ABSTRACT

QUINTANILLA, ADAM LEO. Fundamentals of Particulate-Filled Polymer Composite Fabrication via Continuous Liquid Interface Production (CLIP) (Under the direction of Joseph M. DeSimone)

Over the past 10 years, three-dimensional (3D) printing has evolved beyond prototyping into a growing manufacturing platform with industries including automotive, aerospace, medical, and construction implementing the technology into many applications. Despite excitement for additive manufacturing applications, the presence of slow fabrication rates, low dimensional accuracy, and a lack of materials with industrially relevant properties have long impeded the technology. However, a new 3D printing technology called Continuous Liquid Interface Production (CLIP) debuted in 2015 that balances light and oxygen to improve fabrication rate and dimensionally accuracy without traditional resolution/speed trade-offs. As such, more focus can be directed toward 3D printable material development with industrially relevant properties. A current trend in 3D printing material development is the fabrication of polymer composites using particulate fillers to improve or add new properties to existing materials. The goal of 3D printable composite development is to utilize well-established development practices to further improve the material library for the technology. Thus, knowledge of how fillers and other phases affect the 3D printing process is required for successful and worthwhile material development.

The overall goal of this work was to develop methods of characterizing the effect of adding particulate fillers and other homogenous phases to photocurable CLIP resins. The main objectives of this dissertation research included investigating filler/phase effect on formation of the liquid deadzone during the CLIP process and observe/characterize the flow behavior and ultimate location of filler in fabricated parts. It was hypothesized that the addition of filler would influence the size of the deadzone, which in turn could influence how particles move within the CLIP process. A combination of physical measurements and reaction kinetic characterization techniques revealed that filler affects deadzone depending on loading, size, and its chemical nature (i.e. solid versus liquid microphases). The versatility and design freedom of 3D printing allowed the ability to fabricate custom microchannels for filled fluid flow observation. Consequently, it was revealed that ultimate filler location is heavily dependent on particle size, with clog formations at a constriction point during part fabrication.
leading to uneven filler distribution. Lastly, the techniques learned aided in the development of novel rubber toughened CLIP resins. Microphase separated reactive liquid elastomers were blended into thermosetting resin and printed using the CLIP process, where rubber particles were cured in situ. Average toughness and elongation were found to improve with the addition of rubber. However, thermal imagining and knowledge of resin flow behavior revealed macrophase separation due to heat evolution from photopolymerization reactions during CLIP, resulting in increased phase size, decreased rubber content within the part, thus diminished toughening efficiency. Nevertheless, this work contributes to a better understanding of particulate-filled polymer composite fabrication in 3D printing through implementation and explanation of unique characterization techniques.
Fundamentals of Particulate-Filled Polymer Composite Fabrication via Continuous Liquid Interface Production (CLIP)

by
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DEDICATION

This dissertation is dedicated to my wife, parents, family, and friends who have supported and encouraged me through this whole process.
BIOGRAPHY

Adam Quintanilla was born and raised in Leesburg, Florida by his parents Paula and Eduardo Quintanilla. In 2009, he entered Florida State University where he studied chemical engineering, but also found time to participate in the World-Renowned FSU Marching Chiefs where he met his future wife, Shennie. During this time, he did research under John Telotte, wherein he studied inhibition in enzymatic cellulose hydrolysis via glucose production. He graduated with an honors thesis in 2013, before entering the PhD program at North Carolina State University in chemical engineering. Though he initially intended to continue pursuing research in energy alternatives, he joined Joseph DeSimone’s lab to pioneer studies in a novel form of 3D printing during an exciting time for the technology. Always looking for new and exciting challenges, he intends to pursue a career that values lifelong learning through teaching, mentoring, and leadership in areas of material and process development.
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Chapter 1: Introduction to Additive Manufacturing and Composite Materials

1 Introduction: 3D Printing from Prototyping to Manufacturing

In 1984, Chuck Hull, co-founder and chief technical officer of 3D systems, filed for a U.S. patent describing a technology “for directly producing a three-dimensional object as it is designed by a computer”\(^1\). Three years later and stereolithography was commercialized as a method of for rapid prototyping. Over the next few years, industries began to use the technology to drastically reduce the time and cost of iterative prototyping in part design.\(^2\) Beyond its ability for producing prototypes that would later be fabricated using traditional manufacturing techniques, stereolithography also had the inherent ability to produce structures that were otherwise impossible to fabricate. As more industries adopted the technology, and as it continued to grow as its own industry, it has now led to a booming excitement in what is more commonly known today as three-dimensional (3D) printing.

3D printing can defined as the fabrication of a computer aided design (CAD) file with raw materials printed in a stacked layer-upon-layer process.\(^3\) Since its commercialization nearly 30 years ago, 3D printing has grown and evolved to include many methods and has found use in application areas ranging from art to engineering.\(^4\) This is in no small part due to its versatility and low barrier of entry that allows users to begin printing complex and custom objects sometimes within minutes of being introduced to the technology. Currently, 3D printing adds value to manufacturing through reduced prototype development time, which has been a driving force for the growth of 3D printing industry by a growth average rate of over 25 \%.\(^4,5\) The marked growth of 3D printing has led to the development better iterations within the technology, which has led to its potential to fabricate end-use parts. Consequently, 3D printing has shown potential to be used within and as a standalone manufacturing platform.

Thus, it should not be surprising that research and development globally has been motivated to study 3D printing in all forms from novel and optimized part/process design to a particular interest in developing industrially relevant materials. The impact of 3D printing as a driver for novel material development and as a tool used in research is best evidenced when
one looks at the flux of scientific publications that include 3D printing within the past 20 years, as seen in figure 1.1.

![Figure 1.1: Number of research publications per year involving 3D printing. Data was collected using Web of Science internet search engine using the terms described.](image)

As seen in the figure above, 2013 marked a turning point for 3D printing in terms of its presence as a research tool and topic. This growing research excitement in 3D printing has brought about opportunities wherein it can compete with alternative methods of fabrication. This includes opportunities such as reduction in tooling (versus injection molding or investment casting), or lightweight part fabrication using intricate structures with optimized and/or customized load bearing properties. While the technology cannot (currently) compete with large-scale and high-volume machining processes, such as injection molding, it can only continue to compete as additive manufacturing with the development of worthwhile materials. Thus, 3D printing has shifted to away from improving its use as prototyping, but rather developing industrially relevant materials that can impact all fields including automotive, aerospace, medical, and construction.

The work in this dissertation presents contributions to the material development of 3D printable resins through the study of fundamental factors relating to particulate-filled polymer composites for continuous liquid interface production (CLIP), a novel form of 3D printing. Therefore, chapter 1 will provide the reader with some context of 3D printing general concepts,
specific techniques, the CLIP process, its material development, and the growing interesting in fabricating polymer composites using the technology.

1.1 General 3D Printing Concepts

1.1.1 The fabrication process

Figure 1.2 details the general workflow in 3D printing a physical object.

Figure 1.2: The general 3D printing process from computer design file to physical object.

The first step in 3D printing is choosing or designing a three-dimensional object to be fabricated. Just as a writer uses a word processor to write and format a novel before printing, so too must a 3D object designer use a 3D CAD software to design an object before 3D fabrication. It is in this step that the form and dimensions of an object are developed and finalized. A number of considerations must be applied to the design of the object including, for example, the size constraints and resolution of the 3D printer. Once designed, the CAD file is saved in standard tessellation language (.STL), a format that simplifies complex 3D structures into a series of triangles for easy manipulation. Then, the .STL must be “sliced” into a series of two dimensional cross-sections, a format typically known as scalable vector
graphics (.SVG). In this step, slice thickness is typically a user-defined parameter, with limits varying between the different types of 3D printing, discussed in a later section.

The next step in fabricating an object using a 3D printer is to apply the manipulated design file to the 3D printer control software. For most 3D printing technologies, .SVG file data is uploaded to the software that controls the 3D printer, and printing parameters are chosen based on the size, shape, slice thickness, type of printer, and the material used. Details of fabrication and parameters will be discussed in depth in the next section, however, in general, an object is printed onto a build stage starting with the first slice, or layer, which is the bottom cross-section of the object. Once the layer has been printed, the build platform moves up or down, depending on the method used, an amount equal to the slice thickness and the next layer is printed onto the previous layer. This process is repeated in a layer-by-layer fashion, with each layer representing a different cross-section (or slice) along the z-axis of the 3D object, until the final part has been completed. At this point the object has been converted from virtual data into a physical object. The final step, or steps, involve post-processing of the object for final use. Post-processing techniques vary depending on 3D printing platform and materials used and on the complexity of the object, but typically involve washing, removal of support structures, sanding or polishing, and/or post-curing either thermally or via UV light.

1.1.2 Types of 3D printing

The purpose of this section is to highlight a few of the more widely known methods to show the progress in the technology. There are multiple methods of 3D printing, however the primary difference is in how the fabrication step is executed, which varies depending on the material being used. This is by no means an exhaustive list of techniques, but represents three of the most widely available and used methods. Figure 1.3 details the concepts behind three common methods of 3D printing.
Arguably the most widely known form of 3D printing is Fused Deposition Modeling (FDM). In this method, seen in figure 1.3A, fabrication occurs via deposition of thermoplastic filament, such as acrylonitrile-butadiene-styrene (ABS), through a heated nozzle tip in a raster pattern. In this way, layers are fused together due to rapid heating, which causes fusion between two layers and adjoining filament within a raster, and subsequent cooling to maintain shape. The nozzle moves via motor and deposits a bead of the material in a pattern such that it fills the area of the slice being printed. After a slice has been completed, the build platform is lowered or the nozzle raised an increment equal to slice thickness and the next layer is deposited.\textsuperscript{5,7} The versatility, material handling, and ease of adoption of FDM have made it a tool of consumers ranging from hobbyists and artists, to engineers and scientists.

Selective laser sintering (SLS) is a widely-used method of 3D printing, particularly in small scale prototyping and manufacturing plants.\textsuperscript{8} A major advantage of SLS is its raw material versatility such as thermoplastics, metals (such as steel or titanium), or glass. The SLS process, seen in figure 1.3B, uses laser rastering to locally sinter a shape into a thin layer of fine powder that is kept at temperatures just below its melting point. Similar to FDM, SLS requires rapid heat and subsequent cooling to both fuse and maintain the shape of adjoining layers, and the raster pattern is done in such a way to fill the cross-sectional area of a slice. When a layer has been completed, the build stage is lowered while a stock powder bed material piston moves upward. Then, a roller pushes a new thin layer of powder over the part, and the

\textbf{Figure 1.3: Three types of common 3D printing techniques.} (A) Fused-deposition modeling. (B) Selective laser Sintering. (C) Stereolithography.
rastering process for the next layer and the cycle repeats. Since SLS requires the build volume to be heated, and high powered lasers to achieve proper sintering, printers are often large, thus targeted more towards specialized high end use and low volume manufacturing.\(^7\)

Unlike FDM and SLS, which fuse raw materials, Stereolithography (SLA) uses photochemical reactions of liquid resin to form solid parts.\(^9\) The raw materials used in SLA are typically liquid resins of relatively low molecular weight monomers and oligomers with functionalities that react by photopolymerization. When mixed with an appropriate photoinitiator, resin components react locally when triggered by light to form a high molecular weight cross-linked polymer network. At the beginning of a print a build stage is lowered into a vat of resin and the cross-sectional shape is either rastered via UV laser (Figure 1.3C) or projected as a single UV image using digital light projection (DLP) like that found in modern overhead projectors.\(^7,10\)–\(^12\) Once a layer has been completed, the build platform is moved up or down, depending on the type of SLA, and resin is recoated across the build area and the process repeats in a layer-by-layer fashion. SLA can be used to fabricate parts that have higher resolution compared to FDM or SLS since slice dimensions are not limited by the size of the raw material and are typically 100 microns or smaller.\(^12,13\) The SLA process will be further discussed in a later section, as it is shares similarities to this research.

1.1.3 Advantages of 3D printing

In their book, *Fabricated*, authors Hod Lipson and Melba Kurman list “The 10 principles of 3D printing” to describe its advantages over other traditional fabrication methods.\(^14\) These principles center around the freedoms that are inherent to 3D printing such as freedom in part complexity, virtually unlimited design space, and waste reduction. Historically, part design has had constraints that typically centered around which tools were to be used in fabrication, most of which were subtractive methods that removed material from a piece of stock. 3D printing offers the ability to additively manufacture parts wherein complexity and design freedom unmatched using subtractive techniques. For instance, fabrication of complex scaffold structures, like that seen in figure 1.4, have long been of interest to engineers as lightweight alternatives to solid designs.
Figure 1.4: Complexity and part design freedom in 3D printing. Despite varying complexity, the same unit volume can be printed without the need for re-tooling due to additive manufacturing. Adapted and reproduced with permission from reference.\textsuperscript{15}

The structures above are not feasible to fabricate using subtractive or traditional manufacturing such as injection molding or investment casting. Since additive manufacturing builds parts layers at a time, multiple variations of complex parts with the same external volume but widely varying internal structures can be all be fabricated without a change in fabrication technique. Moreover, multiple parts, or even pre-assembled parts, each with a different structure can be fabricated simultaneously using 3D printing, leading to less manufacturing and/or assembly time.\textsuperscript{14}

Unlike traditional manufacturing, where fabricating small quantity, individualized, or low-demand parts can be time consuming, costly, and require specialized training, 3D printers are essentially ready-to-go at all times, which highlights its advantages in having zero lead time, less required material inventory, and reduced waste.\textsuperscript{14} Fabricating a part via 3D printing requires no human skills since it is the control software’s duty to relay the printing instructions to the printer. Therefore, the lead time between when a part is designed and when it will be fabricated is virtually zero, which allows for fabrication at a moment’s notice. Consequently,
less stock material inventory is needed, not only because parts are printed with the exact volumes required, but also because custom parts are printed when and where they are needed instead of in anticipation. Reduced stock inventories and exact (precise) volume printing emphasize 3D printing’s advantage in reduced waste compared to subtractive techniques that actively produce waste that is not always immediately reusable. Therefore, 3D printing has been considered a greener form of manufacturing.

1.1.4 Limitations of the technology

There are many benefits to fabricating an object via 3D printing, but the technology has not been without its own limitations and concerns. In order for 3D printing to flourish as a manufacturing platform, it must be competitive with traditional techniques by producing high quality parts, be fabricating with a variety of materials from tough to elastomeric, and offer unique fabrication solutions. This section aims to describe limitations that 3D printing has faced as it has attempted to breakthrough into manufacturing.

3D printing has been considered rapid due to reduced time from design to physical object, however fabrication rates are typically slower than traditional techniques.\(^5\) Build rates vary from method to method, and by other factors such as part size and slice thickness. For methods that use raster patterning, the time spent on each layer depends directly with the size of a layers’ cross-section.\(^7,8,16\) Therefore, an increase in cross-sectional area, or printing multiple copies of the same part simultaneously, will increase overall fabrication times. Additionally, tall parts can have an increased number of slices relative to a proportionally smaller (shorter) object, which further increase fabrication time and/or surface finish. Ideally, fabrication of an object would be as dimensionally accurate and highly resolved as the CAD files. Unfortunately, the layer-by-layer process, or repetitive 2D printing, can lead to a staircase effect on the surface of printed parts that is aesthetically undesired.\(^17\text{–}20\) To reduce stair-stepping and achieve good surface finish, slice thickness can be manipulated to be as small as possible, resulting in a smoother surface as described in figure 1.5.
However, a decrease in slice thickness increases the total number of slices for the same part, thus leading to decrease in overall fabrication rate. For example, if the fabrication time per layer is assumed constant regardless of slice thickness, then a doubling in the number of slices equals a doubling in fabrication time. Combined with part size, slice thickness can reduce fabrication speed to as low as a few millimeters per hour. Projection based SLA can eliminate the rate-limiting rastering step by being able to fabricate an entire layer at one time. Therefore, SLA often has improved surface finish due to layer thicknesses typically being <100 microns. Thus, the rate-limiting step in projection based SLA is the recoating/resin renewal process, which can be time consuming because resin must be level to ensure constant slice thickness/part accuracy. Therefore, regardless of the method used, 3D printing is often met with a tradeoff between fabrication rate and highly resolved parts.

Besides surface finish and fabrication rate trade-offs, the layer-by-layer process of 3D printing can also introduce inherent weakness within fabricated parts due to insufficient adhesion between layers. For instance, in fabrication via FDM or SLS, near instant heating then cooling of both the current and previous layer is required for adhesion between layers. Moreover, poor adhesion between layers and within cross-sections often results in porosity within parts that are designed to be solid. Insufficient melting between powder particles in SLS has been shown to result in high porosity within a part, thus decreasing its structural integrity (elongation, tensile strength). Porosity can be reduced using a thermal post cure,
though this too can be challenging with thermoplastics since elevated temperatures can cause part deformation. Poor adhesion between layers and porosity can thus lead to inherent mechanical anisotropy based on layer orientation relative to an applied stress, as shown in figure 1.6.28–31

Figure 1.6: Effect of build orientation on mechanical strength and fracture behavior. (A) Build orientations of tensile testing specimens. (B) Tensile strength as a function of energy density in SLS process. 0° orientation is consistently higher than 90° orientation. (C) Fracture example of a 0° oriented specimen. (D) Fracture example of a 90° oriented specimen. Adapted and reproduced with permission from reference.30

Figure 1.6D shows that fracture occurs directly at the interface of two adjoining layers, unlike figure 1.6C. This intrinsic weakness led to an overall decrease in mechanical properties, such as tensile strength, as seen in figure 1.6B. This effect of decreased structural integrity based on build orientation has been observed in multiple forms of 3D printing, and often mechanical properties are best when tensile stresses are applied parallel to the slices.32 Unlike SLS or FDM, polymer crosslinks are formed in situ during fabrication via SLA, thus each layer interacts with its adjoining layers at a molecular level and reducing anisotropy.28,33–36 However, layer adhesion in SLA requires unreacted functional groups at the surface of a previously printed layer, typically achieved by reducing light exposure and subsequently crosslink density. This reduces the structural integrity of the layer and/or the part, which in turn can be damaged during
the often physically demanding recoating process. Thus, a layer needs to be highly crosslinked to maintain structural integrity, but this can lead to inherently decrease structural integrity similar to FDM and SLS discussed above.\textsuperscript{33}

By themselves, the limitations of 3D printing appear to be subjective to the needs of the individual looking to fabricate a part, but together they have hindered the technology as a potential universal manufacturing technique. An ideal 3D printing platform is one that has removed the trade-offs between material, resolution, and fabrication rate. The processes mentioned so far have lacked in one or more of these ideals, however a new technology developed by startup company Carbon aims to eliminate trade-offs and lift 3D printing into a role that is manufacturing-centered.

1.2 Continuous Liquid Interface Production

Continuous Liquid Interface Production (CLIP) is a 3D printing platform that has the potential be a premier form of additive manufacturing. Developed by the startup company Carbon, CLIP offers 3D part direct fabrication at unparalleled speeds without the traditional tradeoff with resolution or issues with interlayer adhesion leading to structural integrity. Thus, by eliminating trade-offs, CLIP material development can be a primary focus. This section will describe the CLIP process and concepts important this dissertation.

1.2.1 Bottom-up Stereolithography and CLIP

Traditional stereolithography involves parts being lowered into a vat of liquid resin with each layer. After a layer is printed and the stage lowered, a sweeper arm levels the resin surface above the part to ensure uniform layer thickness.\textsuperscript{7,23,24,37} A better way to ensure uniform thickness is to reverse the process and have the part rise out of a vat of liquid. In this process, described in figure 1.7, a build stage lowers into a pool of liquid resin and a layer is projected from below and the part is lifted out of resin to cure the next layer, or rather the bottom of the part moves upward.\textsuperscript{12,38}
Figure 1.7: Traditional bottom-up SLA and comparison to CLIP. (A) Light reflects an entire layer cross-section off a DMD and projects the image through a UV transparent window to build parts. (B) The CLIP process reduces the number of steps involved in layer fabrication due to an oxygen deadzone. Adapted and reproduced with permission from reference.39

Bottom-up SLA typically uses Digital Light Projection (DLP) as opposed to laser line rastering because it can project an entire layer at once. DLP operates by reflecting light off of a digital micromirror device (DMD), which is an array of tiny mirrors that can be individually controlled, creating pixels that form projectable cross-sectional shapes.11 As shown in figure 1.7B, using traditional SLA, each layer image is projected through a rigid UV transparent window and resin cures the full volume between from the window to part. Following each layer cure step, the part must be delaminated from the window before resin can flow or be recoated underneath the part, then the next layer can be projected. Conversely, CLIP utilizes a UV transparent and oxygen permeable window. Diffusion of oxygen through the window causes inhibition of curing in a small volume directly at the window/resin interface. This region of inhibition, known as the deadzone, remains a liquid and allows resin renewal without the need for delamination or recoating.39 As a result, CLIP builds part layers continuously, thus fabrication rates are much higher than traditional techniques.39 An added advantage to the
continuous process of CLIP is that there are no interlayer adhesion issues because the parts are formed monolithically rather than layer-by-layer.\textsuperscript{17} Finally, slice thickness in the continuous process does not affect total build time, removing the trade-off with resolution and enabling smooth surface finishes.\textsuperscript{17}

1.2.2 Free-radical photopolymerization and oxygen inhibition

In its most basic form, a typical CLIP resin formulation is made up of a photoinitiator and monomer with one or more functional groups that can react rapidly via free-radical polymerization.\textsuperscript{40} A typical CLIP photoinitiator is a molecule that creates one or more reactive species when exposed to light radiation, in the form of free-radicals\textsuperscript{41,42} These initiators form radicals as a result of absorbing UV light, typical at 385 nm wavelength. Once a radical has been formed, the reactive species can either self-terminate or interact with a monomer. If the latter event occurs, the mechanism of propagation begins. The general mechanism for free-radical photopolymerization can be seen in scheme 1.1.

\begin{align*}
\text{Initiation} & \quad \text{PI} \xrightarrow{\text{UV}} \text{PI}^* \rightarrow 2\text{R}^* \\
& \quad \text{R}^* + \text{M} \rightarrow \text{R-M}^*
\end{align*}

\begin{align*}
\text{Propagation} & \quad \text{R-M}^* + n\text{M} \xrightarrow{k_p} \text{R-(M)}_n\rightarrow\text{M}^* \\
\text{Termination} & \quad \text{R-(M)}_n\rightarrow\text{M}^* + \text{R-(M)}_m\rightarrow\text{M}^* \xrightarrow{k_t} \text{R-(M)}_{n+m}\rightarrow\text{R}
\end{align*}

\textbf{Scheme 1.1: Free-radical photopolymerization}

The process begins with a high-energy photon from light interacting with a photoinitiator to form and excited state molecule and subsequently a radical initiators species that can then react with a monomer to create an initiated monomer radical species, which will react with other monomers thus forming a polymer chain through propagation.\textsuperscript{43} In most photopolymerizations, initiation propagation, and termination continues as a sample is being exposed to light, so long as monomer concentrations remain high. When the light is triggered off, propagation continues, however no new initiations occur and monomer concentrations begin to decline. The rate constant $k_t$ is typically on the order of $\sim 10^5$ L mol\textsuperscript{-1} s\textsuperscript{-1} versus $\sim 10^3$ L mol\textsuperscript{-1} s\textsuperscript{-1} for $k_p$, therefore termination can occur quickly, though propagation can still occur since radicals are
typically in very low concentrations. In the photopolymerization of multifunctional monomers, which are commonly used as CLIP resins, propagation can also be terminated by becoming physically trapped in crosslinked networks.

The mechanism described above is true for systems within an inert atmosphere, or rather in the absence of oxygen. It is well-known that oxygen inhibits free-radical polymerization by its reaction with radicals as well as excited state initiators as described in scheme 1.2. Oxygen inhibition causes the formation of peroxide radical, causing initiation and propagation to cease until oxygen concentrations decrease.

\[
\text{Inhibition} \\
\begin{align*}
\text{PI} & \xrightarrow{\text{uv}} \text{PI}^* \xrightarrow{} 2R\cdot \xrightarrow{M} R-M\cdot \\
\text{O}_2 & \xrightarrow{} \text{O}_2 & \text{O}_2 & \xrightarrow{\text{O}_2} \\
\text{PI} & \xrightarrow{R-O-O\cdot} \xrightarrow{} R-M-O-O\cdot
\end{align*}
\]

Scheme 1.2: Oxygen inhibition of free-radical photopolymerization.

For most resins at equilibrium, oxygen concentrations within a free-radical polymerizable liquid are typically on the order of \( \sim 10^{-3} \) mol/L. Despite its low concentration, inhibition dominates in the early stages of free-radical polymerization because the rate constant for oxygen inhibition is on the order of \( \sim 10^8 \) L mol\(^{-1}\) s\(^{-1}\), five orders of magnitude higher than propagation. Therefore, propagation occurs only once monomer molecules can compete with oxygen, that is, when \( k_p[M] \sim k_o[O_2] \). Oxygen inhibition is typically diffusion limited, wherein it will only continue to occur within small depths past surfaces that are in contact with an oxygen-rich atmosphere. Consequently, in UV related processes, such as photoimaging and coatings, oxygen inhibition at cured surfaces leads to undesirable surface finishes surfaces that appear and feel tacky due to insufficient curing. As such, oxygen inhibition is typically viewed as a disadvantage in the use of free-radical photopolymerizable systems and has been extensively studied to reduce its occurrence. However, CLIP utilizes oxygen inhibition to form a liquid deadzone underneath growing parts during 3D printing.

1.2.3 Deadzone formation during CLIP

The practice of using oxygen inhibition as a tool in fabrication has been done before. Doyle et al exploited oxygen inhibition within microchannels as a solution to rapid microparticle fabrication. In their method, photoreactive liquids were flowed through
polydimethyl siloxane (PDMS) microchannels and light was projected through a photomask in short concentrated intervals, forming microparticles. Because PDMS is known to be highly gas permeable, oxygen inhibition at the channel surface prohibited particles from adhering within the channels, thus forming a method of continuous microparticle fabrication. The same mechanism is used in CLIP, in that oxygen inhibition stops parts from adhering to the window thus eliminating the need to delaminate and recoat with fresh resin.

Figure 1.8 illustrates the CLIP fabrication process, which begins with liquid resin at equilibrium with the atmosphere.

At time zero (t = 0) the resin contains an equilibrium concentration of oxygen that inhibits curing of the resin. While illuminated, oxygen concentration within the resin decreases as photoinitiated radical species consume it until, after some time (t = t_c), a critical oxygen concentration is reached, and propagation begins to occur. However, due to gas permeation through the window and into the resin, oxygen concentrations remain high enough to maintain inhibition in a volume of resin just above the window, known as the deadzone. The height of this volume is oxygen diffusion limited and remains liquid despite light exposure. Above the deadzone, however, oxygen concentrations are not constantly replenished, thus propagation dominates and the resin cures into a solid. Once cured the build stage and part move up and resin replenishes underneath the part above the deadzone and the process repeats.

The process described above shows how the balance of light and oxygen plays a vital role in CLIP operation, and can be studied by manipulating those factors. Oxygen
concentration beneath the window directly affects deadzone thickness due to diffusion limitation. In their paper detailing the technology, Tumbleston et al described how both oxygen and light concentration also affect deadzone thickness. As seen in figure 1.9, the deadzone did not exist regardless the concentration of photons in pure nitrogen environment. Conversely, when exposed to ambient or pure oxygen atmospheres, deadzone thickness decreased in a power law fashion with increasing light intensity.

The liquid deadzone allows for continuous light projection due to continuous resin renewal and subsequently slice thicknesses of 100 microns or less are enabled without a fabrication rate trade-off, as shown in figure 1.9B. Therefore, it is possible to fabricate parts that are effectively layerless, enabling fabrication of parts with superb surface finish and isotropic mechanical properties.

Figure 1.9: Effect of oxygen concentration on deadzone thickness. (A) Deadzone thickness decreases with photon flux following a power law fit. (B) The deadzone allows fabrication of smooth surface finishes due to fine slicing without the trade-off fabrication rate. Adapted and reproduced with permission from reference.
1.2.4 Governing equations of the CLIP process

Printing parameters, such as light intensity, exposure, or build speed, for CLIP are determined using governing equations related to photon flux modeling.\textsuperscript{39, 54} The working curve for the CLIP process originates from the Beer-Lambert law, as described in equation 1.1.

\[ \Phi = \Phi_0 e^{-\alpha z} \quad 1.1 \]

Where \( \Phi \) is the number of photons per area per time at a depth \( z \), \( \Phi_0 \) is the incident number of photon flux, and \( \alpha \) the total absorption coefficient of the resin. The equation can then be manipulated to describe the number of photons absorbed per unit area per unit depth by taking the derivative of equation 1.1 and multiplying is by light exposure time, as seen in equations 1.2 and 1.3.

\[ A = \alpha \Phi_0 e^{-\alpha z} \quad 1.2 \]
\[ D = \alpha \Phi_0 t e^{-\alpha z} \quad 1.3 \]

An SLA resin solidifies to a particular depth, \( z_{ct} \), at a critical curing dosage, called \( D_c \). Substituting \( D_c \) and \( z_{ct} \) into equation 1.3 and solving for \( z_{ct} \) yields equation 1.4.

\[ z_{ct} = \frac{1}{\alpha} \ln \left( \frac{\alpha \Phi_0 t}{D_c} \right) \quad 1.4 \]

This equation, in tandem with experimental measurement of cured thicknesses at different light intensities and exposure times, is thus used to calculate the exposure time required to solidify a given liquid resin to a certain depth, and thus determine the printing speed at a given light intensity.

1.3 Material Development using Photocurable Resins

1.3.1 Crosslinked polymer networks

As discussed previously, CLIP resins are typically a blend of monomers, oligomers and photoinitiator that react, when exposed to UV light, to form a solid object. Monomers and oligomers in CLIP resin typical have two or more photoreactive groups functional groups
where each group is f=2 and thus form crosslinked networks, also known as thermosets, upon polymerization. Unlike thermoplastics, which are made up of individual chains that can form entanglements, thermosets form covalently bonded crosslinks between neighboring polymer chains. These chemical linkages cause thermoset samples to maintain the shape with which they were cured and can exhibit a wide range of mechanical properties from elastomeric rubbers to rigid plastics.\textsuperscript{40,43} As such, CLIP resin development starts with tailoring the chemical nature of the monomers and oligomers to target final polymer properties such as glass transitions temperature (T\textsubscript{g}), and is then followed by resin additives and the overall cure behavior between constituents.

1.3.2 Material properties and applications of thermosets

From a mechanical standpoint, the main factor in thermoset material properties is the crosslink density, which is a function of the molecular distance between crosslinks (M\textsubscript{c}).\textsuperscript{55} High M\textsubscript{c} means that crosslink density is low, whereas low M\textsubscript{c} results in high crosslink density. In general, the mechanical properties of a thermoset scale with crosslink density, wherein a material stiffens as crosslink density increases. Highly crosslinked thermosets are used in a wide variety of engineering applications because of their high strength and modulus properties, however they often come at the price of brittleness.\textsuperscript{55–57} As such, thermoset material development requires careful consideration in crosslink density in order to ensure a proper balance between strength and ductility. This is often achieved through manipulation of the chemical nature of the monomers, which in turn has led to their use in a wide variety of applications.

Beyond mechanical properties are chemical and thermal properties brought about by changes in the types of monomers used. For instance, CE resins have been known to retain good mechanical properties even after prolonged exposure to temperatures as high as 300 °C.\textsuperscript{55,58,59} Heat resistance is often the result of high T\textsubscript{g} that are inherent of the chemical nature of their backbone. Engineering thermosets can have T\textsubscript{g} values ranging from 150 °C for epoxies to as high as 400 °C in CE resins. As such, many thermosets are used in applications requiring high heat resistance, such as aerospace and automotive industries, with the driving force typically being weight reduction through replacement of heavier ceramic and metallic material.
The coupling of high strength with excellent thermal and chemical stability have thus put thermosets into a variety of applications.

1.3.3 Photocurable materials for 3D printing

Photocurable resin development for 3D printing shares many of the same design principle as conventional thermoset development, wherein material development begins at the molecular level. Unlike conventional thermosets, CLIP resins have the added requirement of containing at least one component that is rapidly photocurable. In systems where the sole functionality is readily photocurable, such as an acrylate or methacrylate, material choices primarily concern the chemical and physical properties of the monomers and oligomers. Typically, this comes in the form of crosslink density manipulation, such as when moderate to high molecular weight oligomers with multiple functional groups ($f > 2$) are blended with low MW monomers. Oligomers typically set the desired mechanical property by varying its chemical backbone and/or molecular weight, whereas the monomers act as chain extenders to manipulate crosslink density to improve material ductility.

Another method of photocurable resin development introducing other components within the resin that can react to form unique structures known as interpenetrating networks (IPNs). An IPN is a blend of two thermoset networks that are combined to take advantage of the properties (physical/mechanical) of both materials. IPNs can form either simultaneously where a mixture of monomers and initiators react to form two crosslinked systems, or sequentially where one polymer network forms within an already existing network. Simultaneous IPN fabrication via photopolymerization has been shown to introduce various chemical and mechanical properties to otherwise structurally or chemically inadequate systems. For instance, Crivello developed photocurable hybrid acrylate-epoxide IPNs using blends of both free-radical and cationic photoinitiators. He detailed how acrylate and epoxy photopolymerization work synergistically in that highly exothermic acrylate reactions markedly increase slow cationic ring opening epoxide reactions. The products of these hybrid photopolymerizations were found to be rigid and optically clear. The study was then further expanded to show that the same mechanism of sequential IPN formation applied to hybrid acrylate-oxetane systems. Several other similar studies have used simultaneous IPN
fabrication techniques to develop photocurable resins that produce parts with unique properties including hydrophobic surfaces using fluorinated acrylate-epoxide hybrids, tissue engineering using unique hydrogel IPNs, and even durable materials with biocidal properties.\textsuperscript{66–68}

Sequential IPN fabrication via photopolymerization has also been shown to improve and even introduce unique properties to photocurable resins. For instance, Berg et al described their combination of a thermoreversible Diels-Alder (DA) network with an acrylate network in an effort to form heat removable support structures for large overhangs in printed parts.\textsuperscript{69} In their system, a mixture of photoinitiator, acrylate monomer, multifunctional furan, and maleimide could be cast in a thin film, which then spontaneously forms a DA network. UV exposed areas of the thin film form IPNs with acrylate while the remaining DA network acted as supporting material. IPNs have also been made specifically for CLIP by Carbon Inc., wherein they introduced a resin technology platform that incorporates both UV curable and thermal curable components as detailed in figure 1.10.\textsuperscript{70}

![Figure 1.10: Dual-cure resin concept.](image)

In these dual-cure resins, the UV curable components set the shape of the part, also known as the green part. Following fabrication and post-processing to remove residual resin, the part is subjected to a thermal cure that forms the secondary polyurethane network. This process allows for the fabrication of polymer parts with unique properties such as dampening elastomers or rigid polyurethanes with high ductility competitive with polyurethanes produced using more traditional processes like injection molding. For instance, a study by Miller et al. showed that
the strain-based fatigue properties of parts made with Carbon’s EPU 40 were very similar to parts made with thermoplastic polyurethanes processed using FDM.\(^1\)

The progress of photocurable resin development for 3D printing has made great strides in the past two decades. The development of resins that offer unique properties, such as those of Carbon’s dual-cure system, has opened new doors to industrially relevant applications. Regardless, the materials developed for CLIP so far have been almost exclusively concerned with chemical manipulation. As such, there are still many untapped material and mechanical properties that can be developed into CLIP resins in the form of polymer composites.

1.4 Polymer Composites in 3D Printing

A composite can be defined as a material that is a blend two or more chemically and physically distinct phases.\(^2\) While composites in an industrial sense are relatively young, the concept of composites has been observed in nature for thousands if not millions of years such as within the complex network of wood found in trees.\(^3\) As such, the inspiration and driving force of composite material development has often stemmed from trying to implement the unique and often desirable properties of the natural materials around us into synthetically designed materials. The purpose of this section is to introduce basic concepts of polymer composites and how their development is relevant to 3D printing material development.

1.4.1 Polymer composites

A polymer composite is a material where at least one of the phases, typically the bulk phase, is a polymer.\(^3\) There are several motivations that drive the development of a composite material, including the need to reduce the cost of materials, to improve mechanical properties, or impart new properties unique to the added filler component.\(^4\) The versatility in the potential benefits of polymer composites has led to their use in a wide variety of application areas including, but not limited to, aerospace and aircraft, automotive, marine, electrical, chemical, and construction.\(^5\)

In general, polymer composites include a dispersed phase, typically known as a filler, is distributed through a bulk polymer phase.\(^6\) The processing of the two materials to produce
the composite structure is different for different types of materials and parts. As described in figure 1.11, the term ‘filler’ is broad in that it includes materials of varying shape, size, material, and function.

![Diagram](image)

**Figure 1.11: General forms and distribution of fillers in polymer composites.**

With the existence of varying forms of filler comes the development of multiple types of polymer composites. For example, epoxy based carbon fiber composites used in aircraft are typically produced by sequentially layering a woven carbon fiber (CF). Meanwhile, fiber reinforced polymers like those in construction of beams for bridges or decks, are typically made by pultrusion as a continuous product. These two examples are both polymer composites with improved mechanical properties over their pure plastic counterpart in the direction of the continuous fibers. However, polymer composites with woven filler exhibits less anisotropy because it reinforces in two directions.

Still there is another type of composite that utilizes particle fillers that will be the focus of this dissertation. A particulate-filled polymer composite is created from a blend of a polymer with discontinuous particles. Particulate fiber fillers come in a range of material, shape, and size, as seen in figure 1.12. Moreover, particulate filler can be categorized into two size regimes as micro- or nanoparticles, which are used in microcomposites and nanocomposites respectively. Microcomposites typically involve the use of relatively short fibers and flakes where at least one dimension is less than a millimeter in length. Nanocomposites are materials that include filler that has at least one of its dimensions on the nanoscale, typically less than 100 nm.
Filler properties such as shape, size, its material or composition, and its interaction with the polymer affect the mechanical properties of the polymer composite being produced.\textsuperscript{77,81} Furthermore, the addition of filler can also affect processing conditions of polymer composite fabrication. For instance, particulate fillers with small particle size (i.e. nanoparticles) are harder to disperse within the bulk phase, even at low loadings, due to increased viscosity.\textsuperscript{79,80,83} The concept of increased viscosity in filled resins will be discussed in greater detail in chapter 3.

Traditionally, spherical or irregular particle fillers have been blended into polymers primarily to reduce the cost of materials, since their often unfavorable geometries only result in moderate improvements to mechanical properties.\textsuperscript{77} However, increasing filler aspect ratio (l/d), particulate fillers can have a reinforcing effect on polymers such as high aspect ratio talc powder blended into brittle polystyrene or polypropylene.\textsuperscript{84,85} This is because, particles with high l/d, such short fibers, or very low l/d, such as platelets, have high surface area to volume ratios, which in turn allows for increased particle-polymer interaction. As such, the typical particulate-filled polymer composite utilizes particles with l/d > 1 in order to achieve qualities such as reinforcement. Simply blending the filler into a polymer is not enough though, as orientation of high or low aspect ratio particles also plays a role in its ability to reinforce. Just as continuous fiber or woven polymer composite reinforcement is noticeably improved along the same axis as the fibers, so too is it important for particle fillers to align in the same direction.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{particulate-fillers.png}
\caption{Types of particulate fillers.}
\end{figure}
to achieve desired mechanical properties. For instance, orientation of talc powder in HDPE due to the shear from injection molding was shown to increase tensile strength to 100 MPa versus 40 MPa for non-shear induced (random) orientation. Therefore, care is often taken to account for how a particulate-filled polymer composite will be processed to ensure that the desired orientation, and subsequently the mechanical properties, will be achieved.

The benefits of polymer composites go beyond just tensile properties such as modulus and strength. For instance, flame retardancy can be imparted into polymer composites with the addition of nanoparticles such as organically modified nanoclays. In flame retardant polymer composites, clays improved char properties at the surface of the nanocomposites decreased the emission of volatile products (fuel), thus self-extinguishing flames. Therefore, high aspect ratio particles were preferred since their high surface area ensured proper coverage at the surface of the composite. A final example of a non-intuitive benefit of polymer composites is the development of electromagnetic interference (EMI) shields for electronics housing using carbonaceous fillers. Carbon fillers such as fibers, graphene, and nanotubes are known to be electrically conductive and can impart this property into polymer composites. Thus when polymers are blended with carbonaceous fillers they can form EMI shielding that is moldable and cost effective.

The polymer composite examples described above are by no means an exhaustive list, but serve to briefly exemplify the range of properties than can be achieved through the addition of filler. The many potential benefits of polymer composite material development have made them attractive to part designers within many industries. It is for this reason that composite material development in 3D printing is of interest.

1.4.2 3D printed composite materials

Polymer composite development for 3D printing has made considerable achievements in terms of fabricating materials with improved or even unique properties. The following are examples of how polymer composites have been used and/or fabricated in 3D printing.

A primary motivation for 3D printable polymer composite fabrication is to improve the mechanical properties (strength/modulus/elongation) of printed parts. In one example, Tekinalp et al showed that carbon short-fibers (CF) could be blended with ABS copolymer
filament prior to its use in a FDM apparatus to produce polymer composites. In their study they showed that tensile strength parallel to layer and subsequently fiber orientation increased from ~36 MPa to ~67 MPa and modulus from 2 GPa to ~14 GPa with the addition of 40 wt% CF. This was in part due to the CF being highly orientated as a result of extrusion through the FDM nozzle. Interestingly, they detailed how the addition of fiber cause the formation of voids within the solid part, which is an indication of poor adhesion of the filler with the polymer matrix. This suggests that mechanical properties could still be improved further with processing modification. Mechanical improvements have also been achieved in polymer composites fabricated via SLA. In their paper, Kumar et. al. described the use of low amounts of cellulose nanocrystals blended into SLA resin to improve mechanical strength and moduli of printed tensile testing specimens by as much as 30 % relative to the pure matrix. Their results also detailed how elongation at break decreased from 3.8 % to 1.6 % after the addition of just 5 wt% filler. This was likely due to increased filler-polymer interactions, which can induce brittle part failure.

One particular application of polymer composites fabrication via 3D printing following cues from nature has been bone regeneration scaffolds with tunable porosity. Inzana et. al. fabricated composite calcium phosphate and collagen scaffold using a powder binding 3D printing method for the purpose of improved bone regeneration. They showed that not only could a 3D printer be modified to fabricate objects using biological material (collagen), but also form complex scaffold structures (like those in figure 1.4) to tailor porosity and further promote bone regeneration through increased surface area. In a similar study, Cox et. al. showed that porosity could be further increased with the addition of hydroxyapatite (HA). In their study, porosity within the scaffolds reached a value of 55 % without losing mechanical strength due to the addition of HA. Bone regeneration polymer composites have also been shown to promote bone regeneration in vivo within rabbit femur, as detailed by Kim et. al. They added tricalcium phosphate filler into an SLA resin and printed cylindrical scaffold structures to be used as implants in femur bones. Using the 3D printed composite structures resulted in improved bone regeneration, replacing 60 % of the biodegradable scaffold after just 6 weeks. Still there are many of examples of 3D printing being used for the purpose of bone
regeneration, as it combines the free complexity of 3D printing and polymer composites to form novel bioengineering structures\textsuperscript{18,99,100}.

3D printable composites have also been shown to exhibit unique non-mechanical properties. Kim et. al. detailed their use of barium titanate (BTO) nanoparticles within propylene glycol diacrylate resins to develop 3D printable structures with piezoelectric properties\textsuperscript{101}. Resin loaded with 10% BTO particles was printed with UV light and photomasks to produce small 3D structures. The addition of BTO particles resulted in a moderate electrical charge following a mechanical stress. Mechanical to electrical conversion was further enhanced by as much 500% through chemical modification of the particles with 3-trimethoxysilylpropyl methacrylate, which allowed particles to form a covalent linkage with the polymer matrix. Kalsoom et. al. developed 3D printable polymer composites filled with microdiamond powder for the purpose of improving thermal properties\textsuperscript{102}. In their method, microdiamond powder was added to SLA resin for bottom-up SLA. They showed that the linear thermal expansion coefficient of the polymer composite decreased by as much as 75% relative to the pure polymer with the addition of 30% (w/v) nanodiamonds. The addition of nanodiamond was also found to impart heat conductive properties to the polymer composite, as pictured in figure 1.13.
The filled polymer heatsink in figure 1.13D shows overall increased temperature compared to the pure polymer heatsink (figure 1.13C) indicating increased heat conductivity. As such discussed the potential for custom heat exchange units with optimized heat dissipation using 3D printable composite materials, as well as other engineering applications.

The addition of fillers into polymers is an avenue for developing potentially unique 3D printable materials and structures. For some, this has meant improving mechanical properties, such as strength or modulus. While others have shown that 3D printing offers opportunity for synergistic enhancement, combining complex structures and materials to produce parts that can mimic nature itself. The opportunities for polymer material improvement, both mechanically and in terms of potential applications, grows by developing new methods for composite fabrication. Given the ever-growing interest in polymer composite development, 3D printing, and the unique properties that have been exhibited with their combination, there is an inherent need for their (polymer composite) development in CLIP.
1.5 Dissertation Overview

Research in 3D printing processes and materials is a relatively new area of study, however many of the same design principles from traditional polymer processes and materials can be applied. Meanwhile, CLIP is a novel 3D printing process with improved fabrication rates and unique resin materials. The materials commercialized for CLIP so far are by no means inadequate for a range of engineering applications, however evidence shows that 3D printable materials can have improved and even unique properties with the addition of fillers. Therefore, the focus of this dissertation will be to understand how the addition of filler affects various aspects of the CLIP process, with the purpose of paving the way for future polymer composite development within the CLIP platform. This dissertation represents the first reported studies that are directly concerned with characterizing the feasibility of polymer composite fabrication using CLIP. As such, fundamental characterization techniques were developed to provide a better understanding of the observed physical phenomena.

In chapter 2, the effect of solid particulate filler on the oxygen deadzone and overall resin cure behavior was investigated in terms of particle size and shape. Their potential effect on gas permeation into resin during CLIP are described. Chapter 3 explores filler distribution in filled parts fabricated via CLIP. The effect of particle size and loading on viscosity and resin flow were observed using rheology and microfluidics to visualize how particles can clog at the interface of a growing part during CLIP fabrication, leading to inhomogeneous filler distribution across its cross-section. Finally, in chapter 4, a new type of filler is introduced in the form of rubber particles formed in-situ for the purpose of toughening a brittle thermoset resin. Characterization techniques and observations from both the previous chapters aided in understanding the limitations of this approach to toughening. The dissertation concludes with a summary and recommendations for future work in chapter 5.
1.6 References


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CHAPTER 2: Effect of Fillers on CLIP Resin Kinetics

2 Introduction

One essential consideration in particulate polymer composite material development is to evaluate how particulate filler affects the fabrication/processing parameters. The addition of filler particles into polymers often dictates changes to manufacturing and processing parameters of a process, including within additive manufacturing methods.\textsuperscript{1-3} For instance, continuous or highly oriented fiber polymer composites can be fabricated via fused deposition modeling (FDM) only once nozzles have been modified to prevent particle clogging or to ensure proper filler mixing and adhesion.\textsuperscript{4,5} In relation to the continuous liquid interface production (CLIP), particulate polymer composites fabricated via stereolithography (SLA) often require changes in UV exposure time because filler can reduce cure depth due to light obstruction.\textsuperscript{6,7} The addition of filler can also alter the rheological properties of a resin, which adds to processing parameter considerations.\textsuperscript{8-10} Rheological properties of filled resins and the flow of particles in resins will be discussed in chapter 3, whereas this chapter will present how the addition of fillers in CLIP resin affects the deadzone formation and how these results relate to CLIP parameters.

2.1 Technical Background

2.1.1 Gas transport in filled systems

As was detailed in chapter 1, the depth of the liquid deadzone increases or decreases based on the rate of oxygen diffusion into the resin from the direction of the highly gas permeable window. Therefore, deadzone formation characteristics depend on the gas permeability of the liquid resin, which is the product of the oxygen diffusivity and solubility in the resin.\textsuperscript{11} The chemical nature of the resin affects gas solubility, where polar molecules exhibit relatively low oxygen solubility compared to their non-polar counterparts.\textsuperscript{12-14} For instance, because of their unique ability to solubilize large quantities of oxygen, highly non-polar fluorocarbons have long been studied as potential emergency blood transfusion substitutes.\textsuperscript{14,15} While measuring gas solubility in liquids have been studied for decades,
literature lacks studies on oxygen diffusivity and subsequently permeation into liquids.$^{11-13,16}$ Therefore, utilizing established techniques is imperative to begin exploring how the addition of filler into resin might affect deadzone formation.

Deadzone thickness is on the order of 10 to 100 microns, making it analogous to thin-film polymer membranes used in various applications.$^{17}$ The food packaging industry is well known for their studies of thin-film polymers designed as oxygen barriers for preservation purposes.$^{18-20}$ It has been shown that the degree of crystallinity in polymers such as poly(vinyl chloride) (PVC) or low density polyethylene (LPDE) directly affects gas permeability.$^{10,21}$ The oxygen diffusivity decreases due to physical obstruction of gas transport pathway (tortuosity), as shown in figure 2.1.

![Figure 2.1: Gas diffusion through polymer membranes.](image-url)

Figure 2.1: Gas diffusion through polymer membranes. (Left) A neat amorphous polymer membrane allows molecules to diffuse effectively in one direction uniformly. (Right) A filled or semi-crystalline polymer obstructs gas diffusion pathways increasing diffusion time.

This concept of tortuosity can also be applied to polymer composites and thus to deadzone formation in filled resins for CLIP. For instance, the food packaging industry has been developing biodegradable alternatives to PVC and LDPE, however these polymers exhibit lower modulus and more importantly, have lower gas and vapor barrier properties.$^{18,19,22}$ One method that has been demonstrated to improve both properties has been the addition of high...
aspect ratio filler such as clays, which reinforces the polymer physically and simultaneously form tortuous pathways for oxygen diffusion. With the addition of filler, oxygen diffusion can be reduced by ≥50% relative to the unfilled polymer and is dependent on the filler aspect ratio. As such, polymer composites have been developed for the specific purpose of reducing the diffusion of oxygen to fabricate flame retardant materials, improve weather stability, and improve the reliability of UV curable dental resins. Even if gas transport in polymer liquids differs from their solid thin-film analog, evidence of the impact of tortuosity from the addition of filler requires that its effect on deadzone formation be carefully studied.

2.1.2 Photopolymerization kinetics of crosslinking systems

The CLIP process uses photocurable liquid resins containing monomers and oligomers with one or multiple photoreactive groups. As such, one method of resin characterization involves studying changes in reaction kinetics upon the addition or removal components. In general, photopolymerization rate equations follow a modified classical model as seen in the following equations.

\[ R_p = \frac{k_p}{k_t^{0.5}} [M] \left( \frac{R_i}{2} \right)^{0.5} \]  \hspace{1cm} (2.1)

\[ R_p = \frac{k_p}{k_t^{0.5}} [M] (\Phi I_0)^{0.5} \]  \hspace{1cm} (2.2)

\[ R_p = \frac{k_p}{k_t^{0.5}} [M] \left\{ \left( 1 - e^{-\varepsilon|\ln|b|} \right) \right\}^{0.5} \]  \hspace{1cm} (2.3)

Where is M is the concentration of functional groups, \( R_i \) is the initiation rate, \( k_p \) and \( k_t \) are the propagation and termination rate coefficients respectively, \( \Phi \) is the quantum yield for initiations, \( I_a \) the absorber light intensity, \( I_0 \) the incident light intensity, \( \varepsilon \) the extinction coefficient, [ln] the photo initiator concentration, and b the layer thickness. Although several attributes of linear polymerization are present in crosslinking reactions, or the increased in crosslink density, causes reaction diffusion to become the dominating termination mechanism as opposed to termination by combination. In this sense, radicals can become trapped within
dense crosslink networks, leading to the onset of reaction autoacceleration at the initial stage of polymerization, demonstrated by a typical kinetic curve (figure 2.2).

Figure 2.2: Typical shape of kinetic curves for polymerization rates. Restricted mobility of radicals within crosslink networks causes an autoacceleration in rate towards the beginning of polymerization, represented by a reaction peak.

Several models and experimental methods have been developed to measure and calculate photoinitiator efficiency, polymerization rates and rate constants, and in the case of vinyl group functionality, double bond conversion.\textsuperscript{31,33,34} One prominent method, known as differential scanning calorimetry, is a thermoanalytical technique which measures the difference in the amount of heat required to increase the temperature of a sample versus a reference.\textsuperscript{35} This method can be modified to use light to cure photoreactive resins, and thus has been utilized as a characterization tool for multiple industries including Stereolithography.\textsuperscript{36–38} In this sense, changes in temperature are due to the reaction of double bonds, such as acrylates or methacrylates, which in turn can be used to produce rates of polymerization graphs like that seen in figure 2.2. Therefore, double bond conversion can be calculated using known sample mass and the heat of reaction per double bond from literature. Differential scanning calorimetry technique can therefore be used to determine how filler affects double bond conversion when blended with liquid resin.
2.2 Materials and Methods

2.2.1 Materials

Ethyl (2,4,6-trimethylbenzoyl) phenylphosphinate (L-TPO, 98 %), 2-tert-Butyl-6-(5-chloro-2H-benzotriazol-2-yl)-4-methyl-phenol (BLS 1326, 98 %), and triethanolamine (TEtOHA ≥99 %) were purchased from Sigma-Aldrich and used without further purification. CN2920 and SR833-S were provided as samples from Sartomer. CN2920, an aliphatic urethane acrylate oligomer, and SR833-S (tricyclodecane dimethanol diacrylate) was used as a reactive diluent. Silica microspheres with average diameters 0.8 microns and 25 microns were purchased from US-nano and used without further modification. Methacryloxy-propyl-trimethyl silane surface treated ECR glass flake with a nominal thickness of approximately 1 micron was provided by Glass Flake Limited. Isopropyl alcohol (IPA, 99%) was used as a cleaning solvent for all samples and were obtained from Fisher Scientific. All resins and blends were mixed using a THINKY ARE-310 centrifugal mixer.

2.2.2 Resin Formulations

The resin used in experimentation was a formulation using CN2920 and SR833-S, labeled VF11. 50 g each of CN2920 and SR833-S were weighed on an analytical balance and added to a mixing cup, followed by 1 g (1 part per hundred; pph) L-TPO as a photoinitiator, 0.5 g (0.5 pph) TEtOHA as a catalyst, and 0.1 g (0.1 pph) BLS 1326 as UV absorber to prevent curing in ambient light. The cup was then placed in the THINKY mixer and blended for 90 seconds at the default setting, wherein the components were mixed by revolving the cup as a centrifuge at 2000 rpm while simultaneously rotating the cup about its center axis in the opposite direction at 200 rpm. Next a filler was chosen and weight to the appropriate amount (in pph) before adding to the mixing cup. The resin and filler were then placed back in the mixer and allowed to mix at default for 3 minutes. This was followed by 7 minutes on the mixer’s “defoam” setting (2200 rpm revolution, 60 rpm rotation).

Viscous resins were prepared to observe the effect of viscosity on deadzone formation. Viscosity was varied by changing the weight ratio of CN2920 to SR833-S. Formulations of 1:1, 2:1, 3:1, and 7:1 CN29020 to SR833-S were mixed. 1 pph L-TPO and 0.5 pph TEtOHA
by weight was added to each formulation and mixed for 90 seconds on a THINKY mixer. Formulations were labeled based on the ratio CN2920 to SR833-S as VF-X1, where X is denoted the ratio of the CN2920 relative to SR833-S (i.e. 2:1 would be VF-21).

2.2.3 Viscosity Measurement

Viscosity of all resin blends was analyzed on a Discovery HR-3 hybrid rheometer from TA Instruments. Shear viscosity measurements were done using a 40 mm diameter parallel plate geometry and a gap height of 500 microns above a Peltier plate accessory. Flow sweep experiments were performed at shear rates between 1 s\(^{-1}\) and 1000 s\(^{-1}\) with 4 points per decade at an isothermal temperature of 25 °C. Each shear rate was equilibrated for 3 minutes, followed by 2 minutes of data collection before averaging.

2.2.4 Deadzone Measurement

Deadzone thickness was calculated using a differential thickness technique, adapted from Tumbleston et al.\textsuperscript{17} The process began with a stainless steel circular shim with thickness of approximately 250 microns glued to a glass disc of the same diameter, figure 2.3A depicts the cross-section of this setup. Liquid resin was then sandwiched between the glass and the oxygen permeable window, forming a control volume and height. Next, resin was exposed to UV light via a CLIP imaging unit that has been programed to display the grid pattern shown in figure 2.3B. The outer ring of 9 dots served as a location reference and was used to account for drift in control height through all experimentation. Each row of the inner 5 by 5 grid represented a different light intensity from 1 mW/cm\(^2\) to 5 mW/cm\(^2\) linearly.
Due to ±10 micron variation in shim thickness around the perimeter, calibration measurements were taken across the grid. Calibrations began by first exposing both the outer ring and the grid to full light intensity for 120 seconds to allow resin to solidify fully from window to glass. A Mitutoyo electronic variance indicator was used to measure the thickness of each dot, with a precision of ±0.5 micron. This process was repeated a minimum of 5 times, and the average thickness of each dot was taken. Calibration measurements were also done at the beginning and end of each set of deadzone measurements for every filled resin blend to further account for potential drift in control height thickness in-between experimentations. Calibration averages were used as the control heights for each dot in deadzone thickness calculation.

Deadzone measurement began by first illuminating the outer ring at full light intensity for 120 s to ensure full solidification from window to glass. Subsequently, the highest light intensity row was exposed as a series of twenty 1-second light pulses with 0.2 seconds between each pulse. The process was repeated for each row (light intensity) until the full grid had been exposed. Following exposure step, the glass was removed from the window and the resin wicked from the cured samples using Kimwipes, followed by IPA wash. Once air-dried, the thickness of each dot was measured using the profiling tool. Deadzone thickness was
calculated as the average thickness from the calibration of an individual dot minus its corresponding experimental dot thickness.

2.2.5 *Resin cure dosage and absorption measurement*

As mentioned in chapter 1, Dosage cure ($D_c$) and absorption ($\alpha$) are empirical measurements of different resins and used as input for printing parameters. The measurement can also serve as an initial evidence of filler effect on curing behavior for CLIP resins, as well as compliment photo-differential scanning calorimetry (p-DSC) data. Thus, $D_c$ and $\alpha$ were measured for all resin blends presented in this study.

Measurement began by placing a thin (1/8 inch) quartz disc onto a CLIP imaging unit window, as detailed in figure 2.4A. Approximately 1 mL of the resin was then placed on the disc and allowed to settle for 30 seconds. Next, the resin was exposed to light in a gradient grid pattern, as depicted in figure 2.4B, for a set amount of time typically between 5 and 30 seconds. Exposure times varies between resins, but by rule of thumb were adjusted such that the highest light intensities (top row) do not cure beyond the thickness of the resin pool. Following exposure, excess resin was wicked away using a Kimwipe and followed by a IPA wash. The thickness of each dot was measured individually using a Mitutoyo variance indicator and the results are plotted as function of dosage. $D_c$ and $\alpha$ are thus determined by a fit line to the experimental data as presented in figure 2.4C.
Figure 2.4: Diagram of Dosage cure and absorption measurement. (A) Resin rests upon a UV transparent quartz, preventing continuous oxygen inhibition from below. (B) Grid pattern exposed unto resin where light intensity increases with each dot. (C) Example curve fit of measured $D_c$ & $\alpha$ data. Resin is exposed from below at a set maximum light intensity and exposure time. $D_c$ and $\alpha$ are determined by measuring cure thickness of each dot in the grid and fitting their results to a semi-log plot.

2.2.6 Photo-differential scanning calorimetry

P-DSC experiments were conducted on a Discovery Series DSC from TA instruments equipped with an Accucure LED light source (385 nm) from Digital Light Lab. Resin was placed in open aluminum pans, allowing light to be exposed from above. First a sample pan was weighed before depositing an aliquot of resin, typically between 7 mg and 10 mg. The sample was then placed in the instrument alongside a previously weighed reference. Next the light fixture was installed such that each pan is directly illuminated when the light is triggered. The sample chamber was held at a constant 25 °C temperature, and light intensity was set to 7 mW/cm$^2$. All experiments were done in a nitrogen atmosphere. The experimental method is seen below.
1. Isothermal for 3 min
2. Light on
3. Light exposure for 0.04 min (~3 seconds)
4. Light off
5. Isothermal 10 min
6. Light on
7. Light exposure for 5 min
8. Light off
9. Isothermal 5 min

The short light exposure was used to simulate the short exposure times seen during CLIP. It should be noted that exposure times during CLIP vary based on resin type and printing style. The long exposure was used to evaluate changes in overall bond conversion between resins.

Double bond conversion (DBC) was calculated based on the sample size and heat data collected during experimentation. A sample calculation for 9.01 mg (0.0091 g) of VF11 filled with 10 pph SS-1 is described here. Acrylated component weight fractions and approximate molecular weights can be seen in table 2.1. It should be noted that the mass of filler within filled resins was removed prior DBC calculation. For this example, filler made up 8.655 % of the total mass of resin, therefore 0.0082 g (91.345 %) of the resin is reactive resin.

<table>
<thead>
<tr>
<th>Acrylated / methacrylated Component</th>
<th>Weight percent in resin (%)</th>
<th># of functional groups</th>
<th>Approximate Molecular Weight (g/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN2920</td>
<td>49.220</td>
<td>2</td>
<td>~863.89</td>
</tr>
<tr>
<td>SR833-S</td>
<td>49.220</td>
<td>2</td>
<td>308.48</td>
</tr>
</tbody>
</table>

First the moles of acrylate were calculated for the reactive portion of the resin. Subsequently, the theoretical heat of polymerization, ΔH_{P.th}, was calculated for the sample, which assumes that 100 % acrylate bond conversion, as shown in equation 2.4. For these calculations a value of 78,230.8 J/mole was used for acrylate double bond heat of conversion.39
\[
\Delta H_{P,th} = \sum_i \frac{H_{pi} \cdot m_i \cdot f}{M_{Wi}} \quad (2.4)
\]

Moles acrylate = \left( \frac{0.0041 \text{ g CN2920} \times 2}{863.89 \text{ g/mole}} + \frac{0.0041 \text{ g SR833S} \times 2}{308.48 \text{ g/mole}} \right) = 3.61 \times 10^{-5} \text{ mole}

\[
\Delta H_{P,th} = 78,230.8 \frac{1}{\text{mole}} \left(3.61 \times 10^{-5} \text{ mole}\right) = 2.82 \text{ J}
\]

Where \( H_P \) is the heat of polymerization of the functional group, \( m \) is the mass of the molecule, \( f \) is the number of functional groups per molecule, and \( M_W \) is the molecular weight of the molecule. Next the heat flow data from the p-DSC for the first pulse (step 3 and 4) was integrated to obtain reaction enthalpy.

\[
\Delta H_{P,ex} = \int Q \, dt \quad (2.5)
\]

\[
\Delta H_{P,Pulse} = \int Q_{pulse} \, dt = 0.964 \text{ J}
\]

Where \( Q \) is the heat flow as recorded by the p-DSC. This integration was done for each peak (pulse and long cure) where each exposure step fully equilibrated back to baseline and the entire peak was integrated. For the long five-minute cure (step 7), there is a small amount of heat added by the light that does not translate to DBC. This value was removed from the data by integrating from the right using a horizontal line from the end of step 7 as a baseline. DBC was calculated as the ratio of experimental heat over theoretical heat.\(^\text{36}\)

\[
DBC = \frac{\Delta H_{P,ex}}{\Delta H_{P,th}} \quad (2.6)
\]

\[
DBC_{pulse} = \frac{\Delta H_{P,Pulse}}{\Delta H_{P,th}} \times 100 \% = \frac{0.9640 \text{ J}}{2.82 \text{ J}} \times 100 \% = 34.18 \% \text{ acrylate conversion}
\]

Total DBC was calculated as the sum of integrated pulse and integrated long cure heat flow data.

\[
\Delta H_{P,Total} = \Delta H_{P,Pulse} + \int Q_{Long \, cure} \, dt = 0.9640 \text{ J} + 0.7996 \text{ J} = 1.7636 \text{ J}
\]

\[
DBC_{Total} = \frac{\Delta H_{P,Total}}{\Delta H_{P,th}} \times 100 \% = \frac{1.7636 \text{ J}}{2.82 \text{ J}} \times 100 \% = 62.54 \% \text{ acrylate conversion}
\]
2.3 Results

2.3.1 Effect of solid filler on deadzone thickness

The first study investigates the effect of increasing filler content on deadzone thickness. Silica was chosen as a preliminary model filler because of its common use in many polymer composite systems. Blends of 25 micron average diameter silica microspheres (SS-25) were tested at concentrations of 0, 10, 20, and 40 pph. Each filler concentration was measured at each light intensity a minimum of 3 times.

SEM micrograph in figure 2.5A shows that SS-25 is comprised of polydisperse silica microspheres with sizes ranging between 5 microns and 26 microns in diameter. In terms of deadzone thickness, each filled resin followed a power law fit, as displayed in figure 2.5B, which falls in line with resin deadzone results reported by Tumbleston et al.\textsuperscript{17} Interestingly,
deadzone thickness decreased as SS-25 loading increased, as plotted in figure 2.5C. At low light intensities the effect appears linear, however higher light intensities reveal exponential decay, suggesting a minimum non-zero deadzone thickness exists.

Next the effect of filler surface area was tested using silica microspheres with a 0.8 micron average diameter (SS-1) at concentrations of 0, 5, 10, 20, and 40 pph. The intermediate 5 pph tests were done to determine if changes could be detected at low concentration.

Figure 2.6: Effect of SS-1 on deadzone thickness. (A) SS-1 particles as received. (B) Deadzone thickness as a function of light intensity. (C) Deadzone thickness as a function of filler loading at varying light intensities.

Similar to SS-25, SEM micrograph in figure 2.6A shows polydisperse particles however the size is smaller ranging between 0.8 micron and 5 microns in diameter. Compared to SS-25 (figure 2.5C), deadzone thickness seem unchanged due to increased surface filler surface area from SS-1 (figure 2.6C). The trend still followed an exponential decay with filler loading, and there was a noticeable change in thickness at the intermediate 5 pph loading.
While microspheres are simple and abundant fillers, they are not commonly used for polymer reinforcement. High aspect ratio filler is preferred as it is better suited for polymer matrix reinforcement.\textsuperscript{40,41} Thus, blends of resin with high aspect ratio glass flake (GF) were tested at concentrations of 0, 10, 20, and 40 pph. The purpose of these tests was to observe the influence of aspect ratio on oxygen diffusion and thus deadzone thickness in comparison to spherical particles.

![Figure 2.7](image)

**Figure 2.7: effect of glass flake on deadzone thickness.** (A) GF particulates as received. (B) GF particulate as viewed close-up from the side. (C) Deadzone thickness as a function of light intensity. (D) Deadzone thickness as a function of filler loading at varying light intensities.

SEM micrographs in Figure 2.7A and 2.7B reveals that GF is a polydisperse yet high aspect ratio filler with areas ranging between 10 microns and 30 microns wide. Again, despite an
increase in average surface area, deadzone thickness of GF filled resins follow a similar trend to SS-25 or SS-1. Nevertheless, the addition of solid filler, whether it is low (spherical) or high (flake) aspect ratio, reduces deadzone thickness. Subsequent experimentation on light absorbance and reaction kinetics help explain these effects, but do not address physical differences such as viscosity or the acrylate content of the resin.

The addition of solid fillers, silica, glass, or other material, increased average viscosity and decreased functional group concentration, as detailed in table 2.3.

<table>
<thead>
<tr>
<th>Loading (pph)</th>
<th>Viscosity (cP)</th>
<th>Viscosity (cP)</th>
<th>Viscosity (cP)</th>
<th>Acrylate Molality (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1583</td>
<td>1560</td>
<td>1510</td>
<td>4.33</td>
</tr>
<tr>
<td>10</td>
<td>1747</td>
<td>1720</td>
<td>1740</td>
<td>3.94</td>
</tr>
<tr>
<td>20</td>
<td>2141</td>
<td>2136</td>
<td>2136</td>
<td>3.61</td>
</tr>
<tr>
<td>40</td>
<td>2860</td>
<td>2886</td>
<td>3490</td>
<td>3.09</td>
</tr>
</tbody>
</table>

It is possible that deadzone thickness decreases because of these changes in resin characteristics. As such, a series of viscous resins were formulated and tested alongside filled resin measurements to explain how changes in viscosity and acrylate concentration affect deadzone thickness. Table 2.4 shows viscosity and acrylate concentration data for VF resins. Deadzone experiments were performed for each formulation displayed in figure 2.8.
Table 2.3 Viscosity and acrylate concentration for VF resins

<table>
<thead>
<tr>
<th>Resin</th>
<th>Viscosity (cP)</th>
<th>Acrylate Molality (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VF-11</td>
<td>1500</td>
<td>4.33</td>
</tr>
<tr>
<td>VF-21</td>
<td>3200</td>
<td>3.65</td>
</tr>
<tr>
<td>VF-31</td>
<td>4800</td>
<td>3.31</td>
</tr>
<tr>
<td>VF-71</td>
<td>9800</td>
<td>2.79</td>
</tr>
</tbody>
</table>

Figure 2.8: Effect of viscosity on deadzone thickness. (A) Deadzone thickness as a function of light intensity. (B) Deadzone thickness as a function of resin viscosity at varying light intensities.

Deadzone thickness versus viscosity and acrylate concentration for filled resin are displayed figures 2.9 and 2.10 respectively. Because CN2920 has a viscosity of 50,000 cP at 25 °C, VF resin viscosity increased with increasing CN2920 content. Consequently, acrylate concentration also decreased with increasing CN2920 because of its higher molecular weight (~863 g/mol) than SR-833S (308 g/mol). Figure 2.8B shows that deadzone decreases with increasing viscosity at all light intensities. Furthermore, figure 2.9 shows that deadzone decreases in a similar trend due to increasing viscosity for all filled resins, albeit over a smaller viscosity range. This suggests that resin viscosity plays a role in deadzone thickness.
Figure 2.9: Effect of viscosity on deadzone thickness in filled resins. (A) SS-25; (B) SS-1; (C) GF. In general, deadzone thickness decreases with viscosity as an exponential decay.
Figure 2.10: Deadzone thickness as a function of acrylate concentration. (A) filled with SS-25; (B) filled with SS-1; (C) filled with GF; (D) VF resins. Acrylate concentration decreases with increasing filler content in filled, or with increasing viscosity in VF resins.

Finally, figure 2.10 shows deadzone thickness increased with increasing acrylate concentrations across all light intensities and for all resin formulations (filled and VF). This is counter intuitive, since an increase in acrylate concentration should increase radical formation, thus reducing oxygen concentrations at a faster rate. Therefore, these results suggest that both viscosity and the presence of filler in resin decrease oxygen permeation into resin.

2.3.2 Effect of solid filler on resin cure dosage and absorption coefficient

Unlike deadzone experiments, which require calibration, DC and $\alpha$ experimentation is done using only a UV transparent oxygen barrier placed on the oxygen permeable window of a CLIP imaging unit. This eliminates the deadzone by removing the sustained inhibition from oxygen diffusion into the resin from below. Thus, these experiments provide the curable
thickness of resin at varying light intensities or exposure times. VF11 resin blends that contain SS-25, SS-1, or GF were tested along with the remaining VF resins, each a minimum of two times. Figures 2.11 – 2.14 depicts the variation in dosage cure and absorption coefficients versus filler loading for fillers SS-25, SS-1, and GF respectively. Experimental results were very reproducible and thus error is omitted, as deviations were minimal.

**Figure 2.11: Effect of SS-25 on resin cure dosage and absorption coefficient.** (A) Dosage cure; (B) Absorption coefficient

**Figure 2.12: Effect of SS-1 on resin cure dosage and absorption coefficient.** (A) Dosage cure; (B) Absorption coefficient
Overall as depicted in figures 2.11A, 2.12A, and 2.13A, results indicate a decreased or constant $D_c$ with increasing filler loading, meaning filled resins require less light exposure to cure the same thickness compared to neat resins. Absorption coefficient remained constant for resins filled with SS-25, suggesting that the particles are not significantly obstructing light. Absorption coefficient increased in resin filled with SS-1, though this only at the highest loading after a slight decrease. Conversely, absorption decreased in resin filled with GF which explains decreased $D_c$ since light can penetrate deeper into resin. This is possibly due to the glass particles reflecting light during illumination, increasing overall cure depths. Meanwhile,
VF resin $D_c$ increased as shown in figure 2.14A with increasing viscosity, which was opposite of that in filled resins. This trend also implies that $D_c$ decreases with increasing acrylate concentration, which again is opposite that of filled resins. Furthermore, absorption remained relatively constant, suggesting the increased cure dosage is a primarily due to decreased acrylate concentration in VF resins, requiring more light exposure to cure the same thickness.
These results show that while decreasing acrylate concentration plays a role in decreased deadzone formation of filled resins, it does not have the same effect in a resins ability to cure a certain thickness.

2.3.3 Effect of solid filler on resin reaction kinetics

The kinetics of the photoactive resins relates to the phenomena observed in the previous two sections. Two stage (pulse, then long cure) p-DSC experiments were conducted for all resin blends, and an example result is shown in figure 2.15. This experiment aimed to compare the double bond (acrylate) conversions of the unfilled and filled resins.

![Figure 2.15: Example heat flow data from p-DSC experiments.](image)

Each resin (filled and unfilled) was tested individually a minimum of 3 times for each loading. Resins were initially compared based on the normalized heat flow peak heights of the first pulse at each filler loading, as shown in figures 2.16 – 2.19 for resin blends that contain SS-25, SS-1, and GF fillers respectively. This was designed to compare changes in heat
generation between filled and unfilled resins and served as an initial comparison between loadings. These changes were further evaluated by calculating double bond conversion (DBC) as described in the methods section of this chapter. First pulse DBC was calculated separately because it is representative of light exposure during CLIP as well as the previously described experiments. The long cure DBC was treated as a continuation of the first pulse, thus representing the combined conversion from both exposures. It should be noted that peak curves seen in the figures below are representatives of the averages calculated for each resin blend.

First pulse normalized heat flow peak heights for SS resins (figures 2.16A and 2.17A) remained relatively constant, only despite increasing filler loading. This agrees with Dc data in that it shows that these filled resins maintain their photoreactivity, requiring no change in light exposure to cure the same thickness. Figures 2.16C and 2.16C show that these resins maintain constant or slight increased DBC, further confirming that filler within these resins has not hindered reaction kinetics. Pulse peak heights for GF filled resins in figure 2.18A decreased with increasing fillers, suggesting that the addition of GF reduces resin reactivity. However, DBC in GF resins maintained a constant value as seen in figure 2.18C.
Figure 2.16: P-DSC heat flow and double bond conversion of resin filled with SS-25. (A) Light pulse heat flow data. (B) Long exposure heat flow data. (C) Double bond conversion for pulse and aggregate total.
Figure 2.17: P-DSC heat flow and double bond conversion of resin filled with SS-1. (A) Light pulse heat flow data. (B) Long exposure heat flow data. (C) Double bond conversion for pulse and aggregate total.
Figure 2.18: P-DSC heat flow and double bond conversion of resin filled with GF. (A) Light pulse heat flow data. (B) Long exposure heat flow data. (C) Double bond conversion for pulse and aggregate total.
Figure 2.19: P-DSC heat flow and double bond conversion of VF resins. (A) Light pulse heat flow data. (B) Long exposure heat flow data. (C) Double bond conversion for pulse and aggregate total.

Meanwhile, pulse peaks for VF resins decreased with increasing viscosity as seen in figure 2.19A. DBC in figure 2.19C show constant or increased value, suggesting that decreased heat flow is primarily due to decreased acrylate concentration, which produces less heat upon reaction. These results, combined with Dc and α data in the previous section, provide more evidence that filler within these resins affect deadzone formation but not resin kinetics.
2.4 Discussion

The work presented here is the first effort in describing changes to fundamental CLIP parameters, particularly the liquid deadzone, due to the addition of filler. Using previously established thickness measuring techniques and well-established thermoanalytical techniques, CLIP deadzone formation and curing behavior have been explored in ways not yet reported. It is intriguing to observe decreased deadzone thickness due to filler loading within resin. Regardless of the filler type, as solid content increased, deadzone thickness decreased at all light intensities. Although the effect appears more pronounced at low light intensities, this is only in terms of magnitude. In general, the percent change increased as light intensity increased. For instance, the percent difference between neat resin and 40 pph GF increased linearly from 32.7 % at 1 mW/cm$^2$ to 45.2 % at 5 mW/cm$^2$. The same trend applies at other loadings for glass and silica filler. Overall, the addition of filler decreased deadzone thickness between 5 % and 45 % relative to neat VF11 resin based on filler loading and type.

Widely-studied filler samples were chosen for these studies for their variation in size and surface area. Both the size of filler and its aspect ratio play a role in gas diffusion into resin and results were discussed in this chapter’s corroborate previous studies.$^{28,42}$ SS-25 has the least surface ($\sim 1250 \text{ cm}^2/\text{g}$) area as it has the largest particles and is spherical in shape, whereas SS-1 ($\sim 7500 \text{ cm}^2/\text{g}$) having a larger surface area due to its smaller size. The thickness of GF is uniform at approximately 2 microns, but the length and width are highly variable, contributing to its high aspect ratio and thus high surface area ($\sim 5700 \text{ cm}^2/\text{g}$) between SS-25 and SS-1. In figure 2.20, blends with the same loading across the three fillers are compared.
Although nominally deadzone appears to decrease with increasing surface area, these results are not statistically significant, and not consistent across all loadings. The lack of a statistically significant trend with increased surface area is likely due to the particles not having large enough aspect ratio (~20 for GF; 1 for SS) and the inability to control particle orientation. Indeed, barrier property enhancement using filler typically involves the use of nanoclays whose aspect ratios are an order of magnitude larger.\textsuperscript{10,18,22,25,43} Nevertheless, decreased deadzone thickness from the addition of filler is likely due to tortuosity within resin, as there are similar studies of UV curable resins used in dentistry that incorporate particles in the same size range to reduce oxygen inhibition.\textsuperscript{29,30} This tortuosity effect was further complemented when considering the effect of increased viscosity and decreased acrylate concentration. Deadzone thickness between VF-11 and higher viscosity resins decreased between 10 % and 50 %. The deadzone results from these experiments suggest that increased viscosity plays a role in oxygen diffusion into resin. However, the effect of increased viscosity in filled resins on deadzone thickness occurred in a narrower range compared to VF resins. Therefore, a closer look at filled resin curing behavior was needed to further explain deadzone thickness due to increased tortuosity.
Dc and p-DSC experiments revealed that resins, in the absence of oxygen inhibition, do not exhibit decreased curing kinetics. This was evidenced by decreased or constant Dc suggesting that resins (filled or unfilled) cure to the same or greater depths at the same light exposure, and by DBC remaining constant relative to neat resin for a single light pulse. On the other hand, VF resins exhibited increased Dc with increasing viscosity thus requiring more light exposure to cure the same thickness, likely due to decreased acrylate concentration. If acrylate concentration or viscosity were the primary reasons for decreased deadzone thickness in filled resins, then their curing behavior should have fallen in line with VF resin curing behavior. The discrepancy between Dc values between the two types of resin (filled and VF), plus that their pulse DBC values remain constant despite decreasing acrylate content, further confirm that filler increases tortuosity in filled resins thus decreasing deadzone thickness.

2.5 Conclusions

This chapter has shown that the CLIP deadzone, though elegantly fundamental, becomes complex with otherwise subtle changes in resin formulation. It is difficult to isolate the root cause of deadzone decreases without affecting other physical and chemical properties in the process. Nevertheless, the experiments detailed here have shown that since curing behavior remains relatively constant, filled resins create tortuous pathways for gas diffusion leading to decreased deadzone thickness. Despite deadzone complexity, simple physical tests and well-established analytical techniques have allowed for a better understanding of the deadzone formation in filled systems. The techniques explored here can be easily translated to any type of filler, resin, or combination thereof, streamlining composite material development and characterization for the CLIP process in the future.
2.6 Acknowledgements

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2.7 References


CHAPTER 3: Filler Distribution and Flow Dynamics

3 Introduction

Particle filler distribution within a polymer matrix, specifically particulates, is an important factor in polymer composite fabrication. Non-uniform filler distribution within a part can result in fabrication failure and/or decreased physical properties.\(^1\)–\(^3\) As such, particle and fiber distribution in 3D printed parts has been studied whenever filler has been added to raw materials. Given the infancy of the process, fundamental studies regarding the distribution efficiency of filler particles in a part fabricated via continuous liquid interface production (CLIP) part have not been reported. The purpose of this chapter will be to study filler distribution in parts fabricated via CLIP using filled resin and use observation of flow through physical models to describe filling behavior during fabrication.

3.1 Background

3.1.1 Filler distribution in 3D printed parts

The process of incorporating filler into 3D printed parts begins with blending the filler into the raw material (resin) used for printing. For extrusion and sintering methods, which utilize thermoplastics, particle or fibrous fillers are typically blended homogeneously into polymer prior to fabrication of the 3D printed part.\(^4\)–\(^7\) The incorporation of filler into the relatively high molecular weight polymer must be accomplished using an extruder or other high energy mixer which then must produce the filled polymer in the form needed for 3D printing. The particle orientation in the printed part can be further manipulated using fused deposition modeling (FDM) as extrusion through the heating nozzle imparts orientation inherently in the direction of deposition and can be used to intentionally develop beneficial anisotropic properties.\(^8\) However, Stereolithography (SLA) typically use liquid resins and thus filler is often more easily blended with the monomer/oligomer prior to photocuring.\(^9,10\) The addition of filler into liquid resins introduces new processing parameter considerations such as the dispersion stability, viscosity, reactivity, and stability under flow conditions during the fabrication process.
3.1.2 Rheology of filled fluids

For CLIP especially, a primary consideration is the effect of filler on the viscosity of a resin. As a rule of thumb, CLIP resins are typically developed with viscosities below 10,000 cP, since resin renewal time therefore print failure increases with viscosity. It is well-known that addition of particles into a liquid can increase its viscosity, as well as introduce non-Newtonian behavior such as shear thinning. Furthermore, as particle concentrations increase, thereby increasing the chance of particle-particle interaction, some suspensions can also develop thixotropic behavior.

Thixotropy is defined as the reversible and time-dependent reduction in viscosity when a liquid experiences stress. As such, thixotropic fluids typically maintain flow under continued stress, but immediately begin to form a pseudo gel at rest. The dynamics of using a thixotropic resin in the CLIP process will be important, as filled resins are likely to exhibit this behavior. The CLIP process does not possess a physical method of agitation, but instead relies on suction force from the upward motion of a part away from the window to initiate resin flow. One method of estimating the suction force exerted on the resin is through using the Stefan adhesion equation, which estimates the force required to separate two plates with a certain gap distance submerged in a liquid media, as seen in equation 3.1 below.

\[ F = \mu \frac{3\pi r^4}{h^3} \frac{dh}{dt} \]  

(3.1)

\(\mu\) is the viscosity of the fluid, \(r\) is the radius of the plane of two equal and parallel plates, \(h\) is the height of the gap between the two plates, and \(dh/dt\) is the rate of separation. Given the relatively small gap between a growing part and the window in the CLIP process, between 10 and 150 microns depending on deadzone thickness and part slice thickness, these forces can become quite large. It should be noted that this force deals with plate separation and therefore can only serve as an approximation of the force exerted on resin. As such, it is unlikely that the full body of resin experiences these forces during part movement upward, but rather in a small radius from the outer edges of a growing parts cross-section. The Stefan equation will be useful when describing the effect of thixotropy on printability of filled resins with CLIP because it provides an estimation of the effective agitation due to resin renewal.
3.1.3 Filled fluid flow in microchannels

The small size of the CLIP deadzone (~10 - 50 microns) plus part slice thickness sets the gap between a growing part and the window, which is comparable in size to microfluidics channel dimensions.\textsuperscript{17,18} Therefore, a microchannel could be used simulate the flow of a filled resin underneath a growing part during CLIP. In the literature, there are many studies on microfluidics channel flow using particles, with emphasis on flow profile, clogging of particles, and interaction of particles with channel features and each other.\textsuperscript{17,19–22} Many of the same methods can be used to explain phenomenon within CLIP with filled resins. The following are examples and explanations pertaining to the studies presented in this chapter.

The flow profile through a microchannel can be characterized by the Reynold’s number (Equation 3.2),

\[
Re = \frac{\rho v h}{\mu} \quad (3.2)
\]

where \( h \) is the height or diameter of the channel, \( v \) is the average velocity, \( \rho \) is the fluid density, and \( \mu \) the fluid viscosity. The small dimensions of a microchannel keep \( Re \) within laminar values, often below 1, which is well below 2000, the typical value for transition into turbulence. Low \( Re \) values are even more likely with CLIP resins, with viscosities that range between 500 cP and 6,000 cP. As such, it will be important to understand how laminar profiles affect filled resin flow in CLIP-like conditions. One difference between microchannel conditions in CLIP and a conventional microchannel is that aspect ratios, or channel height to width ratio, aspect ratio in CLIP are much smaller than traditional microfluidics. This is because resin flowing in CLIP interacts with the growing part above and the window below and in most cases without the constriction of sidewalls like in a microchannel. Few studies have explored complex microfluidic shapes such as rectangular systems with widths greater than 1 mm, however those report unique cross-sectional flow patterns.\textsuperscript{17}

Another area of suspension flow behavior in microfluidic devices has been in studies that analyze clogging behavior.\textsuperscript{22–24} The concept of clogging during the flow of particle filled liquids has been studied in many disciplines, and not surprisingly plays a factor in microfluidic design and utilization. While there may be some situations where clogging is desired, in CLIP,
the particles must remain consistently suspended within the liquid during the process to achieve a uniform distribution in the formed solid parts.\textsuperscript{9,10} Clogging occurs through many mechanisms including sieving where particles create blockage due to size exclusion, bridging of a constriction with a narrow band of particles that often results in intermittent flow, and aggregation of particles due to deposition of one or multiple particles at a constriction.\textsuperscript{23} In general clogging occurs when flow through a large volume suddenly constricts into a volume at least an order of magnitude smaller in size. This abrupt change in volume forces suspended particles closer together, which in turn can lead to the development of a clog.\textsuperscript{25,26} In the CLIP process, resin flows from a liquid pool, typically several millimeters in depth (large volume), to a gap whose height ranges between 10 and 200 microns, therefore the clogging potential is very high. Because of this parallel to constrictions in microfluidics, characterization of filler location in parts fabricated via CLIP will be important in observing the presence, or absence, of clogging at the pool-gap interface.

3.2 Materials and methods

3.2.1 Materials

Isopropyl alcohol (IPA; histological grade, 99 %) was used as a cleaning solvent for all samples and was obtained from Fisher Scientific. PR25 CMYK (urethane acrylate with colored pigment), PR25 white (urethane acrylate with white pigment), and RPU 61 (two-part dual-cure urethane methacrylate) resins were provided by Carbon. CN2920 and SR833-S were graciously provided as samples by Sartomer. Rectangular glass microtubes of varying heights and widths were purchased from Vitrocom. Silica microspheres of four different average diameters 0.8 microns (SS-1), 5 microns (SS-5) 10 microns (SS-10) and 25 microns (SS-25) microns were purchased from US-nano. AR711 fumed silica was acquired as a sample from Evonik. Carbon mesoporous (>99.95 %) was purchased from Sigma-Aldrich. Fluoro-max green dry fluorescent particles with average particle size 6 microns were purchased from Thermo-Fisher scientific. All resins were blended with fillers using a THINKY ARE-310 centrifugal mixer. Carbon’s M1 CLIP unit was used to fabricate parts for testing.
3.2.2 Resin formulation

Filled resins for thermogravimetric analysis were formulated using PR25 white and the desired silica microparticle. Resin and filler were placed in a cup and mixed on a THINKY mixer for 3 minutes wherein samples are centrifuged at 2000 rpm while the cup simultaneously rotates in the opposite direction at a rate of 100 rpm. This was then followed by 7 minutes on the defoam setting (2200 rpm revolution, 60 rpm rotation) to remove air bubbles.

The bulk resin used in rheological and microfluidic experimentation was formulation without photoinitiator or pigment. The formulation blended CN2920 and SR833-S in a 1:1 ratio by weight. The two components were mixed in a THINKY mixer for 90 seconds using the default setting. For microfluidic observations, resin was doped with approximately 0.025 parts per hundred (pph) fluorescent nanoparticles to aid in tracking resin flow behavior.

3.2.3 Resin rheology

Resin viscosity was measured on a TA Instruments Discovery HR-3 hybrid rheometer. Shear viscosity measurements were done using a 40 mm diameter parallel plate geometry and a gap height of 500 microns using a Peltier plate accessory. Flow sweep experiments were done at shear rates between 1 s$^{-1}$ and 1000 s$^{-1}$ with 4 points per decade under isothermal conditions at 25 ºC. Each shear rate was equilibrated for 3 minutes, followed by 2 minutes of data collection before averaging.

3.2.4 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was done using a Q5000 IR from TA instruments. Sample preparation began by fabricating cylinders with a diameter of 7 mm and height of 100 mm using PR25 filled with 5 pph or 20 pph SS-1 or SS-25, printed on the M1 printer at standard slicing (100 microns per slice) and default print profile. After fabrication, the parts were thoroughly washed in an IPA bath for 3 minutes, at which point they were dried with compressed air and UV post cured for 60 seconds. Next a Dremel rotary tool equipped with a stainless-steel cutting blade was used to slice 2 mm sections at locations 5 mm and 95 mm from the beginning of the print (labeled L and H respectively) as depicted in figure 3.1. The sections were then marked down the middle and a Dremel sanding tool was used to file down
the section until a thin strip remained. Finally, the strips were cut into 5 pieces such that filler loading could be measured from three sections: outer, middle, and inner (labeled O, M, and I respectively). The same procedure was done for square solids, with a length, width, and height of 7 mm by 7 mm by 100 mm respectively. Sections were labeled based on shape of print (C for circle and Q for square), z-axis height relative to build platform, and cross-section location. For example, an inner sample from the low position (5 mm) of a cylinder print would be labeled CLI.

![Figure 3.1: Schematic of sample preparation for filler distribution experiments. Cylinders and square columns were printed and cut to assess distribution at the beginning and end of prints, as well as across the cross-section of fabricated parts.](image)

Individual samples were then placed on platinum pans and heated from 25 °C to 650 °C at a rate of 50 °C/min and then held there for 5 minutes in air atmosphere. This procedure was replicated for a minimum of 4 times for all filler sizes, loadings, cross-section and height locations, and part shapes. Samples were taken of each filled resin blend prior to printing and tested by the same procedure to serve as reference loading values.

The effect of print profile and slice thickness on ultimate filler location and distribution was also tested. Print profile is defined as the method with which the build platform moves per projected slice during the printing process, as detailed in figure 3.2.
The default slice thickness and print profile for the samples listed previously were 100 microns and step profile. Slice thickness can change to 50 or 25 microns (fine and superfine respectively), the latter of which changes the print profile to oscillatory. In either case (fine or superfine) print times typically increase because the build stage moves up slower compared to standard slice thickness. This is because the force to move the build stage up from the small gap is much larger than the standard gap, based on Stefan’s adhesion (equation 3.1), which can cause cavitation at the center of the cross-section if the part were to be moved at the same velocity as default. Furthermore, an oscillatory print profile ensures that resin flows to the center of cross-sections because the increased height moves more resin toward the center. Cylinders with diameter 7 mm and height 20 mm were printed and sectioned in the same way as described previously to investigate the effect of decreased slice thickness. However, the height location was based on a 2 mm section taken at 5 mm above the beginning of the print and 2 mm from the end. Part sections were labeled in the same fashion and included either an F or SF for fine and superfine slicing respectively. A minimum of two samples for each section were then tested using the same TGA procedure described previously.
3.2.5  *Low aspect ratio glass microchannel assembly*

Microchannel resin flow observations were done on a Zeiss 800 upright confocal microscope, equipped with an AxioScan camera for video recording. Table 3.1 details the glass microchannel dimensions as received.

<table>
<thead>
<tr>
<th>Channel ID</th>
<th>Inner Width (µm)</th>
<th>Inner height (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GMC-200</td>
<td>2000</td>
<td>200</td>
</tr>
<tr>
<td>GMC-100</td>
<td>2000</td>
<td>100</td>
</tr>
<tr>
<td>GMC-50</td>
<td>1000</td>
<td>50</td>
</tr>
</tbody>
</table>

Tubing was fit to each channel using custom adapters designed on Solidworks software and printed on the M1 using PR25 CMYK, as depicted in figure 3.3. The channels and adapters were then assembled and sealed using silicone adhesive. Next this assembly were fitted into custom frames that were designed and printed to fit within the microscope sample holder. A similar adapter was also designed so that allows resin flow could be observed from the side of a channel. Afterwards, resin was pumped through the channels at a volumetric flow rates such that the average flow velocity was approximately 1,000 microns per second using a NE-200 Just Infusion syringe pump from New Era Pump Systems, Inc. Images and videos were analyzed using Zeiss 2011 software.
3.2.6 **Stepped microchannel fabrication**

Unique microchannels were designed and fabricated using CLIP to simulate and observe filled resin flow at a constriction point similar to flow from a resin pool underneath a growing part in CLIP, as seen in figure 3.4.
The channel was designed using Solidworks software and printed on the M1 printer using dual-cure rigid polyurethane RPU61 resin. Next a glass slide was placed and clamped on the printed part, thus forming the channel. This assembly was then placed in an oven set to 120 ºC for four hours, which exploited the thermal post-cure process to permanently seal the glass and channel together. Custom adapters were then printed using PR25 CMYK and fitted to the assembly to allow tubing connection to the stepped microchannel.
3.3 Results

3.3.1 Effect of filler on resin viscosity and printability

The goal of these studies was to observe the effect that filler particle size, shape, and loading has on resin viscosity. Spherical silica fillers in a range of sizes were chosen first to evaluate the effect of filler particle size and loading on viscosity, as plotted in figure 3.5.

Regardless of particle size, resin viscosity increased from ~1,500 cP to ~3,000 cP with increasing loading level. Resins also maintained Newtonian flow behavior, as evidenced by zero slope, even at high loadings. Furthermore, these viscosities are well within the suggested range for CLIP fabrication. The effect of filler size and loading was further explored using two
nanoparticle fillers: carbon black (CB) with nominal particle size ≤ 500 nm and fumed silica with particle size ≤ 50 nm (FS), figure 3.6 shows rheological profiles of filled resins.

Compared to resins filled with SS, the addition of nanofillers increased the resin viscosity dramatically, even at low loadings. In figure 3.6B carbon black loadings as low as 1 pph resulted in resin that exhibited shear thinning behavior. Physically these resins appeared to flow upon immediate removal from the mixer, however after several minutes at rest the flow was no longer possible without being remixed due to thixotropy.

The printability of resins exhibiting shear thinning or thixotropic behavior was tested using simple 100 mm tall cylinders, printing results can be seen in figure 3.7.

![Figure 3.6: Effect of nanofillers at various loadings on PR25 viscosity. (A) Fumed Silica; (B) Carbon black](image)

![Figure 3.7: Printing with PR25 CMYK filled with 5 pph fumed silica. (A) Resin pool post-print showing flow pattern due to upward movement of build platform. Holes without resin form due to pseudo-gel formation in resin. (B) Parts fabricated during print. Only 8 mm of part successfully printed due to a lack of resin renewal.](image)
Figure 3.7A shows circular holes without resin at the location where each part was being fabricated. The resin settled during fabrication thus forming a pseudo-gel and maintained a cross pattern indicative of flow due to the upward motion of the build platform during fabrication. As a result, part formation stopped after approximately 8 mm of fabrication, as seen in figure 3.7B. Conversely, resins detailed in figure 3.5 printed without issue. Because of this discrepancy, resins exhibiting thixotropic behavior were excluded from subsequent studies involving filler location and flow visualization.

3.3.2 Filler distribution in CLIP printed parts

Filled resins were successfully printed via CLIP using identical print parameters to the unfilled resin. Rectangular solid columns were fabricated with VF11 with SS-25 at various loadings. Filler location and distribution within these samples were visible to naked eye, as shown in figure 3.8.

![Figure 3.8: Cross-sectional images of parts printed using PR25 filled with 10 pph SS-25. (A) Rectangular solid cross-section with a clear region where particle loading is diminished. (B) Square solid cross-section with a region of lower loading, allowing light to shine through.](image)

Regardless of the shape of the solid being printed, a distinct empty region exists at the center of each cross-section. These visual results suggested that particle loading was not uniform within fabricated parts.

Filler loading by position was quantified using TGA. The printed solids were portioned by location and heated to temperatures above the polymer’s degradation point allowing organic polymer to burn and the residual silica to be measured yielding the weight percent silica in the...
sample. Two fillers were chosen for this study to observe the effect of particle size on loading and distribution within the printed parts. The silica particles SS-1 and SS-25 were used, representing small and large particles respectively. Each filler was blended with resin at concentrations of 5 pph and 20 pph to observe the effect of particle loading. Filler incorporation as a function of location within parts fabricated using SS-1 are plotted in figure 3.9.

![Figure 3.9: Filler distribution for parts printed with SS-25 filled resins.](image)

The data in figure 3.9 agrees with the visual images of figure 3.8, revealing decreased filler concentration at the center of a cross-section. Interestingly, the concentration tends to be greater for outer cross-section locations than the starting resin loading. This suggests that particles are also clogging or clinging to the surface of printed parts. Additionally, part height location (high or low) did not appear to affect filler distribution. Next, filler distribution was
observed in parts filled with SS-1, which are an order of magnitude smaller than SS-25, as shown in figure 3.10.

Figure 3.10: Filler distribution for parts printed with SS-1 filled resins. (A) Cylinder prints with 5 pph filler; (B) Square solid prints with 5 pph filler; (C) Cylinder prints with 20 pph filler; (D) Square prints with 20 pph filler. Red line represents resin filler loading prior to fabrication as measured via TGA.

With smaller particles, filler concentration remained constant, even relative to the concentration in resin, across all sections, both high and low, and regardless of loading. This is contrary to that seen in figure 3.8, but shows that even particle loading in parts is achievable with particles sizes smaller than SS-25. It should be noted that the default print style and slice thickness using these resins was step and 100 microns respectively. It is possible that filler loading can be improved in for resins filled with SS-25 by changing print profile. Therefore, a series of subsequent samples were printed to observe small slice thickness: fine (50 microns) and superfine (25 microns), the latter of which forces the fabrication into an oscillatory print
profile. The effect of fine and superfine slicing can be seen in figures 3.11 and 3.12 for parts filled with SS-1.

Figure 3.11: Filler distribution for parts printed with SS-1 and fine slicing (A) Parts filled with 5 pph SS-1. (B) Parts fabricated with 20 pph SS-1. Red line represents resin filler loading prior to fabrication as measured via TGA.

Figure 3.12: Filler distribution for parts printed with SS-1 and superfine slicing. (A) Parts filled with 5 pph SS-1. (B) Parts filled with 20 pph SS-1. Red line represents resin filler loading prior to fabrication as measured via TGA.

In figure 3.11 filler loading was lower than the bulk resin across the entire cross-section and at both high and low locations and with both filler concentrations. It is possible that this is due to decreased gap height compared to default, which in turn caused improper flow of particles underneath the growing part. Furthermore, resin flow underneath the part decreased due to the
reduced upward velocity of the build stage, which may have resulted in further decrease in particle flow within resin. Nevertheless, it is peculiar that this effect is seen on the outer edges of the cross-section since this effect was not observed at standard slicing. This implies filler remained in the resin pool during fabrication. Figure 3.12A shows that this effect did not appear for parts filled with 5 pph SS-1 and using superfine slicing. This suggests that the subsequent change to an oscillatory print profile improved particle flow and mixing during fabrication. On the other hand, figure 3.12B shows that at a loading of 20 pph SS-1, the filler distribution was once again lower across the entire cross-section. As such, there appears to be a connection between high filler loading within resin and distribution in a final part regardless of print profile when slice thickness is less than default. This connection was further explored by fabricating the same parts under the identical conditions using resins filled with 5 pph SS-25, as shown in figure 3.13.

Figure 3.13: Filler distribution for parts printed with SS-25 and fine/superfine slicing. (A) Fine slicing prints with 5 pph filler; (B) Superfine slicing prints with 5 pph filler. Red line represents resin filler loading prior to fabrication as measured via TGA.

Figure 3.13A shows that filler loading was lower than the bulk resin across the whole cross-section, similar to parts filled with 5 pph SS-1. Moreover, figure 3.13B shows that, within some error, superfine slicing did not improve filler distribution, but remained lower than the bulk resin. This is contrary to that seen in parts fabricated with 5 pph SS-1 and superfine slicing, but similar to that seen in 20 pph SS-1 loaded parts. This further suggests the connection between filler loading and distribution has more to do with particle interaction with
itself and its surroundings. It is possible that this behavior is due to increased particle interaction, which could in turn form aggregates that move slower during resin flow both outside and underneath the growing part. Therefore, the outer edges of parts exhibit loadings lower than the bulk resin, since larger aggregates may not be able to fit within the smaller gap heights.

Another intriguing phenomenon was observed between low and high locations within parts, regardless of filler concentration or size. With the exception of 5 pph SS-1 using fine slicing, high location (late in print) samples exhibited increased filler loading compared to low location (early in print). This is possibly due to increased fabrication times due to decreased slice thickness, as described in the methods section. Indeed, fabrication time at default slicing thickness for these parts would be 35 minutes, whereas fine and superfine sliced parts were fabricated in 70 minutes and 120 minutes respectively. In practice these resins were found to exhibit particle sedimentation after one hour of rest. Therefore, it is likely that filler within these resins, which experienced no external agitation during fabrication, began to settle over the course of the much longer prints leading to slightly increased loading at the high location.

3.3.3 Visualizing resin flow in constricted channels

TGA data revealed that particle loading is not always uniform in solid parts fabricated via CLIP, especially with larger particles. As such, an effort was made to characterize the particle flow with filled resins under CLIP-like conditions to help explain the distribution of filler observed in the dynamic process of CLIP. This was achieved by fabricating microchannels utilizing commercially available rectangular glass microtubes where the widths within the channel were at least an order of magnitude large than the height. Unfilled resin was loaded with a dilute amount (0.025 pph) of fluorescent particles and pumped via syringe pump at a flow rate of 100 microliters per min. Example images of videos taken via confocal fluorescent microscopy are shown in figure 3.14.
As predicted, resin exhibits a laminar flow profile at these conditions wherein particles located near the top move slower than fast moving particles in the center. This effect is further exemplified when resin flow is viewed from the side, as detailed in figure 3.15. It should be noted that side view channels are subject to side wall interactions, but served to confirm the flow profile.
Figure 3.15: Snapshots of resin flow (GMC-100, side orientation). A laminar flow profile can be seen when tracking particles from the same starting point.

In the figures 3.14 and 3.15, particles that appeared as streaks were considered to be located within the middle portion of the channel, while slower moving particles that appear as spheres are located near the top of the channel. The average velocity of the slow-moving particles was calculated by measuring the distance a particle travels over a given time. Fast-particle average velocity was calculated by measuring the length of a streak divided by the time scale of fluorescent light exposure, which varied between observations. The same observations were made for each microchannel height, adjusting volumetric flow rates to maintain an average velocity of around 1,000 microns per second. Velocity data was evaluated as the ratio of middle channel velocity over the top channel velocity, as tabulated in table 3.2. This observation enables, to some extent quantification of the relative change in flow characteristics with changing channel height. Thus, a higher ratio would represent channels where discrepancy between top and middle channel velocity is more visually apparent, while lower ratios would be more difficult to tell a difference.
Table 3.2: Velocity ratios (middle/top) for glass microchannels (N≥30 particles tracked)

<table>
<thead>
<tr>
<th>Channel</th>
<th>Velocity Ratio</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>GMC-200</td>
<td>6.5</td>
<td>1.8</td>
</tr>
<tr>
<td>GMC-100</td>
<td>6.9</td>
<td>2.0</td>
</tr>
<tr>
<td>GMC-50</td>
<td>1.5</td>
<td>0.3</td>
</tr>
</tbody>
</table>

It should be noted that these values presented above are for non-filled resins, however the effect is the same regardless. As such, at increasing gap height, the difference in average velocities between the center and edge became more apparent. It is plausible that particles located near the top of a channel, which in this case represent particles near a growing part in CLIP, could move slower and thus contribute to the uneven cross-sectional loading. However, the snapshots in figure 3.14 reveal that fast particles outnumber slow particles 10:1. This means that, in general, the fast-moving particles are more abundant than slow moving particles located only in the top and bottom of the channel. Furthermore, slow moving particles would only account for uneven loading at points where two layers are joined, a concept which is detailed in figure 3.16 below.

![Figure 3.16: Schematic of uneven loading due to laminar flow profile.](image)

Relative to slice thickness, the height of the circled gap in figure 3.16C would be small and likely only on the order of the particle size. Therefore, it seems unlikely that laminar resin flow
behavior underneath growing parts is the primary cause for uneven filler loading in part cross-sections.

3.3.4 Constricted flow of filled resins.

Constricted flow at the interface of bulk resin and the growing part was successfully observed using a custom-made stepped microfluidic channel. The channel simulated resin flow from a large volume into a small volume like that experienced during CLIP. A resin blended with 20 pph SS-1 was syringe pumped through the channel at a volumetric flow rate of 100 microliters per min, snapshots of which can be seen in figure 3.17 below.

![Figure 3.17: Filled resin (SS-1) flow a stepped channel.](image)

After 20 minutes of continuous flow resin is diverted around a small unseen blockage.

After 20 minutes of continuous resin flow, resin began to flow around a concealed obstruction, as evidenced by particle streak angle changes. Nevertheless, resin flow was maintained throughout observation, which agrees with TGA data that revealed homogeneous loading using small particle size silica filler.

A resin blended with 20 pph SS-25 was pumped through the two-part channel at a volumetric flow rate of 100 microliters per minute. Snapshots of a video can be seen in figure 3.18 below.
Within 30 seconds of resin flow a visible clog formed at the interface between the two volumes. The clog diameter continued to grow along with several other smaller clogs, all of which diverted resin flow in non-linear pathways. After two minutes of clog development, pressure build-up resulted in microchannel failure. The same phenomenon occurred with a 5 pph SS-25 blend yielding similar results. Given that clogs formed nearly instantaneously in flowing resin, it is reasoned that a similar phenomenon occurs during CLIP part fabrication.
3.4 Discussion

The work presented in this chapter evaluated the effect of adding filler to resin on viscosity and flow behavior and its relation to filler distribution in parts fabricated via CLIP. Fillers with particle sizes larger than a micron had a relatively small influence on resin viscosity, maintaining Newtonian behavior and printability. Shear thinning or thixotropic resins, such as resins that contain nanoparticles, could not be used for printing with CLIP. This is likely due to the yield stress of the resin exceeding the suction force exerted on the resin as the build platform moves upward during fabrication. Thus, part fabrication with thixotropic resins can only occur during the beginning of a print due to the large cross-sectional area of the build platform. The force exerted by the upward movement of the build platform is four orders of magnitude greater than that by the cylinder. Furthermore, using the shear thinning resin formulation presented in figure 3.7 as a model, the force exerted by the build platform decreases rapidly from $10^6$ N to $10^2$ N after just 1 mm of fabrication. After the build platform no longer exerts appreciable force to initiate resin flow, part fabrication occurs only for as long as the time limit set by the transient transition of a flowing thixotropic liquid into a pseudo gel. Therefore, in order for a thixotropic resin to flow during CLIP the force exerted by the part cross-sectional area moving upward must be greater than the yield stress of the fluid, or the resin must be continuously agitated by an outside force.

Filler distribution within cross-sections of parts fabricated via CLIP was found to be lower in the center when using particles SS-25, the largest particles used in this study. Conversely, small particles, like SS-1, uniformly load across a part cross-section. It is possible that the laminar profile of flowing resin underneath a growing part could cause particles located close to the part to move slowly causing incomplete filling. However, if this were the case, then particle loading would be varied regardless of filler size. Instead, filled resin flow through a constriction observation revealed near instant formation of clogs as larger particles reach the gap underneath a growing part. It is important to note however, that filler loading never reaches zero because gap height is kept effectively constant as a part moves upward during fabrication. Therefore, it would seem as a though a clog could not maintain itself during fabrication since channel height is constantly being reset. However, studies in microfluidic clogging due to
aggregation have shown that clogs begin with the deposition of a single particle on a microchannel surface.\textsuperscript{23,25–27} It is reasoned that particles near the window also move slower since laminar flow would be symmetrical from the center of channels, even in CLIP. Therefore, slower moving filler particles within the deadzone have a higher chance of deposition. And since the deadzone is presumed to be continuously present, this deposition could be a starting point for aggregate clog formation, thus leading to uneven loading, as detailed in figure 3.19.

![Figure 3.19: Schematic of filled resin clog formation during CLIP.](image)

(A) Single particles deposit onto window surface. (B) Aggregation forms as resin continues to flow underneath a growing part. (C) Over time the aggregation grows to form a clog, reducing the concentration of particles flowing underneath a growing part.

As a result of this clog formation, the effective entrance height underneath a growing part would decrease, leading to fewer particles reaching the center before the resin solidifies. This process never forms a complete clog since the upward movement of part fabrication would break newly formed, and often fragile, closed clogs at the entrance.

Particle deposition on the window and the growing of aggregates can be explained when the process is compared to gravitational field flow fractionation (Gr-FFF), as seen figure 3.20.
A typical Gr-FFF experiment involves the injection of particles into a channel, followed by a relaxation period determined by equations 3.3.\(^{28,29}\)

\[
t_{\text{relax}} = \frac{18\mu h}{d^2 \Delta \rho g} \tag{3.3}
\]

In equation 3.3, \(\mu\) is the fluid viscosity, \(h\) the channel height, \(d\) the diameter of the relaxing particle, \(\Delta \rho\) the difference in density between the particle and the fluid, and \(g\) is gravitational acceleration. Using 110 microns (approximate gap height based on deadzone and slice thickness using standard print condition) as the channel height, for a resin filled with SS-25 the particle settling time ranges between 0.5 minutes for 25 micron diameter particles and 8 minutes for 5 micron particles. Given that much the resin remains stationary during fabrication, it is conceivable that some sedimentation occurs near the entrance of the gap between the growing part and the window.

In Gr-FFF experiments following relaxation, separation of particles from the accumulation wall (bottom-surface) occurs due to fluid flow. The velocity of a (spherical) particle in this instance depends on the distance from the center of the particle to the wall. An approximation of this velocity can be calculated from equation 3.4.\(^{29}\)

\[
v_{\text{particle,separation}} = \frac{3 \cdot v_{\text{avg}} \cdot (d)}{h} \tag{3.4}
\]
In equation 3.4 \( d \) is the diameter of a particle, \( h \) is the height of the channel, and \( v_{avg} \) is the mean average velocity. Using the same channel dimensions as before, and assuming a mean velocity of 1000 microns per second (from experimentation), larger particles (25 micron diameter) begin to move first with an average velocity 681 microns per second.\(^{29,30}\) Conversely, small particles (~1 micron diameter) that have deposited on the window surface move slowly at 27 microns per second. Lift forces, and subsequently particle elevation, occurs as a result of increased pressure behind the moving particles during flow, and increase with particle size.\(^{31}\) In theory this indicates that particles never adhere to the window. Still, these approximations assume that all particles will move upon resin flow initiation due to the upward movement of a growing part. In reality however, there are additional effects occurring during particle flow and hydraulic lift such as viscous drag near the wall, or particle-wall attractive forces that can further slow or even halt particle movement.\(^{29}\) Given that the resin viscosity used in these experiments was quite high (~1000 cP versus), it is likely that particle deposition, especially at small radius, would be effectively permanent due to their close proximity to the window. Thus, once particles begin to sediment near the gap, aggregates can form due to attractive forces between particles as described previously, resulting in a pseudo-clog that ultimately results in an uneven loading at the center of parts.

### 3.5 Conclusions

CLIP part fabrication with filled resins is possible so long as changes in resin flow behavior are considered. The thixotropic nature of filled liquids can cause print failures; however, this will vary between bulk resins, fillers, and combinations thereof. As was detailed above, filler distribution is affected by particle size, wherein large particles can clog during the flow underneath a growing part, particularly within the deadzone and restrict the flow of other particles to the inner area of a growing cross section. The work presented here offers fundamental tools for observing and characterizing filled resin restricted flow that can be related to conditions in CLIP. These fundamental observations of restricted particle flow related to CLIP can be applied toward informed choices regarding fillers appropriate for CLIP resins, thus ensuring better printability and filler distribution in fabricated parts.
3.6 Acknowledgements

The author would like to thank Bob Geil from UNC CHANL for his assistance and guidance on microfluidic fabrication techniques and limitations, as well as Richard McLaughlin from the department of mathematics at UNC for his advice and guidance on the use of glass microchannels to observing resin flow. A special thanks to Robert Currin from the Hooker Imaging Laboratory, part of the imaging core for the school of medicine at UNC, for his training and help with operating the confocal microscope in an uncommon application. We acknowledge Carbon for providing a state-of-the-art CLIP machine and resins used in part fabrication. This research was funded by a sponsored research agreement with Carbon, Inc.

3.7 References


CHAPTER 4: Rubber Toughening of CLIP Resins

4 Introduction

One of the primary motivations for polymer composite material development is to manipulate mechanical properties beyond that of the neat polymer.\textsuperscript{1-3} Indeed, the addition of filler has been found to enhance or modify polymer mechanical properties including tensile strength and modulus, flexural strength, toughness or impact strength, and elongation.\textsuperscript{1} Because of this, early studies in material improvement for 3D printing showed that the addition of filler could improve mechanical properties of printed part, thus compensating for some mechanical drawbacks in the technology.\textsuperscript{4-7} Given the infancy of the continuous liquid interface production (CLIP) process, few studies have investigated the effect of filler on mechanical properties of printed with this new technology. The purpose of this chapter is to explore the mechanical improvement using filler within parts fabricated via CLIP, with a focus on toughening a brittle thermosetting resin. This chapter introduces the development of microphase separated liquid resins for the purpose of fabricating rubber toughened thermosets. The microphase discussed here is an immiscible reactive liquid oligomer that crosslinks to form elastomeric particles during the CLIP process. While their processing and development differ from solid fillers discussed previously, the characterization techniques developed in the previous chapters will prove useful in evaluating their potential as a CLIP resin toughener.

4.1 Background

4.1.1 Mechanical properties in polymeric materials

The mechanical properties of polymeric materials are of great importance for engineering applications.\textsuperscript{8-10} In its simplest form, the deformation mechanism of a polymeric material can be described as its stress-strain behavior. A simple definition of stress is a force per unit area, or negative pressure, normal to the cross-sectional area of material. Equation 4.1\textsuperscript{11} presents the relationship where $\sigma$ is the stress, $F$ is the force or load, and $A$ is the cross-sectional area.
\[ \sigma = \frac{dF}{dA} \quad (4.1) \]

If the stress is assumed to be distributed uniformly over the cross-section, then stress acts constant. Thus, integrating for force as in equation 4.2 yields equation 4.3.

\[ F = \sigma \int dA = \sigma A \quad (4.2) \]

\[ \sigma = \frac{F}{A} \quad (4.3) \]

The stress can be further correlated to the strain, which relates the change in dimension of a specimen to its original length, also known as Hooke’s Law.

\[ \sigma = E \varepsilon \quad (4.4) \]

\[ \varepsilon = \frac{\Delta l}{l_i} \quad (4.5) \]

In Equation 4.4 E is constant of proportionality, known as Young’s Modulus, \( \varepsilon \) the strain, \( \Delta l \) the change in length of specimen, and \( l_i \) the initial length of the specimen. These equations assume that the dimensions of tested material do not change drastically, only the cross-sectional area change before fracture. While this may be true for very brittle materials, polymers can exhibit many different characteristics under uniaxial stress, as seen in an example stress-strain curve in figure 4.1.

**Figure 4.1: Examples of stress-strain curve behavior plots.** (A) General representation of tensile curve; (B) typical tensile curve for polystyrene, a brittle polymer, and high-impact polystyrene, a toughened polymer blend.
Early in polymer deformation, stress increases proportionally to strain and behave according to Hooke’s Law. This continues until a yield point, or the maximum stress before the stress-strain relation is no longer linear. At this point a polymer may begin to deform and may not require additional load to continue increasing strain. Therefore, the maximum stress is called the ultimate tensile strength (UTS).

\[ \sigma_{UTS} = \frac{F_{\text{max}}}{A_0} \]  

Equation 4.6 UTS where \( A_0 \) is the area before deformation begins. After this point, the area begins to change in a process known as necking. This continues until the sample can no longer sustain the applied load, thus resulting in fracture. The stress at this point is known as the fracture strength, and the strain as the elongation shown in equation 4.7.

\[ e = \varepsilon_f \times 100\% = \frac{\Delta l}{l_i} \times 100\% \]  

As such, elongation is a measure of a materials ductility, or its ability to stretch without failure. Polymer toughness is defined as the amount of energy a material can absorb before failure, typically expressed as the area under the stress-strain curve as seen in equation 4.8.

\[ U_T = \int_0^{\varepsilon_f} \sigma d\varepsilon \]  

\( U_T \) is toughness which represents energy per unit volume to fracture. Polymers that absorb large amounts of energy before failure are considered tough, typically indicated by high fracture strength and ultimate elongation (ductility). Conversely, brittle materials experience failure at relatively low deformation, such as polystyrene in figure 4.1B.

There are many factors that affect the toughness of a polymer, such as chemical composition, morphology (i.e. semi-crystallinity, phase separation), molecular weight, and topology. As was mentioned in chapter 1, the CLIP process can produce parts that exhibit isotropic properties regardless of part orientation during fabrication. This is because CLIP uses photocurable resins and a deadzone which allows fast resin renewal and layer adhesion issues seen in thermal 3D printing print. Consequently, monolithic and layerless structures can
be fabricated that exhibit mechanical properties similar to traditional polymer molding techniques. As such, developing tough polymers for CLIP focuses on manipulation of morphology.

Most photocurable materials for 3D printing utilize resins which form thermoset polymers. Thermosets differ from thermoplastics in that polymer chains are chemically linked together during polymerization, forming crosslinked networks. While there are many benefits to thermoset materials such as their high strength, resistance to flow, and solvent resistance, high crosslink density can limit polymer deformability, which in turn leads to brittle materials. Consequently, the toughening of thermosets is a continuously studied area of polymer material development. Arguably the most frequently studied thermoset materials in need of toughening are epoxies, which are used in a wide range of engineering applications. The CLIP process does not utilize epoxide functionality during photopolymerization fabrication because its ring-opening reaction typically utilizes cationic photoinitiators and these reactions are not inhibited by oxygen. As such, few studies have explored rubber toughening in acrylate or methacrylate based photopolymerized thermosets. Nevertheless, many of the same strategies applied to the rubber toughening of epoxy thermosets can be applied to developing rubber toughened CLIP resins.

4.1.2 Fundamentals of microphase separation

Polymer blends, or polymer alloys as they are sometimes called, are the combination of two or more polymers into one solid for the purpose developing a new material with improved properties over the individual components. Microphase separation in thermosetting polymers is a subset of polymer blends. Thus, the formation of microphases lies in the dynamics of polymer-polymer miscibility, which will be discussed here briefly.

The primary relationship governing mixtures of dissimilar components is the Gibbs free energy of mixing equation.

\[ \Delta G_m = \Delta H_m - T \Delta S_m \]  

\( \Delta G_m \) is the free energy of mixing, \( \Delta H_m \) is the enthalpy or heat of mixing, and \( \Delta S_m \) is the entropy of mixing. For mixing (miscibility) to occur, free energy must be negative. The Boltzmann
relationship can derived to denote the entropy of mixing two molecules based on mole fractions.

\[ \Delta S_m = -k (N_1 \ln x_1 + N_2 \ln x_2) \quad (4.10) \]

The multiplier \( k \) is the Boltzman constant, \( N_i \) and \( x_i \) are the number of molecules and molar fraction of component i, respectively. This equation is reliable for low molecular weight components, but polymers are large molecules and thus it fails to predict miscibility. The equation is modified to account for the volume.

\[ \phi_i = \frac{V_i N_i}{V}; \quad V = V_1 N_1 + V_2 N_2 \quad (4.11) \]

As shown in equation 4.11 \( \phi_i \) and \( V_i \) are the volume fraction and the volume occupied by component i, and \( V \) is the total volume occupied by the components. This assumes that each polymer molecule occupies a certain number of volume units, thus volume fraction can substitute for mole fraction as seen equation 4.12.

\[ \Delta S_m = -k (N_1 \ln \phi_1 + N_2 \ln \phi_2) = -kV \left[ \frac{\phi_1}{V_1} \ln \phi_1 + \frac{\phi_2}{V_2} \ln \phi_2 \right] \quad (4.12) \]

Meanwhile, the enthalpy of mixing (\( \Delta H_m \)) is derived from the exchange energy between interacting components as seen in equations 4.13 and 4.14.

\[ w_{12} = \frac{1}{z} (\varepsilon_{11} + \varepsilon_{22}) - \varepsilon_{12} \quad (4.13) \]

\[ \frac{\Delta H_m}{V} = \frac{zw_{12}}{v_r} \phi_1 \phi_2 \quad (4.14) \]

\( \varepsilon_{ij} \) is the energy of contact between components i and j, \( w_{12} \) is the exchange energy of interacting components, \( z \) is the coordination number, and \( v_r \) is the reference volume. The exchange energy and coordination number are related to the Boltzman constant through the Flory-Huggins interaction parameter, and thus can be substituted into equation 4.14 as shown below.

\[ \chi_{12} = \frac{zw_{12}}{kT} \quad (4.15) \]
Thus, the equation for the free energy of mixing for two polymers can be modeled by substituting entropy and enthalpy for mixing as defined above, known as the Flory-Huggins theory.

\[ \Delta G = kTV \left[ \frac{\phi_1 \ln \phi_1 + \phi_2 \ln \phi_2}{V} \right] + \phi_1 \phi_2 kTV \frac{\chi_{12}}{V_r} \]  

This expression, which is on a molecular basis due to the Boltzman constant, can be written on a molar basis as well by substituting \( k \) with \( R \), the gas constant, and \( V \) (molecular volume) with molar volume, \( v \).

\[ \Delta G = RTV \left[ \frac{\phi_1}{V_1} \ln \phi_1 + \frac{\phi_2}{V_2} \ln \phi_2 \right] + \phi_1 \phi_2 RTV \frac{\chi_{12}}{v} \]

By making this substitution, the miscibility of two polymers can be related to their molecular weight realizing that \( v = M_i/\rho_i \).

\[ \Delta G = RTV \left[ \frac{\rho_1 \phi_1}{M_1} \ln \phi_1 + \frac{\rho_2 \phi_2}{M_2} \ln \phi_2 \right] + \phi_1 \phi_2 RTV \frac{\chi_{12}}{v} \]

Where \( M_i \) and \( \rho_i \) are the molecular weight and density of component \( i \), respectively. The first part of equation 4.19 is the entropy of mixing, and it will always be negative given since \( \ln(\phi_i) \) is negative (\( \phi_i \leq 1 \)). Moreover, as the molecular weight of one or both the components increases, the magnitude of the entropy of mixing becomes quite small. Therefore, polymer-polymer miscibility is often most influenced by the enthalpy of mixing, specifically in relation to the interaction parameter, \( \chi_{12} \). If the interaction between two polymers is assumed to be dispersive and/or non-polar, then the interaction parameter can be estimated as the square difference of the Hildebrand solubility parameter of each component.

\[ \frac{\chi_{12}RT}{v_r} = (\delta_1 - \delta_2)^2 \]

Hildebrand solubility parameter of component \( i \) is \( \delta_i \). Substituting equation 4.20 into equation 4.19 further demonstrates that the enthalpy of mixing will always be greater than zero.
Therefore, high molecular weight polymer blends are almost always immiscible, even at elevated temperatures. Conversely, low molecular weight blends can achieve miscibility quite easily when interaction parameters are similar. This of course assumes that component interactions are dispersive. Indeed, enthalpy of mixing values can be negative when specific interactions between polymers, such as hydrogen bonding, play a significant role during mixing. Thus, the equation for the enthalpy of mixing should include an enthalpy for specific interactions.

\[
\Delta H_m = \Delta H_{m,\text{dispersive}} + \Delta H_{m,\text{specific}} \quad (4.21)
\]

4.1.3 Rubber toughening in thermosetting resins

Rubber toughened epoxy utilizes microphase separated elastomeric particles to improve inherent brittleness of the thermoset, by increasing crack growth resistance.\textsuperscript{18} The most widely used method of incorporating rubber microphases into epoxy networks utilizes miscible low Tg reactive oligomers formulated with the bulk epoxy resin. During the cure, microphase separation due to ever increasing molecular weight of the epoxy and formation of in situ rubber crosslinking yields discrete rubber particles within the matrix.\textsuperscript{16,18,27} As such, effective toughening of these crosslinked networks has been achieved and appears to be a function of a variety of factors including the chemical composition of the starting materials and the size and distribution rubber particle phases.

The mechanism of toughening has been highly debated, with early studies proposing that the crosslinked particles dissipated fracture energy by rubber stretching and tearing.\textsuperscript{22,28,29} Based on the size and concentration of the particles however, the microphase are not enough of an energy sink to account for the experimentally observed toughness improvement. Instead, studies have shown that the mechanism of toughening has more to do with shear deformation zones within thermoset, which relates to its ductility.\textsuperscript{18} In general, decreased crosslink density, or increasing the molecular weight between chemical crosslinks, of thermoset increases its ductility.\textsuperscript{16,18,30,31} This phenomenon is thought to occur because matrix ductility increases plastic deformation zone in the presence of a crack tip. Chen et. al. studied the effect of matrix ductility on rubber toughening efficiency by varying the amount of long (325 g/mole epoxy
equivalent) or short crosslinker (125 g/mole epoxy equivalent) to an epoxide of moderate molecular weight (187 g/mole epoxy equivalent).\textsuperscript{32} Crosslink density was found to have little effect on the neat epoxide polymer fracture energy, staying constant at \(\sim 150 \text{ J/m}^2\). The addition of 10 part per hundred (pph) reactive liquid elastomer oligomer to highly crosslinked samples resulted in a moderate increase in fracture energy to 376 J/m\(^2\). Whereas addition of 10 pph reactive liquid elastomer to the specimen with relatively lower crosslink density increased fracture energy to 5000 J/m\(^2\).

In terms of the rubber phase, molecular weight, topology, phase size and distribution, interfacial adhesion, and its \(T_g\) all contribute to its toughening ability on thermoset resins. Since primary goal of rubber microphase incorporation is to exploit its crosslinked elastomeric behavior, the \(T_g\) of rubber particles are typically in the range of -25 °C and lower.\textsuperscript{8,33,34} With that in mind, microphase size ranging between 500 nm and 5 microns have been found to best improve fracture toughness. In terms of loading, studies have shown that fracture toughness increases linearly up to a 10 pph reactive liquid oligomer. However this typically comes at the consequence of a linear decrease in modulus and strength because crosslink density is displaced by a lower crosslink density rubber, and slightly decreased \(T_g\).\textsuperscript{18} Beyond size and loading however, interfacial adhesion, or the interaction of the reactive liquid elastomer oligomer with the thermoset matrix, is considered a fundamental importance in toughness enhancement.\textsuperscript{18,27,35,36} Consequently, reactive liquid oligomers require functionality that allows an adequate covalent bonding with the thermoset matrix. In epoxy thermosets, this functionality is typically a carboxyl or amine group, whereas with CLIP, this will likely come in the form of an acrylate or methacrylate group.

Proper particle size and distribution, as well as interfacial adhesion, often requires presence of a compatibilizer. Compatibilization typically involves the use of an extra component within a blend that lowers interfacial tension between immiscible components, thus leading to smaller particles and better dispersion.\textsuperscript{37} In a sense, the compatibilizer, takes on the role of a surfactant, whose role is to stabilize multiphase morphology at the interface between two phases. Indeed, compatibilization is a common technique in rubber toughened polymer development.\textsuperscript{38,39} There are many methods of compatibilization, however a common method
is the addition of a block copolymer.\textsuperscript{37} In this method, a compatibilizer is chosen or designed such that it includes at least one block of each phase to be blended. A classic example is the compatibilization of high density polyethylene (HDPE) and high impact polystyrene (HIPS) using a styrene/ethylene-butylene/styrene (SEBS) block copolymer as a compatibilizer. The addition of SEBS to the polymer blends lead to an improvement in impact strength by as much as 4 times.\textsuperscript{40} Given that the CLIP process utilizes liquid resins, a compatibilizer will likely be necessary when developing rubber toughened resins, as a microphases will need to be formed prior to the curing of each layer.

4.2 Materials and Methods

4.2.1 Materials

Isopropyl alcohol (IPA; Histological Grade, 88\% - 91\%), anhydrous tetrahydrofuran (THF), was purchased from Thermo-Fisher Scientific. Trisobutylaluminum (TIBAL; 1 M in hexanes), 1,3-butadiene (\geq 99\%), Anhydrous toluene (ACS HPLC grade), propylene oxide (\geq 99.5\%), Ethyl (2,4,6-trimethylbenzoyl) phenylphosphinate (L-TPO; 98\%), 2-tert-Butyl-6-(5-chloro-2H-benzotriazol-2-yl)-4-methyl-phenol (BLS 1326; 98\%), triethanolamine (TEtOHA; \geq 99 \%) were purchased from Sigma-Aldrich. Toluene was stirred over calcium hydride overnight and vacuum distilled onto molecular sieves. 3-(t-butyldimethylsilyloxy)-1-propyllithium (BPL; 10 M in cyclohexane, 18 \% active weight) was purchased from FMC Lithium. RPU80, a two-part dual-cure rigid polyurethane methacrylate resin, was provided from Carbon. CN307, CN303, CN301, CN2920 (urethane acrylate oligomer), and SR833-S (tricyclodecane dimethanol diacrylate) were graciously donated by Sartomer. Ricon 130 and 130MA8 were provided by Cray Valley.

Table 4.1 lists the molecular weight and functionality of polybutadienes used in these studies, as documented in their technical data sheets.
Table 4.1: Polybutadiene properties

<table>
<thead>
<tr>
<th>Name</th>
<th>Provider</th>
<th>Molecular weight, $M_n$ (x 1000)</th>
<th>Functionality</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN307</td>
<td>Sartomer</td>
<td>~2.6</td>
<td>Diacrylate</td>
</tr>
<tr>
<td>CN303</td>
<td>Sartomer</td>
<td>~15</td>
<td>Dimethacrylate</td>
</tr>
<tr>
<td>CN301</td>
<td>Sartomer</td>
<td>~7.5</td>
<td>Dimethacrylate</td>
</tr>
<tr>
<td>Ricon 130</td>
<td>Cray Valley</td>
<td>2.5</td>
<td>Non-functional</td>
</tr>
<tr>
<td>Ricon 130MA8</td>
<td>Cray valley</td>
<td>2.7</td>
<td>Maleinized, to MA groups per chain</td>
</tr>
</tbody>
</table>

PBD-Poly (propylene oxide) diblock copolymers were synthesized in lab as described in the following section.

4.2.2 Synthesis of polybutadiene – poly (propylene oxide) diblock copolymer

A PBD-PPO diblock polymer was synthesized as a potential compatibilizer in microphase separated resins, as detailed in scheme 4.1. Anionic polymerization of 1,3-butadiene was chosen in order to obtain high 1,4-isomer content, which has been shown to have lower glass transition resulting in improved mechanical properties compared to its vinyl-1,2 counterpart.41

\[
\begin{align*}
\text{Si-O-Li} & \quad + \quad \text{1,3-butadiene} \\
& \quad \text{toluene} \\
& \quad \text{propylene oxide} + \text{triisobutyl aluminum} \\
& \quad \text{(1) 2-propanol, (2) HCl} \\
\end{align*}
\]

Scheme 4.1: Synthesis of polybutadiene with primarily 1,4-butadiene repeat units via anionic polymerization using alkyl-lithium initiator.

15 g of 1,3-butadiene (54.04 g/mol, 0.278 moles) was cryogenically distilled into the PARR reactor. The lecture bottle was weighed on an analytical balance before and after the addition
to determine the amount of butadiene. 3.82 mL of BPL (180.12 g/mol, 0.003 moles, 18% solution in cyclohexane) was measured via syringe and injected into the reactor, followed by addition of 90 mL of toluene. The reaction mixture was allowed to reach room temperature, then the reactor was heated to 45 ºC while mechanically stirring at 200 rpm. The reaction proceeded for 4 hours. Reaction progress was monitored by observing drop in pressure from approximately 40 psi to 1 psi. The reactor was then cooled down to 25 ºC. Subsequently, 30 g propylene oxide (58.08 g/mol, 0.516 moles) was injected into the reactor at 25 ºC. 60 mL of TIBAL solution (0.06 moles, 20-fold excess relative to BPL) was then injected into the reactor, and the reaction was allowed to proceed overnight at 25 ºC while stirring at 200 rpm. The next day, the polymerization was terminated by adding 10 mL of 1 % HCl (v/v) in 2-propanol to the reactor via syringe to neutralize the polymer. Al(OH)₃ salt formed as a result of alcohol quench, thus the reaction mixture was diluted with toluene to obtain a ~5 % polymer solution. The mixture was then passed through filter paper twice and third time through Celite to remove the salt. Then toluene was evaporated via rotary evaporator. Afterwards, product was dissolved in 1 M HCl in THF to obtain a 30 % polymer solution by weight. Tert-butyl dimethyl silyl groups were cleaved by refluxing this solution at 65 ºC overnight. Theoretical targets for PBD and PPO were 10k g/mol and 5k g/mol respectively, for a total diblock Mₙ of 15k g/mol. Size exclusion chromatography (SEC) with light scattering detector revealed monomodal distribution and a measured Mₙ of 13k g/mol with a PDI of 1.16, as seen in figure 4.2.
4.2.3 Resin formulation

The resin for studies described here on was a formulation labeled VF11 consisting of blend of CN2920 and SR833-S as the reactive resin, L-TPO as a photoinitiator, and TEtOHA as catalyst. 50 g each of CN2920 and SR833-S was added to a mixing cup, followed by 1.0 g (1 pph) of L-TPO as an initiator, 0.5 g (0.5 pph) of TEtOHA as a catalyst, and 0.1 g (0.1 pph) BLS 1326 as a UV absorber. The cup was then placed in a THINKY mixer where the components are blended by centrifuging the cup at a rate of 2000 rpm while simultaneously rotating the cup about its center axis in the opposite direction at a rate of 100 rpm, which is the default setting. Components blended for 90 seconds using the mixer default setting. Two additional variations of VF11 were formulated to investigate the effect of the absence of doubling of UV absorber on PBD-loaded resin deadzone formation. VF11-N-UV (no UV absorber) was formulated with a 1:1 blend of CN2920 and SR-833-S, followed by 1 pph L-TPO and 0.5 pph TEtOHA. Whereas VF11-D-UV (double UV absorber) included 0.2 pph BLS 1326. Table 4.2 details resin formulation and nomenclature of the VF resins.
Table 4.2: VF resin formulations

<table>
<thead>
<tr>
<th>Formulation</th>
<th>UV absorber (pph)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VF11</td>
<td>0.1</td>
</tr>
<tr>
<td>VF11-N-UV</td>
<td>0</td>
</tr>
<tr>
<td>VF11-D-UV</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Microphase separated resins were formulated by first choosing a PBD resin and adding the desired amount to one of the resins listed in Table 4.2. The two components were then mixed in a THINKY mixture for 5 minutes at default setting.

4.2.4 Microscopy

SEM micrographs were obtained on a Hitachi S-4700 cold cathode field emission Scanning Electron Microscope (SEM). Samples were made by using a razorblade to cut printed specimens. Images were taken of the cut surface closest to the center of the cross-section of the printed parts. Phase morphology images were obtained on cryo-microtomed samples via transmission electron microscope (TEM), a JEOL 100CX II.

4.2.5 Deadzone thickness and resin parameter measurements

Deadzone thickness, resin cure dosage ($D_c$), and absorption coefficient (alpha) was measured according to methods described in chapter 2.

4.2.6 Photo-differential scanning calorimetry

Photo-differential scanning calorimetry (p-DSC) measurements were done using the equipment and sample size described in Chapter 2 and by the following experimental method:

1. Isothermal for 3 min
2. Light on
3. Light exposure for 0.04 min (~3 seconds)
4. Light off
5. Isothermal 10 min
6. Light on
7. Light exposure for 5 min
8. Light off
9. Isothermal 5 min
The short light exposure was used to simulate the short exposure times seen during CLIP. It should be noted that exposure times during CLIP vary based on resin type and printing style. The long exposure was used to evaluate changes in overall bond conversion between resins.

Double bond conversion was calculated in a similar way as described in chapter 2. Unlike solid filler, CN303 and CN307 have photoreactive functionality and was therefore not removed during (DBC) calculation. An example calculation for a 7.80 mg (0.0078 g) sample of VF11 loaded with 10 pph CN307 (wt% and approximate MW in table 4.3) is provided below.

<table>
<thead>
<tr>
<th>Acrylated / methacrylated Component</th>
<th>Weight percent in resin (%)</th>
<th># of functional groups</th>
<th>Approximate Molecular Weight (g/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN2920</td>
<td>44.580</td>
<td>2</td>
<td>~863.89</td>
</tr>
<tr>
<td>SR833-S</td>
<td>44.583</td>
<td>2</td>
<td>308.48</td>
</tr>
<tr>
<td>CN307</td>
<td>9.411</td>
<td>2</td>
<td>~2600</td>
</tr>
</tbody>
</table>

First moles of acrylate bonds for a sample mass was calculated using the known amounts of monomer, oligomer, and PBD added to resin. Subsequently, a theoretical heat of polymerization (assumes 100 % acrylated conversion) was calculated using a acrylate heat of polymerization value of 78,230.8 J/mole.42

\[
\Delta H_{P.th} = \sum_i \frac{H_{Pi} \cdot m_i \cdot f}{M_{Wi}}
\]

\[
Moles\ acrylate = \left( \frac{0.0035 \text{ g} \cdot \text{CN2920} \cdot 2}{863.89 \text{ g/mole}} + \frac{0.0007 \text{ g} \cdot \text{CN307} \cdot 2}{2600 \text{ g/mole}} \right) = 3.06 \cdot 10^{-5} \text{ mole}
\]

\[
\Delta H_{P.th} = 78,230.8 \text{ J/mole} \cdot \left( 3.06 \cdot 10^{-5} \text{ mole} \right) = 2.395 \text{ J}
\]

Heat flow data from the DSC was then integrated for the first pulse to obtain an enthalpy of polymerization, as seen below.

\[
\Delta H_{P.\text{pulse}} = \int Q_{\text{pulse}} \, dt = 0.5305 \text{ J}
\]
DBC was calculated as the experimental heat of polymerization of the first pulse divided by the theoretical heat of conversion calculated previously.

\[ DBC_{\text{pulse}} = \frac{\Delta H_{P,\text{pulse}}}{\Delta H_{P,\text{th}}} \times 100 \% = \frac{0.5305 \text{ J}}{2.395 \text{ J}} \times 100 \% = 22.15 \% \text{ acrylate conversion} \]

Total DBC was calculated as the sum of the integral of pulse cure heat flow peak and the integral of long cure heat flow peak divided by the theoretical heat of conversion.

\[ \Delta H_{P,\text{Total}} = \Delta H_{P,\text{pulse}} + \int Q_{\text{Long cure}} dt = 0.5305 \text{ J} + 1.0475 \text{ J} = 1.5780 \text{ J} \]

\[ DBC_{\text{Total}} = \frac{\Delta H_{P,\text{Total}}}{\Delta H_{P,\text{th}}} \times 100 \% = \frac{1.5780 \text{ J}}{2.395 \text{ J}} \times 100 \% = 65.87 \% \text{ acrylate conversion} \]

4.2.7 Tensile testing specimen fabrication

ASTM standard D638 type V tensile specimens were fabricated on the M1 printer from Carbon as detailed in figure 4.3. First a resin blend was poured into a resin cassette. Next the resin parameters (resin cure dosage, absorption coefficient, and viscosity), which were measured as described above, were entered into the printer interface using the “custom resin” option. A viscosity of 1200 cP (VF11 viscosity) was used for all resins using VF11 as the base resin. It should be noted that specimens printed with RPU80 as a base resin were printed using the “RPU80” preset printing conditions regardless of PBD loading. Next, STL file of ten tensile specimens, oriented along their longest axis (figure 4.3) was uploaded onto the control interface. The part was sliced using Carbon’s integrated software at 100 microns per slice. Fabrication rate varied depending on the amount of PBD loaded into resin, decreasing linearly from 70 mm/hour to 47 mm/hr as PBD loading increased from 0 pph to 15 pph. Following fabrication, parts were washed for 3 minutes in an IPA bath using an orbital mixer. RPU80 specimens were subject to an additional thermal post cure in a programmable forced-air convection oven by heating to 120 °C in 15 minutes, isothermal at 120 °C for 4 hours, and cooling to room temperature.
4.2.8 Mechanical testing

Mechanical testing was done using an Instron 5566 Universal Test Machine equipped with a 10 kN load sensor. Machine operating parameters were controlled using Instron’s Bluehill 3 software. Testing was conducted according to the ASTM D638 standard, wherein a dogbone specimen was subject to an upward uniaxial stress at a constant strain rate such that failure occurred between 30 seconds and 5 minutes. Specimens fabricated with VF11 base resin were pulled at strain rate of 1 mm/min, and RPU80 specimens at 5 mm/min. A minimum of 5 (out of 10 specimens fabricated) were tested for each resin blend. Stress-strain data was analyzed using the integrated analysis tools on Bluehill 3 software.

4.2.9 Thermal macrophase separation experimentation

Macrophase separation of the liquid PBD phase out of the bulk phase was observed on a localized resin heating apparatus as detailed in figure 4.4.
A 6 mm diameter cylindrical heating cartridge was controlled using variable voltage output power unit. The cartridge was placed in a petri dish filled with resin at a depth of approximately 4 mm. Power was applied to the cartridge and changes in the resin were observed. Infrared video images were captured with a FLIR model E40 infrared imaging camera. Complimentary still images were captured with a Nikon digital camera.

4.3 Results

4.3.1 The effect of polybutadiene on deadzone thickness

It was imperative to evaluate the effect of added PBD on the deadzone thickness to understand the impact of added material phase on the printing process. A high molecular weight blend of VF11 and polybutadiene dimethacrylate (CN303) was analyzed first. The VF11 formulation that contain 0.1 pph UV absorber was then blended with 0, 2, 5, 10, 15, and 20 pph CN303. Each blend was tested a minimum of 3 times and results can be seen in figure 4.5.
Figure 4.5: Deadzone thickness experimental data for VF11 loaded with CN303 (polybutadiene dimethacrylate, $M_n \sim 15000 \text{ g/mol}$). (A) Deadzone thickness as a function of light intensity at various PBD loadings. (B) Deadzone thickness as a function of PBD loading at various light intensities. (C) Reference dot and grid structure used in deadzone experiment light exposure.

Unlike solid fillers, which were shown in chapter 2 to decrease deadzone thickness, polybutadiene increased deadzone thickness as loading increased, at all light intensities. Another notable difference was in the solidified thickness of the reference dots. The reference dots, figure 4.5C, were exposed to full light intensity (~6.0 mW/cm$^2$) for 120 seconds to ensure that the dots form a solid across the entire control height. Even with 4 minutes of full light intensity exposure, these reference dots, when PBD was added to resin, were consistently lower than calibrated control height measurements. As such, internal calibrations in-between deadzone measurement experiments, were done using only neat resin to ensure accurate account of potential control height drift. The deadzone measurements of resin PBD-VF11 resin blends is depicted in figure 4.5A and 4.5B. PBD addition resulted in a drastic deadzone...
thickness increase to as much as 500% at low light intensities relative to neat resin. Deadzone thickness at 1 mW/cm² for 10, 15, and 20 pph CN303 loading were not reported because little to no solid sample formed following light exposure. These results suggest that reaction kinetics have changed with the addition of CN303, which was confirmed using resin cure dosage measurements, displayed in figure 4.6.

Figure 4.6: Dosage cure and absorption cure experimental data for VF11 loaded with CN303 (polybutadiene dimethacrylate; $M_n \approx 15000$ g/mol)

Figure 4.6A shows $D_c$ increased linearly with increasing CN303 loading, doubling in value at the highest loading. Resin absorption displayed a similar increasing trend. These results suggest that increasing the loading of CN303 decreases the cure rate and increases the amount of light absorbed by the resin which in turn decreases the distance that the light penetrates into resin.

Two additional resins were formulated to further investigate and explain the effect of PBD addition on resin deadzone formation and cure dosage cure and absorption. The first was VF11-D-UV whose dosage cure and absorption values were similar to 10 pph CN303 loaded resin. The second was the base VF11-N-UV resin, the purpose of which was to determine if overall increased reaction rates (due to the absence of UV absorber) balance out the negative effect of PBD loading. Therefore, the VF11-N-UV resin was also blended with 10 pph CN303 and tested. The cure dosage and absorption coefficient for these resins and their deadzone thickness measurements for both resins can be seen in table 4.4 and figure 4.7 respectively.
Table 4.4: VF resin cure dosage and absorption comparison

<table>
<thead>
<tr>
<th>Resin Blend</th>
<th>Cure Dosage (# cm(^{-2}) s(^{-1}))</th>
<th>Absorption Coefficient (µm(^{-1}) x 10(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>VF11</td>
<td>7.50</td>
<td>1.00</td>
</tr>
<tr>
<td>VF-11 w/ 10 pph CN303</td>
<td>11.20</td>
<td>1.35</td>
</tr>
<tr>
<td>VF11-D-UV</td>
<td>11.50</td>
<td>1.80</td>
</tr>
<tr>
<td>VF11-N-UV</td>
<td>1.50</td>
<td>0.55</td>
</tr>
<tr>
<td>VF11-N-UV w/ 10 pph CN303</td>
<td>2.90</td>
<td>0.55</td>
</tr>
</tbody>
</table>

Figure 4.7: Deadzone thickness experimental results as a function of light intensity for resins with altered UV absorber. (A) Compares neat VF11 resin with VF11-D-UV (double UV absorber), whose D\(_c\) and alpha matches that of VF11 with 10 pph CN303. (B) VF11-N-UV resin (no UV absorber) neat and blended with 10 pph CN303.

Figure 4.7A shows that increased UV absorber did increase deadzone thickness, however the effect is less pronounced when compared to 10 pph CN303. At low light intensity, the solid thickness was not always measurable or present following exposure, due to high error involved with these measurements. However, except for 1 mW/cm\(^2\), deadzone thickness only increased an average of 20 % relative to the original neat resin across all light intensities. VF11-N-UV light absorption is primarily due to the photoinitiator, thus should have increased cure rates.
overall, even in the presence of PBD. In Figure 4.7B however, the addition of 10 pph CN303 still resulted increased deadzone thickness by an average of 90% across all light intensities relative to neat resin.

CN303 is a bimodal blend of high molecular weight polybutadiene ($M_n \approx 15,000$ g/mole), and thus is much larger than VF11 (~850 g/mole) molecular weight. Therefore, the addition of CN303 to VF11 displaces resin and decreases acrylate concentration from 4.33 mmol/g for neat resin to 3.63 mmol/g when loaded at 20 pph. Moreover, methacrylate reactivity has been quantified to be lower than acrylate. As such, a lower molecular weight PBD relative to CN303 (CN307, $M_n \approx 2600$ g/mol, diacrylate) was blended into the base resin at loadings of 0, 2, 5, 10, 15, and 20 pph. For comparison’s sake, the average acrylate concentration when CN307 was loaded at 20 pph was 3.75 mmol/g. Figures 4.8 and 4.9 demonstrates deadzone and cure dosages results of CN307 loaded resins respectively.

Figure 4.8: Deadzone thickness experimental data for VF11 loaded with CN307 (polybutadiene diacrylate, $M_n \approx 3000$ g/mol). (A) Deadzone thickness as a function of light intensity at various PBD loadings. (B) Deadzone thickness as a function of PBD loading at various light intensities
The addition of CN307 into VF11 increased deadzone thickness at all light intensities and loadings. Compared to CN303, the effect of CN307 loading is less pronounced, with increased deadzone thickness between 25 % and 300 % relative to neat resin. Furthermore, dosage cure and absorption increased in the same way compared to CN303 loaded resins. Despite relatively low PBD molecular weight (increased acrylate concentration) deadzone thickness still increased when blended into VF11 resin.

Increased deadzone thickness suggests that the addition of PBD changes resin cure kinetics and double bond conversion, largely independent of PBD molecular weight. Therefore, both CN303 was loaded into VF11 at loadings of 0, 2, 5, 10, 15, and 20 pph and were tested using p-DSC to observe changes in double bond conversion (DBC) due the addition of PBD. The same loadings of CN307 in VF11 were also tested to investigate the effect of PBD molecular weight on resin DBC and cure rates. Additionally, CN303 was blended at the same loadings into VF11-N-UV to further investigate the effect of a theoretically more reactive resin loaded with PBD on DBC and cure rates. The results of these experiments can be seen in the following figures.
Figure 4.10: P-DSC heat flow and double bond conversion of VF11 resin loaded with CN303 (polybutadiene dimethacrylate; $M_n \sim 15000$ g/mol) (A) Light pulse heat flow data. (B) Long exposure heat flow data. (C) Double bond conversion for pulse and aggregate total.
In figures 4.10A and 4.11A, the first pulse peak height decreased as PBD content increased. Similarly, DBC in the first pulse (figures 4.10C and 4.11C) also decreased as PBD increased by as much as 60% relative to the neat resin. This is similar to the near doubling in $D_c$ with the addition of PBD seen previously, which indicates that resins require 50% more as exposure time to UV light to solidify the same depth of resin. Interestingly, overall DBC following a long exposure for both sets of resin blends remained constant near 65% regardless of PBD loading. This suggests that PBD addition only reduced initial DBC, but not overall conversion.
The results in figure 4.12 for PBD-loaded VF11-N-UV revealed similar results, however the effect of increasing PBD on first pulse cure behavior was even greater, decreasing peak height and DBC by as much as 80 % relative to neat resin.

The resins with or without added CN303 show equivalent DBC following a long cure, which explains a previously noted phenomenon at the beginning of this section. Reference dot thickness in the resin cure dosage tests were consistently lower for all resins blended with PBD by as much as 15 microns, regardless of extended exposure time. However, the fact that there is constant total DBC suggest that the addition of PBD in some way increased oxygen content within the resin. Indeed, polybutadiene has been studied as a potential additive in polymer
films for food packaging for the purpose of oxygen scavenging due to its ability to uptake large amounts of oxygen.\textsuperscript{44–46} Therefore, it is possible that PBD loaded resins exhibit increased oxygen concentration and permeation, which in turn could lead to increased deadzone thickness. This result explains why reference dot thicknesses were unable to solidify fully from window to glass, as increased oxygen permeation would keep oxygen concentrations high enough to sustain inhibition at the window/resin interface. It is also possible that this effect was further compounded by decreased acrylate concentration in PBD loaded resins leading to a decrease in radicals during cure, shifting the critical oxygen concentration for propagation lower. This does not explain however why first pulse kinetics change and DBC appear to be lower, especially in p-DSC experiments that were conducted under nitrogen atmosphere. Though it can be reasoned that saturated oxygen in resin does not fully diffuse out of resin between the time it is loaded in the instrument and when the light is triggered, considering that typical degassing techniques occur over extended time spans.\textsuperscript{47} Nevertheless, the addition of PBD to resin increased deadzone thickness regardless of PBD molecular weight or base resin curing behavior, most likely due to increased oxygen permeation into resin at the window-resin interface.

4.3.2 \textit{Mechanical properties of rubber toughened CLIP resins}

Despite the changes in deadzone thickness and diminished pulse curing behavior, PBD loaded resins were successfully used to fabricate tensile testing specimens on an M1 CLIP printer. The first experiment was designed to observe the effect of PBD functionality on toughness. The base resin was VF11-N-UV, with which 5 pph of a non-functional (Ricon 130), maleated (Ricon 130MA8), Diacrylate (CN307), and two Dimethacrylate (CN303 and CN301) PBD resin were each blended. It should be noted that, in terms of specific PBD MW and distribution, both Dimethacrylate resins were the same, however CN301 includes between 10 % and 20 % by weight hexanediol Diacrylate as a diluent. A minimum of five samples were tested for each resin blend, and toughness was evaluated by calculating area under the stress-strain curve. Results and SEM micrographs of each blends fabricated cross section are presented in figure 4.13.
Figure 4.13: Effect of PBD on resin toughness and particle size/distribution within printed parts. (A) Effect of PBD resins with various functional groups on toughness relative to neat resin. (B) SEM micrograph example of a specimen internal cross-section printed with non-functional or maleated PBD loaded resin. (C) SEM micrograph of specimen internal cross-section printed with Diacrylate PBD loaded resin. (D) SEM micrograph of specimen internal cross-section printed with dimethacrylate (neat or diluted) PBD loaded resin. All data and images blended are based on 5 pph PBD loaded resin. Arrows point at microphases within the image area.

In figure 4.13A, non-functional and maleated PBD containing specimens exhibited drastically decreased toughness compared to neat VF11-N-UV specimens. SEM images of these dogbones, like that in figure 4.13B, revealed an average PBD phase size in the printed parts of 18 microns, and a range between 10 microns and 40 microns. Moreover, the phases also appear
as micro voids, suggesting that PBD was not adhered to the bulk polymer matrix, nor were the phases internally crosslinked, thus diminishing toughness. On the other hand, the addition of PBD with photoreactive functional groups improved toughness of VF11 dogbones in comparison to their non-functionalized PBD. Among those, high molecular weight PBD dimethacrylate CN303 showing the most promise. SEM micrograph images of these PBD loaded specimens, like those in figures 4.13C and 4.13D, revealed average particle sizes of 3.45 micron and 3.25 micron for CN307 and CN303 loaded resins respectively. Furthermore, fewer micro void formations were observed and many particles appeared to adhere to the surrounding bulk matrix, suggesting good particle-matrix adhesion and that particles were crosslinked internally as a result of photo polymerization.

Next, the toughening effect of photoreactive PBD, and consequently molecular weight, was further explored at concentrations of 5 and 10 pph using the VF11-N-UV resin, as seen in figure 4.14.

![Figure 4.14: Effect of photoreactively functionalized PBD molecular weight on toughness of neat VF11-N-UV. Red line and value represents the neat resin control value. Note: 7 kDa PBD actually contains the same distribution as 15 kDa, but with added non-PBD reactive diluent. 5 pph and 10 pph denotes loading of CN307, CN301, and CN303.](image)

Decreased toughness of samples that contain CN307 relative to neat specimens as shown in figure 4.14, is likely due to the physical properties of the rubber being insufficient for toughening. For instance, the cured $T_g$ of CN307 and CN303 networks are -40 °C and -80 °C.
respectively. Higher $T_g$ can be attributed to higher crosslink density of CN307 chains. These results would be expected given that CN307 has relatively lower molecular weight than CN303. Consequently, crosslinked samples of neat CN307 are mechanically weak elastomers. CN303 and CN301 containing dogbones both exhibited improved mechanical properties compared to CN307 loaded specimens, though not much greater than neat resin. Regardless, CN301 was chosen to observe the effect of rubber content within VF11-N-UV on mechanical properties.

The effect of PBD loading level on VF11-N-UV mechanical properties was tested using at loadings of 0, 2, 5, 10, and 15 pph CN301. This translates to PBD loadings of 1.4, 4, 8, and 12 pph due to CN301 containing $\leq$ 20 wt% hexanediol dimethacrylate. Figure 4.15 details the changes in tensile strength, modulus, strain at break, and toughness due to the addition of CN301.
Figure 4.15: Effect of PBD (CN301; HDDA diluted polybutadiene dimethacrylate M_n ~15000 g/mol) on VF11-N-UV mechanical properties. (A) Toughness as calculated by the area under the stress-strain curve. (B) Elongation at break. (C) Tensile Strength. (D) Modulus.

As is typical in rubber toughened systems, the tensile strength and modulus decreased with increasing PBD content, as seen in figures 4.15C and 4.15D. By magnitude, figure 4.15B shows that the average elongation increased from 9 % to 12.5 %, which led to a slightly increased toughness (figure 4.13A) though small at about 20 % greater than neat resin. It should be noted that based on error bars of strain-at-break and toughness, there appears to be no statistical difference. This high error could be due to the low ductility of thermosets, which often yields in inconsistent or premature failure without warning during tensile testing. Given that VF11 is between 50 % and 60 % by weight low molecular weight (~300 g/mol) reactive diluent, it is possible that the high crosslink density potential of the base resin reduces overall
toughening effect of the rubber. Therefore, the toughening effect of PBD loading into RPU80 resin was measured as it yields initially more ductile specimens than VF11, a property which has been shown to be linked to thermoset toughen via rubber.\textsuperscript{30} CN301 was blended at loadings of 0, 5, 10, and 20 pph into RPU80 resin (0, 4, 8, and 16 pph PBD) and tensile testing samples were printed and subjected to a 4-hour thermal post-cure at 120 °C. A minimum of 5 samples were printed and tested, tensile property results can be seen in figure 4.16.

![Figure 4.16: Effect of PBD (CN301; HDDA diluted polybutadiene dimethacrylate M\textsubscript{n} ~15000 g/mol) on RPU80 mechanical properties. (A) Toughness as calculated by the area under the stress-strain curve. (B) Elongation at break. (C) Tensile Strength. (D) Modulus.](image-url)
In figures 4.16C and 4.16D, tensile strength and modulus of RPU80 decreased with increasing PBD content, similar to VF11. The average strain increased from 45 % to 60 % as PBD increased, which in turn lead to an increase in toughness, as presented in figures 4.16B and 4.16A respectively. These observations were also met with high error, despite exhibiting a yield point. This could be due to the hexanediol diacrylate in CN301, which may have increased crosslink densities. Overall, PBD shows promise as a toughening agent, however mechanical testing revealed toughness did not increase appreciable amounts in these particular formulations.

4.3.3 Macrophase separation of rubber toughened resins during CLIP

Further examination of SEM micrographs from figure 4.13 show that rubber particle size within parts fabricated via CLIP ranged between 1 micron and 10 micron and interparticle distances were inconsistent. Moreover, the content of PBD within the observed cross-sections appeared low relative to the amount loaded within resin. Therefore, samples of freshly blended PBD loaded resin were flood cured and imaged using SEM. A comparison of flood cured freshly blended (static) and printed (dynamic) specimen PBD microphase content and distribution can be seen in figure 4.17.
Unlike printed PBD loaded resin, freshly blended PBD loaded resin SEM images, like that in figure 4.17A, exhibited monodisperse particles with an average size of 1.05 micron with even distribution. Furthermore, it appears that the total amount of PBD that is contained within a printed part is lower than what is loaded into resin. This implies that increased phase size and reduced distribution occurs at some point during the dynamic CLIP process. Figure 4.17C shows the resin pool used to fabricate six tensile specimens immediately after the completion of a print. The darker region located at the center of the resin pool appears to be macrophase separation of PBD from the bulk resin. The macrophase separated region is localized only in a small diameter from where the rectangular cross-sections of the growing parts once were, with resin blend surrounding the area. Additionally, bulk phase separation in PBD loaded resin
causes the rubber phase to float upward, as seen in figure 4.17D, since it is less dense than VF11. Thus, macrophase separation near the base of a growing part would both increase phase size and reduce PBD loading due to phase coalescence and larger phases rising to the top of the resin pool.

Macrophase separation appears to accelerate within resin in a localized region around growing parts during the CLIP process. The cause of this phenomenon can be traced to heat generated during resin photoreactions, like that seen in figure 4.18.

Figure 4.18: Infrared thermal imaging of CLIP fabrication and macrophase separation. (A) Heat is generated during the CLIP process due to exothermic photopolymerization. Heat is localized toward the bottom near window. (B) Physical model of heat generated during the CLIP process. A dark ring forms outward from the heated tip of a cartridge due to macrophase separation.

Elevated temperatures develop at the site of polymerization in the resin and form a small heat ring emanating outward from the part, seen in figure 4.18A, that is of similar shape and size to phase separation observed in the resin pool. This observation was replicated using a controlled
heat source with a similar cross-sectional area to a tensile testing specimen. The photographs in figure 4.18B show that localized heating caused a darkened ring to form from the cylindrical cartridge outward due to phase separation, similar to that seen post-fabrication. Additionally, phase separation occurs within 5 minutes of heating, suggesting that PBD loading within printed parts begins to diminish early in fabrication. Therefore, it can be concluded that heat generated by photocuring resin during fabrication accelerated macrophase separation locally around the part, which decreased phase size and diminished rubber quantities within parts, thus at least contributing to insufficient toughening.

4.3.4 Compatibilization of rubber microphases via diblock copolymer

A PBD-PPO diblock copolymer was successfully synthesized, the purpose of which was to compatibilize microphase separation and maintain their stability within resin. PPO was chosen because of its miscibility in VF11 resin, but not within PBD. Therefore, VF11 resin was used as a base resin, to which 5, 10, and 20 pph of CN303 was loaded. A second set of blends were also formulated at the same loadings but included an additional 5 pph of the PBD-PPO compatibilizer each. Mechanical property results and SEM/TEM micrographs of specimen cross-sections can be seen in figures 4.19 and 4.20.
Figure 4.19: Effect of PBD (CN303; polybutadiene dimethacrylate $M_n \sim 15000$ g/mol), with and without PBD-PPO copolymer compatibilizer, on VF11 mechanical properties. (A) Toughness as calculated by the area under the stress-strain curve. (B) Elongation at break. (C) Tensile Strength. (D) Modulus. Red lines represent the measured average value for neat VF11.

Figure 4.19 shows that the addition of the block copolymer did not enhance compatibility of the PBD and bulk matrix interface and in fact produced decreased toughness relative to parts loaded with neat PBD. SEM images in figures 4.19A and 4.19B show that phase size remained unchanged and that the PBD microphases appeared to have either a granular texture and/or microvoid formation within their centers.
Iodine stained TEM images of specimens that contain compatibilizer in figures 4.20D and 4.20E, revealed that the centers of the microphases tore during cryomicrotome slicing, indicating that liquid compatibilizer was likely trapped within microphases. This reduced the structural integrity of both the microphase and the part, leading to decreased and ineffective overall toughening effect.

4.4 Discussion

Rubber toughening of parts fabricated via CLIP was found to be dynamic in that each component and the process itself influence toughening efficiency. PBD with high/moderate molecular weight and photocurable functionality showed the most promise as a toughener. However, there was a visible disparity between the PBD loading within resin and content within printed parts. One particular challenge in controlling and achieving proper particle size and distribution within parts printed via CLIP is the method with which microphases form. Unlike rubber toughened epoxies, which form microphases over several hours due to slow step growth build up in polymer molecular weight in epoxy reactions, the cure time per layer in
CLIP is often on the order of seconds.\textsuperscript{16,18} Therefore, PBD microphases must form within the liquid resin prior to print. In this sense, microphases are frozen in place within a cured layer and subsequently within the final part.

In practice, PBD loaded resins used in these studies exhibited stability, or lack of bulk separation, for several hours at ambient conditions, much longer than the 40-minute average fabrication time for tensile testing specimens. Despite this stability, macrophase separation was consistently seen within resin in a localized area around the growing parts both during and after fabrication. This phenomenon was replicated using a heating cartridge as a model of reaction heat, though visually the macrophase separation differed from that seen in post-fabrication in both size and shade. This shows that heat accelerates phase separation, but also works in tandem with the process of resin renewal underneath a growing part to form localized macrophase separation. It is conceivable that, just as fillers aggregate in a constriction as discussed in the previous chapter, the combined effect of slower moving resin at the window interface and constricted flow underneath the part lead to a higher chance of microphase coalescence. The same phenomenon can be seen in studies where emulsions microphases were shown to have an increased likelihood of re-coalescence, both at the entrance of a constriction and within shear flow near surfaces.\textsuperscript{48–51} Therefore, a major requirement for rubber toughened CLIP resin development is for microphases to be stable in both thermally and physically changing environments.

A significant challenge in compatibilizer development, and thus the formation of microphase separated PBD, was that the bulk matrix was not a single component. Instead, the majority of VF11 was low molecular weight reactive diluent (~60 wt%; 85 mol%), with the remainder a urethane acrylate oligomer. Moreover, after test results were analyzed it was discovered that the miscibility of PBD in resin was more complex than originally realized. It was demonstrated that PBD was miscible to at least 20 wt% within SR-833-S reactive diluent. Additionally, hexanediol diacrylate is listed as a reactive diluent in CN2920, which PBD is also known to be miscible such as in CN301. This could mean that, within VF11, only part of the PBD formed microphases, while low/moderate molecular weight PBD was slightly solubilized. While it is possible for PBD to microphase separate during crosslink network
formation, the rates of photopolymerization are too fast for this to occur. This behavior, at least partially, explains why the addition of PBD into RPU80 resulted in increased elongation that was larger in magnitude compared to VF11 resins, since the 4-hour thermal post-cure slows network formation. Overall, these experiments and observations further emphasize the need for microphase separations to be present within the liquid resin and/or have the freedom in mobility to microphase separate during a prolonged thermal post-cure.

4.5 Conclusion

To the best of the author’s knowledge, the work presented here represents the first efforts in developing a rubber toughened photoreactive thermoset resin via microphase separation of reactive liquid elastomer oligomers for the purpose of additive manufacturing via CLIP. Characterization techniques from previous work on filled CLIP resins was applied to the systems presented here providing quantitative data useful in describing and understanding reactivity and complex phase behavior changes taking place during fabrication with these heterogeneous formulations. Effects on ultimate strain and toughness due to the addition of polybutadiene into CLIP resins suggest that the formation of microphases within liquid resin to form rubbers within solid parts shows promise. However, heat from the resin reaction and the increased chances of droplet coalescence due to constricted flow show that resin must be robust in order to achieve microphases of the right size and distribution within CLIP parts. As such, careful choice of base resin and rubber, taking into consideration molecular weight, component miscibility, and stability in thermal and constricted environments could lead to increased toughness similar to that seen in rubber-modified epoxies. With proper decisions at every point in resin formulation, rubber toughening of CLIP resins shows potential as an added design choice for material development.
4.6 Acknowledgements

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4.7 References


Chapter 5: Summary and Recommendations

5  Summary and Recommendations

5.1  Summary

The main objectives of this dissertation were to characterize the effect of the addition of inorganic solid fillers and liquid oligomeric rubbers to resins on the dynamics of Continuous Liquid Interface Production (CLIP). The work presented here is the first study in developing particulate composites directly for CLIP, and understanding their impact on the process from deadzone formation to filler location in fabricated parts. Utilizing an established technique, deadzone formation was found to decrease with the addition of filler, likely due to reduced oxygen permeation into resin. Moreover, decreased and/or constant resin cure dosage and constant double bond conversion (DBC) from a UV light pulse confirm that the addition of filler into resin can cause tortuosity within resin (Chapter 2). With this in mind, parts were successfully fabricated using particulate filler loaded resins for the purpose of describing ultimate filler location (Chapter 3). Small particles (~1 micron diameter) exhibited even loading across the entirety of parts, whereas large particles (~10-25 microns) where found to exhibit drastically decreased loading at the center of cross-sections. Custom microfluidic channel fabrication and observation via microscope revealed that large particles were susceptible to clogging when flowing through a constriction similar in dimension to the gap during CLIP. Thus, it was concluded that particle deposition at the window/resin interface caused the formation of an intermittent clog, resulting in heterogeneous particle distribution within CLIP fabricated parts.

Finally, the techniques described above were used to aid in the development and characterization of parts fabricated using resins blended with reactive liquid elastomers via CLIP. The addition of reactive elastomer oligomers caused deadzone thickness to increase regardless of molecular weight or functionality, even at high light intensities. This was likely due to increased oxygen solubility within polybutadiene, leading to an overall increased oxygen permeability into the resin. Nevertheless, tensile testing specimens using (liquid) polybutadiene- resin blends were fabricated using Carbon’s M1 CLIP printer and tested to
evaluate the toughness due to in situ rubber microparticle formation. PBD with photoreactive functional groups resulted in specimens with increased toughness (calculated as the area under the stress-strain curve) compared to the specimens that contain PBD that lacks photoreactive functional groups. Average elongation and area under the stress-strain curve increased with the addition of high molecular weight PBD, though with high standard deviation. This was at least partially attributed to accelerated macrophase separation near the growing parts due to heat generated during photopolymerization. Furthermore, partial miscibility of PBD within the bulk resin likely reduced the content of microphase separations during fabrication. Nevertheless, the addition of reactive microphase liquid elastomers shows potential as method of toughening brittle thermosetting resins for CLIP.

5.2 Recommendations

5.2.1 Improving deadzone thickness formation and characterization

The technique used to measure deadzone thickness was adapted from a previously established technique and used as a tool in describing the influence of solid filler and liquid microphases on oxygen permeability in resin.\(^1\) Experimental results with particulate-filled resins agreed with previous studies suggesting that the addition of filler, even in the micro range, can reduce oxygen permeability.\(^2\)–\(^4\) While kinetic data and cure dosage experiments helped confirm this phenomenon, oxygen diffusivity, and subsequently permeation, into these resins was not directly measured. Thus, the measurement of gas diffusivity through liquid resin, filled or unfilled would complement the results presented in this dissertation. Several techniques exist for measuring gas diffusivity through polymer thin films, and some have been adapted for use with shallow liquids.\(^5\)\(^,\)\(^6\) Furthermore, few studies have explored the effect of particulates, micro or nano, on gas transport in liquids. Therefore, the direct measurement of oxygen diffusivity in filled resins would allow predictions to be made prior to experimentation. These measurements would resin development and deadzone modelling for both filled and unfilled systems, thus further improving overall CLIP material development.
5.2.2 Development of filled resins with high aspect ratio particulates

Studies in this dissertation focused almost exclusively on the use of spherical fillers and phases within resins. As mentioned in chapter 1 however, the use high aspect ratio fillers is preferred in composites because of their larger surface area, which allows for bulk reinforcement. Figure 5.1 shows an initial investigation on the effect of the addition of 15 pph high aspect ratio glass flake (GF) in RPU80 resins.

![Figure 5.1: Mechanical properties of RPU80 loaded with 15 pph glass flake.](image)

Average Young’s modulus increased at all orientations about 10 %, and average tensile strength increased in X and Y orientations by ~8 % in parts filled with GF relative to neat RPU80. These results show that parts can be reinforced with the addition of filler. Moreover, elongation at break for these samples drastically decreased from an average 50 % to 7 %. This is common in polymer composites, as filler acts increases stiffness (modulus) and has been shown to decrease elongation in parts fabricated with filled photocurable resins. It should be noted however, that SEM micrographs of the neck portion of tensile testing specimens (figure...
5.2) revealed that filler orientation was effectively random regardless of the orientation during fabrication.

![Figure 5.2: SEM micrographs of RPU80 filled with 15 pph glass flake. Filler orientation is unchanged across three orientations.](image)

The example above serves to point out the challenge of filler orientation during fabrication particulate-filled resins for CLIP using high aspect ratio filler. Unlike extrusion based 3D printing that can orient fibers inherently through filament deposition, CLIP does not introduce external mechanical agitation to the resin during fabrication. It could be argued the suction force during resin renewal could aid in filler orientation, but this would likely only occur in parts with large (>10 mm diameter) cross-sections. This relates back to issues in printing with thixotropic resins, where the suction force experienced by resin decreases greatly with even small decreases in cross-sectional area (Stefan Adhesion equation 3.1, Chapter 3). Moreover, figure 5.3 shows how resin renewal under a growing part occurs toward the center of a cross-section from its perimeter.
Inherent filler orientation due to the CLIP process would only ever be radially inward for simple shapes like circles or squares. Long shapes like rectangles may exhibit orientation, though their ends would also exhibit varied orientation. Additionally, complex shapes with concave features would exhibit effectively random orientation.

Particulate orientation in filled part fabrication via CLIP must therefore be achieved by other means. One potential would be to move the part and/or the resin cassette laterally during fabrication to introduce shear unto the resin. This could be done during the or immediately after a part has stepped or oscillated up. Empirical measurements using a shearing instrument such as a photorheology could help determine the shear rates and shearing time needed to achieve filler alignment. In this way, a shear could be applied at a certain rate and time to a thin film of filled photocurable resin, then stopped and cured using UV light. Filler orientation could then be determined using microscopy. A challenge with this method would be potentially high required shear rates or shearing times, which could result in damage to thin or fragile parts with low green strength.

There also exist non-mechanical methods of filler orientation in photocurable resins, demonstrated using controlled magnetic fields. Martin et. al. detailed the use electromagnetic solenoids to monolithically align of magnetically labeled alumina particles with high aspect ratio in photocurable 3D printing resins.\textsuperscript{12} They were able to achieve highly orientated particles with increased modulus and hardness over an unfilled control. Moreover, they show that particles aligned parallel to tensile stress exhibited modulus and hardness by 29 % and 23 %
respectively over perpendicular alignment. Interestingly, their method was able to control alignment of multiple areas of a layer (figure 5.4) to produce patterns with unique predictable failure mechanisms.

![Figure 5.4: Crack steering with magnetically aligned filler in 3D printed parts. Scale bar = 4mm. Reprinted from reference.](image)

Filler alignment times vary depending on fluid viscosity, magnetic field strength and direction, and the initial position of the particles. As such, alignment time can vary between a few seconds at low viscosity (~1 cP) to over a minute (> 1000 cP). This could be viewed as a potential drawback, since alignment times will decrease overall fabrication rates.

5.2.3 Microphase separation stabilization via the addition of filler

As discussed in chapter 4, microphase size and distribution in parts fabricated via CLIP was found to be larger than desired. One method of improving compatibilization is through the
addition of solid fillers within the polymer blend.\textsuperscript{13–15} Physically, the filler acts to break-up larger phases into smaller phases. Chemically and thermodynamically, the addition of filler can decrease the free energy of mixing by introducing interactions between each polymer and the filler, as shown in equation 5.1.

\[
\Delta G_{\text{mix}} = \Delta G_{AS} + \Delta G_{BS} - \Delta G_{AB} \tag{5.1}
\]

Where $\Delta G_{AB}$ is free energy of mixing the two polymer components, and $\Delta G_{AS}$ and $\Delta G_{BS}$ are the free energy of mixing between either component and the solid filler.\textsuperscript{16} Thus, in one case the $\Delta G_{\text{mix}}$ will always be negative when both polymers absorb on the filler surface. Alternatively, if only one component is attractive, then the miscibility will depend on the strength of interaction and the interaction parameters. High aspect ratio nanoclays are often the filler of choice due to their high surface area potential and ability to be organically modified to better interact with a wide variety of polymers.\textsuperscript{13,17} Therefore, it is conceivable that the combination of solid fillers and reactive liquid microphases would result in more stable resins. One can imagine the two additions acting synergistically, where the high aspect ratio nanoclay would act to reinforce and potentially increase tensile strength, while the rubber phase would improve toughness and impact strength. The main challenge in developing these sorts of materials would be maintaining resin viscosity. Work in Chapter 3 showed that nanoparticles can lead to thixotropy in liquid resins which greatly reduced their printability in CLIP. This could also become a potential benefit in the case of rubber toughened systems. Thixotropic resins could maintain microphases size and distribution by reducing the chance of phase interaction (coalescence). In this way, the fabrication process would have to be adapted to introduce intermittent agitation near the growing parts to ensure the resin will flow.

### 5.3 References


