lower temperature. This will form polymer microspheres for any given polymer. Moreover, guidelines provided in this study will be used to access polymer particles that are the proper size for SLS.

Reducing Anisotropy with Reactive Processing Summary

In Chapter 3, reactive processing protocols in the FFF printing of polycarbonate are investigated. In particular the impact of exposure to UV light, incorporation of a photoinitiator and a crosslinker on the anisotropy of a printed part are examined. These results show that the filament that consists of photoinitiator blended with PC that is printed while exposed to UV light shows the least anisotropic mechanical behavior. The filament that contains a crosslinker and photoinitiator blended with the PC exhibit performance that is similar to that of the neat PC filament.

This behavior is attributed to the competition of two possible crosslinking reactions, one that occurs at the interlayer interface and one that occurs throughout the filament. The filament that contains the crosslinker and initiator blended with the PC will be able to form crosslinks throughout the filament, which will inhibit the viscosity and diffusion of the polymer during the deposition process. This, in turn, will limit the diffusion between filaments and the formation of entanglements between layers, creating a weaker interface. The filament formed from the photoinitiator blended with PC, on the other hand, will only form crosslinks at the filament interface due to the high peripheral temperature and oxidation of the printed filament.

This competition between potential crosslinking reactions must be taken into consideration when designing future reactive processing protocols. These

studies strongly suggest that surface segregating crosslinkers are preferred to bias the formation of crosslinks at the interlayer interface. To further test the interpretations presented here and expand this mechanism, the following experiments are proposed.

Future Plan for Reducing Anisotropy with Reactive Processing

Verify the Potential of Crosslinkers to Self-crosslink

The thermal initiation of the photoinitiator and crosslinking reaction are hypothesized in the proposed crosslinking reactions. Differential scanning calorimetry (DSC) experiments will be completed to test this hypothesis. Precise ratios of crosslinker and photoinitiator will be weighed into a sample pan. To better mimic the printing process, DSC measurements will be carried out with the sample exposed to a flow of air.

Thermal stability of the crosslinker and initiator will be monitored by analysis of the recorded flow of energy curve. If a the photoinitiator or the crosslinker thermally initiates, a crosslink reaction will occur and an exothermic peak will be observed. The temperature range of the DSC experiment will be guided by the general printing temperature for PC, which is 290°C at the nozzle and 135°C on the print bed. So, the samples will be ramped up to 290°C, cooled down and reside at 135°C.

Measure the Viscosity of Polymer Melts

The interpretation described above hypothesizes that crosslinks formed in the filament with photoinitiator and crosslinker will increase the viscosity of the polymer in the printed structure. To test this hypothesis, the viscosity of the polymer in the printed cubes will be determined to elucidate the viscosity properties of the cube printed for the PC samples at different stages. Each of the

printed materials will be examined before printing and after printing (with or without UV).

The temperature of the viscosity experiments will be guided by the temperature of the actual printing process which is about 290°C. The construction of high temperature viscometer can be found from previous work¹¹⁵. In this paper, they have modified their viscometer and performed viscosity test at 300°C.

The PC samples examined after printing will be removed from the middle of the cube as shown in Figure 3.6 so that all samples will have similar thermal and UV exposure history. Most importantly, these sections are the “neck” of the dogbone samples for transverse tensile strength which is the portion of the sample that responds to the mechanical tests. These data, combined with previous oxidation data, will provide us further information to understand the impact of the complex thermal history and UV exposure on the properties of the printed polymer.

LIST OF REFERENCES

1. Wendel, B., Rietzel, D., Kühnlein, F., Feulner, R., Hülder, G., & Schmachtenberg, E. (2008). Additive processing of polymers. *Macromolecular Materials and Engineering*, 293(10), 799-809.
2. Jungst, T., Smolan, W., Schacht, K., Scheibel, T., & Groll, J. (2016). Strategies and molecular design criteria for 3D printable hydrogels. *Chemical Reviews*, 116(3), 1496-1539.
3. Appleyard, D. (2015). Powering up on powder technology. *Metal Powder Report*, 70(6), 285-289.
4. Dawood, A., & Marti, B. M. (2015). Sauret-Jackson V, Darwood A. 3D Printing in Dentistry Brit. *Br Dent. J.*, 219(11), 521-9.
5. Wong, J. Y. (2015). Ultra-portable solar-powered 3D printers for onsite manufacturing of medical resources. *Aerospace Medicine and Human Performance*, 86(9), 830-834.
6. Jacobs, S., Grunert, R., Mohr, F. W., & Falk, V. (2008). 3D-Imaging of cardiac structures using 3D heart models for planning in heart surgery: a preliminary study. *Interactive Cardiovascular and Thoracic Surgery*, 7(1), 6-9.
7. Fedorovich, N. E., Alblas, J., Hennink, W. E., Öner, F. C., & Dhert, W. J. (2011). Organ printing: the future of bone regeneration? *Trends in Biotechnology*, 29(12), 601-606.
8. Mironov, V., Kasyanov, V., & Markwald, R. R. (2011). Organ printing: from bioprinter to organ biofabrication line. *Current Opinion in Biotechnology*, 22(5), 667-673.
9. Ceccanti, F., Dini, E., De Kestelier, X., Colla, V., & Pambaguian, L. (2010, August). 3D printing technology for a moon outpost exploiting lunar soil. In *61st International Astronautical Congress, Prague, CZ, IAC-10-D3* (Vol. 3, pp. 1-9).

10. Lim, S., Buswell, R. A., Le, T. T., Austin, S. A., Gibb, A. G., & Thorpe, T. (2012). Developments in construction-scale additive manufacturing processes. *Automation in Construction*, 21, 262-268.
11. Bos, F., Wolfs, R., Ahmed, Z., & Salet, T. (2016). Additive manufacturing of concrete in construction: potentials and challenges of 3D concrete printing. *Virtual and Physical Prototyping*, 11(3), 209-225.
12. Pegna, J. (1997). Exploratory investigation of solid freeform construction. *Automation in Construction*, 5(5), 427-437.
13. 3D Printing: Food in Space. www.nasa.gov/directorates/spacetech/home/feature_3d_food.html (Accessed: August 8, 2021)
14. Bitter Sweet - 3D Systems Acquires the Sugar Lab. <https://3dprintingindustry.com/news/bitter-sweet-3d-systems-acquires-the-sugar-lab-16923/> (Accessed: August 8, 2021)
15. <https://www.ornl.gov/blog/3d-printing-races> (Accessed: August 8, 2021)
16. Ligon, S. C., Liska, R., Stampfl, J., Gurr, M., & Mülhaupt, R. (2017). Polymers for 3D printing and customized additive manufacturing. *Chemical Reviews*, 117(15), 10212-10290.
17. Zocca, A., Colombo, P., Gomes, C. M., & Günster, J. (2015). Additive manufacturing of ceramics: issues, potentialities, and opportunities. *Journal of the American Ceramic Society*, 98(7), 1983-2001.
18. Frazier, W. E. (2014). Metal additive manufacturing: a review. *Journal of Materials Engineering and performance*, 23(6), 1917-1928.
19. Hague, R., Campbell, I., & Dickens, P. (2003). Implications on design of rapid manufacturing. Proceedings of the Institution of Mechanical Engineers, Part C: *Journal of Mechanical Engineering Science*, 217(1), 25-30.
20. Campbell, R. I., Hague, R. J., Sener, B., & Wormald, P. W. (2003). The potential for the bespoke industrial designer. *The Design Journal*, 6(3), 24-34.

21. ASTM International - Standards Worldwide; <http://www.astm.org/> (Accessed: August 8, 2021)
22. ASTM F2792-12a. Standard Terminology for Additive Manufacturing Technologies; *ASTM International: West Conshohocken, PA*, 2012.
23. <https://3duniverse.org/2013/12/14/3d-printed-chess-piece/> (Accessed: August 8, 2021)
24. Zhang, Y., Dong, Z., Li, C., Du, H., Fang, N. X., Wu, L., & Song, Y. (2020). Continuous 3D printing from one single droplet. *Nature Communications*, 11(1), 1-10.
25. *Wohlers Report 2009*. Wohlers Associates. 250 p.
26. Kruth, J. P., Levy, G., Klocke, F., & Childs, T. H. C. (2007). Consolidation phenomena in laser and powder-bed based layered manufacturing. *CIRP Annals*, 56(2), 730-759.
27. Agarwala, M. K., Jamalabad, V. R., Langrana, N. A., Safari, A., Whalen, P. J., & Danforth, S. C. (1996). Structural quality of parts processed by fused deposition. *Rapid Prototyping Journal*, 2, 4-19.
28. Tang, H. H., Chiu, M. L., & Yen, H. C. (2011). Slurry-based selective laser sintering of polymer-coated ceramic powders to fabricate high strength alumina parts. *Journal of the European Ceramic Society*, 31(8), 1383-1388.
29. Krznar, M., & Dolinsek, S. (2010). Selective laser sintering of composite materials technologies. *Annals of DAAAM & Proceedings*, 1527-1529.
30. Kotlinski, J. (2014). Mechanical properties of commercial rapid prototyping materials. *Rapid Prototyping Journal*, 20, 499-510.
31. Kim, G. D., & Oh, Y. T. (2008). A benchmark study on rapid prototyping processes and machines: quantitative comparisons of mechanical properties, accuracy, roughness, speed, and material cost. *Proceedings of the Institution*

of Mechanical Engineers, Part B: Journal of Engineering Manufacture, 222(2), 201-215.

32. Kumar, S., & Kruth, J. P. (2010). Composites by rapid prototyping technology. *Materials & Design*, 31(2), 850-856.
33. Gao, W., Zhang, Y., Ramanujan, D., Ramani, K., Chen, Y., Williams, C. B., ... & Zavattieri, P. D. (2015). The status, challenges, and future of additive manufacturing in engineering. *Computer-Aided Design*, 69, 65-89.
34. Deckard, C. R. (1988). *Selective laser sintering* (Doctoral dissertation, The University of Texas at Austin).
35. Levy, G. N., Schindel, R., & Kruth, J. P. (2003). Rapid manufacturing and rapid tooling with layer manufacturing (LM) technologies, state of the art and future perspectives. *CIRP Annals*, 52(2), 589-609.
36. du Plessis, P., Avitronics, S. A. A. B., & Arena, R. (2008, October). A functional application of RM in a military environment. In *TCT Conference* (pp. 1-13). Ricoh Arena Coventry.
37. Hopkinson, N., Hague, R. J. M., & Dickens, P. M. (2006). Rapid manufacturing. *An Industrial Revolution for the Digital Age*. Chichester, England: John Wiley and Sons, Ltd.
38. Montgomery, J. T., Vaughan, M. R., & Crawford, R. H. (2010). Design of an actively actuated prosthetic socket. *Rapid Prototyping Journal*, 16(3), 194-201.
39. Williams, J. M., Adewunmi, A., Schek, R. M., Flanagan, C. L., Krebsbach, P. H., Feinberg, S. E., Hollister, S., & Das, S. (2005). Bone tissue engineering using polycaprolactone scaffolds fabricated via selective laser sintering. *Biomaterials*, 26(23), 4817-4827.
40. Hollister, S. J. (2005). Porous scaffold design for tissue engineering. *Nature Materials*, 4(7), 518-524.

41. Rogers, B., Stephens, S., Gitter, A., Bosker, G., & Crawford, R. (2000). Double-wall, transtibial prosthetic socket fabricated using selective laser sintering: a case study. *JPO: Journal of Prosthetics and Orthotics*, 12(3), 97-103.
42. Evans, R. S., Bourell, D. L., Beaman, J. J., & Campbell, M. I. (2005). SLS materials development method for rapid manufacturing. In *2005 International Solid Freeform Fabrication Symposium*.
43. Prescott, J. K. (2000). BRA, On powder flowability. *Pharmaceutical Technology*, 60-84
44. Schulze, D. (2008). *Powders and bulk solids. Behaviour, Characterization, Storage and Flow*. Springer, 22.
45. Yang, S., & Evans, J. R. G. (2007). Metering and dispensing of powder; the quest for new solid freeforming techniques. *Powder Technology*, 178(1), 56-72.
46. Ziegelmeier, S., Wöllecke, F., Tuck, C., Goodridge, R., & Hague, R. (2013, August). Characterizing the bulk & flow behaviour of LS polymer powders. In *Proceedings SFF Symposium, Austin (TX), USA*.
47. Amado, F., Schmid, M., Levy, G., & Wegener, K. (2011). Advances in SLS Powder Characterization. In *Proceedings of the International Conference on Solid Freeform Fabrication 2011 (SFF'11)* (pp. 438-452). University of Texas
48. Schmid, M., Amado, A., & Wegener, K. (2014). Materials perspective of polymers for additive manufacturing with selective laser sintering. *Journal of Materials Research*, 29(17), 1824-1832.
49. Berretta, S., Ghita, O., & Evans, K. E. (2014). Morphology of polymeric powders in Laser Sintering (LS): From Polyamide to new PEEK powders. *European Polymer Journal*, 59, 218-229.

50. <https://www.energy.gov/eere/amo/3d-printed-shelby-cobra> (Accessed: August 8, 2021)
51. <https://edition.cnn.com/2021/02/07/us/3d-printed-house-united-states-for-sale-trnd/index.html> (Accessed: August 8, 2021)
52. Ahn, S. H., Montero, M., Odell, D., Roundy, S., & Wright, P. K. (2002). Anisotropic material properties of fused deposition modeling ABS. *Rapid Prototyping Journal*, 8(4), 248-257.
53. Sun, Q., Rizvi, G. M., Bellehumeur, C. T., & Gu, P. (2008). Effect of processing conditions on the bonding quality of FDM polymer filaments. *Rapid Prototyping Journal*, 14(2), 72.
54. Chacón, J. M., Caminero, M. A., García-Plaza, E., & Núñez, P. J. (2017). Additive manufacturing of PLA structures using fused deposition modelling: Effect of process parameters on mechanical properties and their optimal selection. *Materials & Design*, 124, 143-157.
55. Perryman, S. C., & Dadmun, M. D. (2021). Incorporating crosslinks in fused filament fabrication: Molecular insight into post deposition reactions. *Additive Manufacturing*, 38, 101746.
56. Levenhagen, N. P., & Dadmun, M. D. (2019). Improving Interlayer Adhesion in 3D Printing with Surface Segregating Additives: Improving the Isotropy of Acrylonitrile–Butadiene–Styrene Parts. *ACS Applied Polymer Materials*, 1(4), 876-884.
57. Levenhagen, N. P., & Dadmun, M. D. (2017). Bimodal molecular weight samples improve the isotropy of 3D printed polymeric samples. *Polymer*, 122, 232-241.
58. Levenhagen, N. P., & Dadmun, M. D. (2018). Interlayer diffusion of surface segregating additives to improve the isotropy of fused deposition modeling products. *Polymer*, 152, 35-41.

59. Vanderhoff, J. W., El-Aasser, M. S., & Ugelstad, J. (1979). *U.S. Patent No. 4,177,177*. Washington, DC: U.S. Patent and Trademark Office.
60. Blouza, I. L., Charcosset, C., Sfar, S., & Fessi, H. (2006). Preparation and characterization of spironolactone-loaded nanocapsules for paediatric use. *International Journal of Pharmaceutics*, 325(1-2), 124-131.
61. Kim, E., Yang, J., Choi, J., Suh, J. S., Huh, Y. M., & Haam, S. (2009). Synthesis of gold nanorod-embedded polymeric nanoparticles by a nanoprecipitation method for use as photothermal agents. *Nanotechnology*, 20(36), 365602.
62. Yordanov, G. G., & Dushkin, C. D. (2010). Preparation of poly (butylcyanoacrylate) drug carriers by nanoprecipitation using a pre-synthesized polymer and different colloidal stabilizers. *Colloid and Polymer Science*, 288(9), 1019-1026.
63. Mishra, B. B. T. S., Patel, B. B., & Tiwari, S. (2010). Colloidal nanocarriers: a review on formulation technology, types and applications toward targeted drug delivery. *Nanomedicine: Nanotechnology, Biology and Medicine*, 6(1), 9-24.
64. Chronopoulou, L., Fratoddi, I., Palocci, C., Venditti, I., & Russo, M. V. (2009). Osmosis based method drives the self-assembly of polymeric chains into micro-and nanostructures. *Langmuir*, 25(19), 11940-11946.
65. Hornig, S., & Heinze, T. (2008). Efficient approach to design stable water-dispersible nanoparticles of hydrophobic cellulose esters. *Biomacromolecules*, 9(5), 1487-1492.
66. Reverchon, E. (1999). Supercritical antisolvent precipitation of micro-and nano-particles. *The Journal of Supercritical Fluids*, 15(1), 1-21.

67. Mishima, K. (2008). Biodegradable particle formation for drug and gene delivery using supercritical fluid and dense gas. *Advanced Drug Delivery Reviews*, 60(3), 411-432.
68. Sun, Y. P., Rolling, H. W., Bandara, J., Meziani, J. M., & Bunker, C. E. (2002). Preparation and processing of nanoscale materials by supercritical fluid technology. *Supercritical Fluid Technology in Materials Science and Engineering: Synthesis, Properties, and Applications*, 491-576.
69. Asua, J. M. (2004). Emulsion polymerization: from fundamental mechanisms to process developments. *Journal of Polymer Science Part A: Polymer Chemistry*, 42(5), 1025-1041.
70. Thickett, S. C., & Gilbert, R. G. (2007). Emulsion polymerization: State of the art in kinetics and mechanisms. *Polymer*, 48(24), 6965-6991.
71. Muñoz-Bonilla, A., van Herk, A. M., & Heuts, J. P. (2010). Preparation of hairy particles and antifouling films using brush-type amphiphilic block copolymer surfactants in emulsion polymerization. *Macromolecules*, 43(6), 2721-2731.
72. Kim, S. W., Cho, H. G., & Park, C. R. (2009). Fabrication of unagglomerated polypyrrole nanospheres with controlled sizes from a surfactant-free emulsion system. *Langmuir*, 25(16), 9030-9036.
73. Wang, S., Wang, X., & Zhang, Z. (2007). Preparation of polystyrene particles with narrow particle size distribution by γ -ray initiated miniemulsion polymerization stabilized by polymeric surfactant. *European Polymer Journal*, 43(1), 178-184.
74. Bardajee, G. R., Vancaeyzeele, C., Haley, J. C., Li, A. Y., & Winnik, M. A. (2007). Synthesis, characterization, and energy transfer studies of dye-labeled poly (butyl methacrylate) latex particles prepared by miniemulsion polymerization. *Polymer*, 48(20), 5839-5849.

75. Yildiz, U., & Landfester, K. (2008). Miniemulsion polymerization of styrene in the presence of macromonomeric initiators. *Polymer*, 49(23), 4930-4934.
76. Crespy, D., & Landfester, K. (2009). Synthesis of polyvinylpyrrolidone/silver nanoparticles hybrid latex in non-aqueous miniemulsion at high temperature. *Polymer*, 50(7), 1616-1620.
77. Baruch-Sharon, S., & Margel, S. (2010). Synthesis and characterization of polychloromethylstyrene nanoparticles of narrow size distribution by emulsion and miniemulsion polymerization processes. *Colloid and Polymer Science*, 288(8), 869-877.
78. Puig, J. E. (1996). Microemulsion polymerization. The polymeric materials encyclopedia. *Synthesis, Properties and Applications*, 6, 4333-4341.
79. Matsuyama, H., Teramoto, M., Kuwana, M., & Kitamura, Y. (2000). Formation of polypropylene particles via thermally induced phase separation. *Polymer*, 41(24), 8673-8679.
80. Van de Witte, P., Dijkstra, P. J., Van den Berg, J. W. A., & Feijen, J. (1996). Phase separation processes in polymer solutions in relation to membrane formation. *Journal of Membrane Science*, 117(1-2), 1-31.
81. Schaaf, P., Lotz, B., & Wittmann, J. C. (1987). Liquid-liquid phase separation and crystallization in binary polymer systems. *Polymer*, 28(2), 193-200.
82. Hou, W. H., & Lloyd, T. B. (1992). A new technique for preparing monodisperse polymer particles. *Journal of Applied Polymer Science*, 45(10), 1783-1788.
83. Deckard, C. R. (1991). *U.S. Patent No. 5,017,753*. Washington, DC: U.S. Patent and Trademark Office.
84. <https://www.sigmaaldrich.cn/CN/en/substance/polypropylene123459003070?context=product> (Accessed: August 7, 2021)

85. Siggia, E. D. (1979). Late stages of spinodal decomposition in binary mixtures. *Physical Review A*, 20(2), 595.
86. Matsuyama, H., Maki, T., Teramoto, M., & Asano, K. (2002). Effect of polypropylene molecular weight on porous membrane formation by thermally induced phase separation. *Journal of Membrane Science*, 204(1-2), 323-328.
87. Wolf, B. A., & Jend, R. (1979). Pressure and temperature dependence of the viscosity of polymer solutions in the region of phase separation. *Macromolecules*, 12(4), 732-737.
88. Caulfield, B., McHugh, P. E., & Lohfeld, S. (2007). Dependence of mechanical properties of polyamide components on build parameters in the SLS process. *Journal of Materials Processing Technology*, 182(1-3), 477-488.
89. Zaeh, M. F., & Branner, G. (2010). Investigations on residual stresses and deformations in selective laser melting. *Production Engineering*, 4(1), 35-45.
90. Es-Said, O. S., Foyos, J., Noorani, R., Mendelson, M., Marloth, R., & Pregger, B. A. (2000). Effect of layer orientation on mechanical properties of rapid prototyped samples. *Materials and Manufacturing Processes*, 15(1), 107-122.
91. Lee, C. S., Kim, S. G., Kim, H. J., & Ahn, S. H. (2007). Measurement of anisotropic compressive strength of rapid prototyping parts. *Journal of Materials Processing Technology*, 187, 627-630.
92. Yin, J., Lu, C., Fu, J., Huang, Y., & Zheng, Y. (2018). Interfacial bonding during multi-material fused deposition modeling (FDM) process due to inter-molecular diffusion. *Materials & Design*, 150, 104-112.
93. Davidson, J. R., Appuhamillage, G. A., Thompson, C. M., Voit, W., & Smaldone, R. A. (2016). Design paradigm utilizing reversible Diels–Alder reactions to enhance the mechanical properties of 3D printed materials. *ACS Applied Materials & Interfaces*, 8(26), 16961-16966.

94. Yang, K., Grant, J. C., Lamey, P., Joshi-Imre, A., Lund, B. R., Smaldone, R. A., & Voit, W. (2017). Diels–Alder reversible thermoset 3D printing: isotropic thermoset polymers via fused filament fabrication. *Advanced Functional Materials*, 27(24), 1700318
95. Shaffer, S., Yang, K., Vargas, J., Di Prima, M. A., & Voit, W. (2014). On reducing anisotropy in 3D printed polymers via ionizing radiation. *Polymer*, 55(23), 5969-5979.
96. Meng, S., He, H., Jia, Y., Yu, P., Huang, B., & Chen, J. (2017). Effect of nanoparticles on the mechanical properties of acrylonitrile–butadiene–styrene specimens fabricated by fused deposition modeling. *Journal of Applied Polymer Science*, 134(7), 44470.
97. Gao, X., Zhang, D., Qi, S., Wen, X., & Su, Y. (2019). Mechanical properties of 3D parts fabricated by fused deposition modeling: Effect of various fillers in polylactide. *Journal of Applied Polymer Science*, 136(31), 47824.
98. Bhandari, S., Lopez-Anido, R. A., & Gardner, D. J. (2019). Enhancing the interlayer tensile strength of 3D printed short carbon fiber reinforced PETG and PLA composites via annealing. *Additive Manufacturing*, 30, 100922.
99. Nguyen, N. A., Bowland, C. C., & Naskar, A. K. (2018). A general method to improve 3D-printability and inter-layer adhesion in lignin-based composites. *Applied Materials Today*, 12, 138-152.
100. Dul, S., Fambri, L., & Pegoretti, A. (2016). Fused deposition modelling with ABS–graphene nanocomposites. *Composites Part A: Applied Science and Manufacturing*, 85, 181-191.
101. Brenken, B., Barocio, E., Favaloro, A., Kunc, V., & Pipes, R. B. (2018). Fused filament fabrication of fiber-reinforced polymers: A review. *Additive Manufacturing*, 21, 1-16.

102. Levenhagen, N. P., & Dadmun, M. D. (2019). Reactive processing in extrusion-based 3D printing to improve isotropy and mechanical properties. *Macromolecules*, 52(17), 6495-6501.
103. Lee, L. H. (1964). Mechanisms of thermal degradation of phenolic condensation polymers. I. Studies on the thermal stability of polycarbonate. *Journal of Polymer Science Part A: General Papers*, 2(6), 2859-2873.
104. Kuroda, S. I., Nagura, A., Horie, K., & Mita, I. (1989). Degradation of aromatic polymers—III. Crosslinking and chain scission during photodegradation of polysulphones. *European Polymer Journal*, 25(6), 621-627.
105. Mehr, M. Y., Van Driel, W. D., Jansen, K. M. B., Deeben, P., Boutelje, M., & Zhang, G. Q. (2013). Photodegradation of bisphenol A polycarbonate under blue light radiation and its effect on optical properties. *Optical Materials*, 35(3), 504-508.
106. Kousiatza, C., & Karalekas, D. (2016). In-situ monitoring of strain and temperature distributions during fused deposition modeling process. *Materials & Design*, 97, 400-406.
107. Wang, P., Zou, B., Xiao, H., Ding, S., & Huang, C. (2019). Effects of printing parameters of fused deposition modeling on mechanical properties, surface quality, and microstructure of PEEK. *Journal of Materials Processing Technology*, 271, 62-74.
108. https://www.horiba.com/en_en/applications/materials/chemicals/polymers-plastics/laser-diffraction-analysis-of-measurement-of-pvc-powder/ (Accessed: August 8, 2021)
109. https://www.horiba.com/en_en/products/detail/action/show/Product/partica-la-960v2-1944/ (Accessed: August 8, 2021)

110. Kloos, S., Dechet, M. A., Peukert, W., & Schmidt, J. (2018). Production of spherical semi-crystalline polycarbonate microparticles for Additive Manufacturing by liquid-liquid phase separation. *Powder Technology*, 335, 275-284.
111. www.mt.com/us/en/home/products/Laboratory_Analytics_Browse/FP_family_browse/Excellence_Melting_Point_Systems.html (Accessed: August 8, 2021)
112. Dechet, M. A., Goblirsch, A., Romeis, S., Zhao, M., Lanyi, F. J., Kaschta, J., Schubert, D. W., Drummer, D., Peukert, W., & Schmidt, J. (2019). Production of polyamide 11 microparticles for Additive Manufacturing by liquid-liquid phase separation and precipitation. *Chemical Engineering Science*, 197, 11-25.
113. Kloos, S., Dechet, M. A., Peukert, W., & Schmidt, J. (2018). Production of spherical semi-crystalline polycarbonate microparticles for Additive Manufacturing by liquid-liquid phase separation. *Powder Technology*, 335, 275-284.
114. Dechet, M. A., Demina, A., Roemling, L., Bonilla, J. S. G., Lanyi, F. J., Schubert, D. W., Bück, A., Peukert, W., & Schmidt, J. (2020). Development of poly (L-lactide)(PLLA) microspheres precipitated from triacetin for application in powder bed fusion of polymers. *Additive Manufacturing*, 32, 100966.
115. Modaresghazani, J., Moore, R. G., Mehta, S. A., Van Fraassen, K. C., Ursenbach, M. G., Van Dorp, J., & Laureshen, C. J. (2018). Investigation of the viscosity and density of heavy oil/water blends at elevated temperatures and pressure; Part 1: Oil-only sample (absence of water). *Fuel*, 227, 6-12.

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