The Pennsylvania State University

The Graduate School

INDEPENDENT AND INTERCONNECTED INTERPENETRTING POLYMER NETWORK FORMATION IN DUAL-CURE THERMOSET RESINS

A Dissertation in

Materials Science and Engineering

by

Jessica W. Kopatz

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Submitted in Partial Fulfillment

of the Requirements

for the Degree of

Doctor of Philosophy

May 2021

The dissertation of Jessica W. Kopatz was reviewed and approved by the following:

Michael Lanagan Professor of Engineering Science and Mechanics Associate Director, Materials Research Institute Associate Director, Center for Dielectric Studies Dissertation Advisor Chair of Committee

Michael Hickner Professor of Materials Science and Engineering, Chemical Engineering Corning Faculty Fellow

Robert Hickey Assistant Professor of Materials Science and Engineering

Ram Rajagopalan Assistant Professor of Materials Science and Engineering Assistant Professor in the Department of Engineering Applied Materials

Leah N. Appelhans Special Member R&D S&E in Organic Materials Science Sandia National Laboratories

John C. Mauro Professor of Materials Science and Engineering Chair of the Intercollege Graduate Degree Program in Materials Science and Engineering

ABSTRACT

Thermoset polymers are of interest for many structural applications due to their mechanical, thermal, and chemical resiliency in comparison to thermoplastic polymers. However, utilizing thermosets in the realm of additive manufacturing is still a developing field, especially when using viscous thermosets where long cure times can limit the shape retention of 3D printed parts. There has been increased interest in the development of direct-ink-write (DIW) methods for thermoset resins in the last several years. The approaches generally fall into two categories; dual-cure systems or filled resins.

Dual-cure resins are comprised of multiple thermoset polymers that are cured using different stimuli or variations of the same stimuli (i.e. temperatures, wavelengths, etc.). Common dual-cure thermoset resins consist of a photo-curable acrylate and a thermally-curable epoxy. For sequential dual-cure systems, the photo-cure mechanism can be rapidly completed immediately after extrusion from the print tip in order to lock-in the desired structure, while the sequential thermal cure forms the epoxy network and enhances the composite properties. Sequential curing of the resin, via UV exposure followed by thermal exposure, creates interpenetrating polymer networks (IPNs), which can enhance the overall thermomechanical properties compared to either parent material.

IPNs consist of two or more networks that are interwoven on a molecular scale. Though the networks are not covalently bound to each other, they cannot be separated unless chemical bonds are broken. Independent IPNs exist where there are two separate but interwoven networks, while interconnected IPNs form by the addition of a heterobifunctional monomer that links the two networks together. Interconnected IPNs are expected to result in the best properties due to the tethering of the two otherwise separate networks. The filled resins approach to the DIW of thermosets generally require the material to possess high zero-shear viscosity, shear thinning behavior, and controlled curing. High zero-shear viscosity permits shape retention post-extrusion, while shear thinning enables the fluid to flow easily through the print head. To enable shear thinning, fillers such as clay or silica are added, where the filler is usually modified to enable better dispersion within the polymer matrix. Not only does the addition of inorganic fillers alter the rheology and printability of the resin, the fillers can also impact the thermomechanical properties of the composite.

This thesis describes the influence of resin composition on the printability and 'green strength' of printed parts. After the sequential thermal cure in the dual-cure system, the impact of acrylate network formation on the evolution and formation of independent IPNs was investigated. Moving to a more simplified dual-cure acrylate-epoxy resin system, the impact of acrylatefunctionalized and epoxy-functionalized filler particles as network crosslinkers was explored. Finally, the influence of heterobifunctional acrylate-epoxy hybrid monomers with differing backbones on the formation of interconnected IPNs was investigated.

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ACKNOWLEDGEMENTS

To start off, I would like to thank my Penn State advisor, Mike Lanagan, and Sandia advisor, Leah Appelhans. Without your help, guidance, and encouragement, I would not have been able to obtain this degree. I would like to thank Mike for being willing to advise me from the other side of the country. He mirrored my excitement and did an amazing job navigating through these uncharted waters. Mike has an incredible amount of patience, kindness, and wisdom of which I am eternally grateful. Thank you, Dr. Lanagan, – it has been a thrilling adventure and a joy learning from you.

Additionally, I would like to thank Leah for investing a tremendous amount of time in me during my graduate internship at Sandia. I met Leah at a CDP conference that we were both attending, and from her presentation and our conversations, I realized she was a brilliant, dedicated, hardworking, and humble individual. These qualities make her an incredible scientist and had me asking her for a summer internship. That internship led to the contents of this theses, and for that I am indebted. Leah has challenged me, taught me, and encouraged me throughout the course of the Ph.D., and I would not have flourished without her. Thank you, Leah, for taking me on and for teaching me how to become an incredible scientist.

I would also like to thank the staff members in my Sandia department who have helped me, taught me, and supported me throughout my thesis work. First, I would like to thank Patti Sawyer, you were the first individual I befriended, and I'm so happy to call you my close friend. You are one of the smartest and most kind-hearted individuals that I know. Erica Redline, I would like to thank you for your constant willingness to meet with me and answer random questions, regardless of the time of day. Adam Cook, I am so grateful for our conversations, your honesty, and your guidance. You made printing samples a blast and you taught me how to be a more effective communicator. Brad Jones, I would like to thank you for the many polymer physics conversations we had and for also answering random questions when they arose. John Schroeder, I would like to thank you for our many conversions, book suggestions, cryptograms, and for offering never-ending support throughout my internship. Robert Bernstein, I would like to thank you for your honesty and never waning support. I am forever thankful for all our conversations.

I would like to thank other past and present Sandians that helped with this work. Jackie Unangst, who was a postdoctoral scholar and was always willing to have me bounce ideas off her. Shelby Beasley, who was an undergraduate intern and spent a summer helping me functionalize and print fumed silica. Eric Coker, Jessica Kustas, Sara Dickens, Samantha Rinehart, and Ana Baca, who helped run analysis on a few samples.

I am very grateful for my Penn State friends who have helped me in one way or another and have made this experience one for the books. Thank you: Travis Carroll, William Ferrell, Zelong Ding, Kathleen Coleman, Mike Vecchio, Tom Nigl, Sarah Masters, Joseph Roth, Amy Goodling, Alex Molina, Ian Campbell, Josh Bostwick, and many others.

I would also like to my family – especially my Rosh family. 'Mom', you are always so supportive, and you keep me grounded. You helped me through all the ups and downs, no matter the situation, and always managed to make me smile. Anya, you're my best friend and always helped me, no matter what. Uncle Larry, I owe you a pair of golf clubs when this is over. I haven't forgotten. Brooke, my little 'mini-me', this was all for you. I hope you strive to be the best that you can be, and never let anyone hold you back.

Last, but certainly not least, I would like to thank my husband. Jeff, you have done nothing but support and encourage me, even as we spent the duration of this thesis on opposite sides of the country. You have been my sounding board and have been my rock during stressful times. I love you. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Note: The findings and conclusions do not necessarily reflect the view of the funding agency.

CHAPTER 1 : MOTIVATION AND THESIS ORGANIZATION 1.1 Introduction

Direct-ink write (DIW) of thermoset materials relies on the extruded material to maintain shape after extrusion. Dual-cure thermoset resins offer a solution where two curing mechanisms simultaneously or sequentially polymerize two different monomers. For use in DIW, there must first be a rapid curing mechanism of one resin constituent to enable the shape retention of a green body. Following the print, the second resin constituent can be activated by a slow curing mechanism to transform the green body into a fully cured component. Additionally, dual-cure printing of thermosets can overcome typical 3D printed component inhomogeneity by allowing the diffusion of monomers across the interfaces during the formation of the second network after the second cure step. The property homogeneity of the dual-cure DIW thermosets has not been extensively studied in literature. The resulting network formed via dual-cure systems is known as an interpenetrating polymer network (IPNs), and the formation and homogeneity of this network dictates the material properties of the printed component.

The current thesis extends on previous research by investigating the influence of resin composition, *in situ* UV print intensity, functionalized filler materials, and heterobifunctional monomers on the formation of independent and interconnected IPNs of dual-cure thermoset materials used in DIW. This thesis explores how the green strength and print fidelity of the print cured parts are impacted by acrylate content and *in situ* UV cure intensity. The green strength of the printed part dictates the complexity of the prat that can be printed.

This thesis also aims to understand how the extent of acrylate network formation impacts the IPN homogeneity and thermomechanical properties after the sequential cure step and after the epoxy network has formed. The thermal cure profile chosen to cure the epoxy network can significantly impact the phase separation and mechanical properties of the resulting IPN. Additionally, this thesis investigates how the type of filler and filler surface modification influences the rheology, cure kinetics, and post-print properties in dual-cure thermoset materials. In DIW, fillers are added for the primary purpose of controlling rheological properties, but this thesis goes one step further and gives the fillers a dual-purpose. Functionalizing the filler surface with acrylate groups and epoxy groups will allow the filler to form parts of their respective networks. Therefore, a fundamental understanding of how surface functionalization impacts dispersion and network formation is necessary.

Lastly, this demonstrates the influence of two different heterobifunctional monomers on the formation of interconnected interpenetrating polymer networks. This work extends on prior research by understanding the influence of heterobifunctional monomer structure on the rheology, cure kinetics, and thermomechanical properties. The formulations investigated contain either glycidyl methacrylate or bisphenol A epoxy-acrylate as the heterobifunctional monomers.

1.2 Goals

The goal of this dissertation is to further the fundamental understanding of the formation of independent and interconnected interpenetrating polymer networks (IPNs) in dual-cure thermoset resin systems and how IPN formation effects the resulting cure kinetics, rheology, and thermomechanical properties. There are three major areas of research focus in this dissertation, with the commonality of understanding the formation and properties of interpenetrating polymer networks (IPNs) in dual-cure thermoset resins for use in direct ink write additive manufacturing. The first part of this thesis explores new dual-cure thermoset resin formulations to understand how composition and cure profile impacts the formation of independent interpenetrating polymer networks (Figure **1-1** left). Having studied the behavior of unmodified IPN networks, the next step was to investigate the addition of surface functionalized fillers on the formation and properties of IPNs. The second part of this thesis involves utilizing epoxy-functionalized and acrylate-functionalized fillers to crosslink the epoxy network and acrylate networks, respectively, with the goal of achieving improved material properties by controlling network formation and improving filler-matrix adhesion (Figure 1-1 middle). Having investigated the properties of independent IPNs, the next step was to investigate the formation and properties of interconnected IPNs using heterobifunctional monomers. The final part of this thesis explores the influence of hybrid monomers on the formation and properties of interconnected interpenetrating polymer networks (Figure 1-1 right), where the two independent networks are linked together using hybrid monomers.



Figure 1-1: Types of interpenetrating polymer networks explored

1.3 Thesis Organization

This following chapters of this thesis examine the relationship between dual-cure resin formulation and the material properties of the resulting independent or interconnected interpenetrating polymer networks.

- Chapter 2 outlines the background and previous work done in the field of dual-cure thermoset resins and interpenetrating polymer network formation. Additionally, Chapter 2 introduces additive manufacturing techniques with an emphasis on direct ink write, interpenetrating polymer networks, surface functionalization of filler materials, and hybrid heterobifunctional monomers.
- **Chapter 3** discusses the filler functionalization procedure and reaction chemistry in addition to the experimental set-up and characterization used thought-out the remaining chapters of this thesis. Chapter-specific procedures are discussed in detail in the respective chapter.
- **Chapter 4** explores the influence of acrylate content and *in situ* print intensity on the cure kinetics, printability and green strength of a dual-cure thermoset resin. The acrylate resin content and print conditions were shown to affect both the green strength and printability of the DIW parts. These results suggest that mechanical properties of a green part can be tailored by changing the resin formulation and *in situ* print intensity.
- **Chapter 5** investigates the formation and homogeneity of independent IPNs after the sequential thermal cure and epoxy network formation of the samples investigated in **Chapter 4**. The impact of acrylate network formation and thermal cure profile on the thermo-mechanical properties of the fully cured components are studied. These results suggest that the IPN homogenization

is dependent upon the thermal cure profile, but that the thermomechanical properties are not.

- Chapter 6 explores the influence of epoxy-functionalized and acrylatefunctionalized fumed silica and montmorillonite clay on the cure kinetics, network formation, and mechanical properties of particle-integrated independent IPNs. The TGA/MS results show successful silane grafting to the surfaces of the filler materials. The addition of the functionalized fillers altered the rheology of the resins. The results also suggest that the surface functionalization does not significantly influence the cure kinetics or thermomechanical properties of the composite. This is likely due to insufficient surface functionalization and particle agglomeration.
- Chapter 7 examines the influence of two heterobifunctional monomers on the formation of interconnected interpenetrating polymer networks. The rheology, cure kinetics, green strength and thermomechanical properties of are investigated. These results suggest the addition of the heterobifunctional monomers do not significantly influence the thermomechanical properties or mitigate phase separation within the composite, likely due to the inherent highly crosslinked acrylate and epoxy networks.
- **Chapter 8** summarizes the findings of this thesis and outlines proposed future work that relates to the studies that are presented in this thesis.

CHAPTER 2 : BACKGROUND

2.1 Additive Manufacturing

Additive manufacturing (AM) is rapidly drawing interest as a method to create costeffective prototype parts [2] or low-volume, custom, and complex geometrical parts. One huge benefit of AM is that it results in minimal material waste compared to injection molding or subtractive manufacturing methods, such as milling or machining. AM produces parts made of many different materials ranging from metals, polymers, ceramics, and composites [3]. The four most commonly used methods of AM consist of fused filament fabrication (FFF), stereolithography, selective laser sintering (SLS), and direct-ink write (DIW). While these methods result in 3D structures, they rely on very different printing approaches and printing materials [4].

2.1.1 FFF

FFF, also known as fused deposition modeling, involves printing with a continuous

filament composed of a thermoplastic polymer [5]. The thermoplastic nature of the polymer enables it repeatedly to flow when heated and solidify when cooled, compared to a thermoset which solidifies under heat and cannot be melted. Thus, a thermoplastic polymer can be compounded and melted, then extruded into a roll of filament. As demonstrated in Figure **2-1** [6], this roll of solid filament then gets fed into a printer nozzle where it is locally heated, re-melted, and then



Figure 2-1:Example of an FFF set-up

extruded onto a print bed platform or previously extruded layers where it then solidifies [7]. The fusing of layers is dependent on crystallization and chain entanglement of the thermoplastic [3].

The layer thickness, gap size between printed layers, print speed, and print bed temperature are all parameters that can be adjusted to change the mechanical properties of the printed parts [8]. A few challenges of FFF consist of limited material variety due to the material needing to be a thermoplastic, anisotropic mechanical properties, inhomogeneity in microstructure, as well warpage and delamination of the part as it is being printed. As the number of printed layers increases the thermal differential within the part increases resulting in variable shrinkage as it cools. The thermal gradient increases as the distance between the heated nozzle and heated print bed increases. This causes differences in microstructure, which directly impact the mechanical properties of the printed parts. The resulting thermal strain often causes warpage and occasional cracking of the printed part. Delamination can also be a result of shrinkage of the printed part as well as poor adhesion of the thermoplastic material to the print bed material. When the printed part begins to delaminate, the dimensions of the printed shape are altered to where it no longer matches the intended design that was created in the CAD/SolidWorks/etc. software. If the part completely delaminates, the part can be dragged around with the print nozzle and can clog the nozzle, which could potentially damage the machine.

2.1.2 SLA

Stereolithography (SLA) utilizes UV radiation to progressively cure thin layers of UVreactive polymers to build a 3D shape. The liquid monomers, usually acrylate-based or epoxybased, polymerize into polymer chains via free-radical polymerization when exposed to UV light [5, 9]. The print platform begins submerged in a bed of liquid resin where a light source locally polymerizes the resin into a pattern onto the print bed [10]. The platform then ascends a distance of a single layer where the photopolymer recoats the printed part, as the laser cures each sequential layer to the previously cured layer [9]. The two types of SLA are bottom-up, where the laser cures resin from the top as the print bed moves down into the resin bed, and top-down,



where the laser cures the resin from the bottom of the resin bed as the part is pulled up out of the resin bed, shown in Figure **2-2** [9].

Figure 2-2: SLA techniques, bottom-up (Left) and top-down (Right)

The polymer typically must have low viscosity for the excess, unreacted polymer to be removed after the part is printed as well as to allow for easier molecular alignment during cure resulting in improved electrical and piezoelectric properties [11]. The cure kinetics of the polymer material, the choice of light source, the exposure time and the shelf-life of the resin are the main parameters that control the properties of the printed parts[12]. To improve mechanical properties, a post-print curing step(s) may be necessary due to incomplete conversion of reactive groups. SLA can have a resolution of around to 20 microns, and the technique uses small amounts of resin material compared to SLS [9], but larger amounts compared to DIW or FFF. Currently, SLA only allows use of a single resin at a time [9].

2.1.3 SLS

Selective laser sintering (SLS) is a type of process that falls under the umbrella of powder bed fusion processes. This technique relies on a laser to selectively sinter powdered material forming a 3D structure via a particle-particle fusion binding mechanism. Each subsequent layer is created by rolling loose powder across the previously printed layer and then fusing the powder via a laser source as shown in Figure 2-3 [6]. The laser locally elevates the temperature at the surface of the powder causing local melting and fusion. Excess, unfused powder is then removed by blowing air, vacuuming, or vibration [13]. SLS is generally used for thermoplastic polymers, metals, and alloys that have relatively low melting/sintering temperatures and for ceramic powders dispersed in a liquid

binder [14]. The properties of the printed parts depend on





the laser power, scanning speed, particle size distribution and packing of the powder, where the latter two significantly impact part density. Post-print sintering of the printed part is sometimes used to enhance mechanical properties, especially in processes where a liquid binder was used. While SLS parts can have a resolution of around 100microns [3], the printed parts tend to have high porosity [14]. The amount of material necessary for SLS is generally much greater than that required of DIW, FFF, or SLA.

2.1.4 DIW

DIW involves the continuous extrusion of a viscous ink that is generally composed of a shear-thinning material. DIW is similar to FDM in that both are extrusion-based methods [7]. In DIW as pressure is applied, the ink flows out of the nozzle, due to the shearthinning induced decrease in viscosity, while quick viscosity recovery enables shape retention post-extrusion, as seen in Figure **2-4** [15]. The extrusion of the ink in a layer-by-layer sequence then creates a 3D shape[16-18]. Post-print, the parts generally undergo an additional cure process, such as a UV or thermal cure, to completely lock-in the printed structure and to remove binding medium, while also improving mechanical properties [5, 10]. Nozzle size, pumping



Figure 2-4: Direct-ink write printer example

ratio, table speed, and bead overlap are printing parameters that can be varied to impact the resulting properties of the printed part, while the cure profile impacts the final properties of the printed part[19]. One major advantage to DIW is the variety of materials that can be printed using this method, which range from ceramics, to metals, to polymers. The inks are generally loaded with ceramic- or metal-particles, which are then thermally converted into ceramics and metals. Polymer resins are mixtures of acrylates, epoxies, and other oligomers that are often silica- or clay-loaded to achieve desired rheological [1], mechanical [20], and thermal properties[2]. Some challenges with printing materials, such as acrylates, are shrinkage during printing and polymerization reactions that are inhibited by oxygen [21]. Shrinkage causes a build-up of residual stresses, as the part is printed layer-by-layer, and results in warpage of the printed part. The inhibition of polymerization can result in parts that are not fully cured and therefore do not retain shape while being printed. One way to combat such challenges are by adding epoxy to the otherwise neat-acrylate system. One major printing concern is clogging, which can occur if the

ink does not experience shear thinning or if the particle diameters are close in size to the nozzle diameter [16]. Another concern is the resin viscosity being too low, which would leak out of the nozzle, or too high which would require dangerously high pressures to be extruded [22]. Print resolution for DIW depends on the ink selection and nozzle size, which can range from as small as 160 microns to as large as 1.55mm in diameter. The resolution of DIW is dependent upon the choice of ink material and nozzle size [23]. DIW is discussed in more detail in section 2.2 Direct-Ink Writing.

Each individual AM technique has its own benefits and drawbacks. The main benefit of AM processes is the freedom to design complex custom parts, where the printed structures are limited by printer technology, materials properties, and CAD design [3]. However, like any process, AM does have its drawbacks. Currently, AM methods tend to be costly, time consuming, and have limited applications in mass production [3]. AM printed parts also can have more defects and possess anisotropic mechanical, electrical, and thermal properties, compared to traditionally molded parts [14]. These anisotropic properties can result from the layer-by-layer nature of the printing techniques, if the interlayer or inter-filament adhesion is poor relative to inlayer adhesion. This can cause the interlayer adhesion to dominate the mechanical properties and result in significant anisotropy relative to the print direction.

2.2 Direct-Ink Writing

This thesis work will focus on the development of thermoset resins for DIW, thus a more in-depth examination of the resin material properties, such as rheological requirements and cure kinetics, as well as understanding the capabilities of the printer itself is presented here.

Epoxy and composite materials have been sought after for many structural, mechanical, and thermal applications due to their inherent material properties [2]. Traditionally, epoxies and other thermoset materials have been fabricated via curing reactive materials in a mold [2]. Directink writing offers a low-cost method to construct either simple or geometrically complex threedimensional structures having a wide range of material properties based upon ink or resin material selection [5]. Thus far, most DIW material research has been primarily focused on printing colloidal gels and metal alloys in liquid forms [17]. A post-print cure step is usually necessary to solidify the ink through evaporation, gelation, or exposure to elevated temperature or to form a secondary network as is common in dual-cure systems. While many materials are being studied in research applications, there are few commercially available materials that can fulfill desired properties [24] or be printed unmodified using DIW. This is often due to the short shelf lives and specialized rheological properties required for the neat inks. Therefore, there is a need for materials innovation.

2.2.1 DIW Printing Process and Material Requirements

The process involved in DIW requires the design of a part, determination of resin printability, and post-print characterization. To design a desired object, a design software such as CAD or SolidWorks is utilized where an STL file is exported. Once designed, the STL file is then opened using a slicer program which slices the designed structure into individual layers. The properties of these layers, such as the distance between layers and individual bead overlap which influences the resulting mechanical properties, can be manipulated in the slicer software. Once the designed part is ready, it can be printed.

The printability of resin was investigated by Duty *et al.* [7] and is determined by pressure-driven flow at the printer's steady-state flow rate, shape retention post-extrusion, the ability of the resin to span unsupported gaps, and dimensional stability. The viscosity must be such that the resin reaches the volumetric flow rate required for printing at steady-state as pressure is applied to the ink-filled syringe without maxing out the pressure of the machine [7]. The stead-state flow results in a consistent volumetric extrusion of the resin. If too high of a

pressure is required to reach steady-state flow, then the syringe could plastically deform or break, resulting in an un-printable resin. As the material is extruded, it is also important that the bead maintain its shape and dimension, rather than thinning out under gravity. Spanability measures the ability of the resin material to support the entire weight of the deposited bead or filament across a gap or unsupported space without sagging or geometric change. This requires the printing speed and rate of solidification of the spanned bead to be similar, so that the bead geometry is maintained [3]. Dimensional stability means that the resin does not excessively shrink when subsequent layers are deposited or when the bulk printed part is cured. Excessive shrinkage will result in parts with dimensions that do not match that of the original design. These printability properties are largely determined by the rheological properties and cure chemistry of the inks or resins.

A fundamental knowledge of the rheological properties is essential when designing inks or resins for DIW because this property dominates all the printing criteria previously mentioned. DIW resins are usually shear thinning materials, also known as pseudoplastics, where the shear thinning behavior can be quantified using the Equation **1-1**.

Equation 1-1: Power Law Equation

$$\eta = K \dot{\gamma}^{n-1}$$

Where η is the viscosity, $\dot{\gamma}$ is the shear rate, n is the shear thinning exponent, and K is the consistency index. When n is <1, then the material exhibits shear thinning behavior, while n>1 for shear thickening fluids. Pseudoplastic resins exhibit a decrease in viscosity while exposed to a shear stress, but quickly recover their initial viscosity upon removal of the shear stress [25]. This viscosity recovery enables the materials to 'set' rapidly after being extruded. Most DIW shear

thinning inks are types of colloidal suspensions. For printing of pre-ceramics or metal inks, the metal/ceramic particles themselves make up the colloidal suspension. However, DIW of polymer resins is possible through the incorporation of fillers, resulting in shear-thinning behavior and an

increase in the zero-shear viscosity as demonstrated in Figure **2-5** [1]. The shear thinning behavior in colloidal suspensions is believed to result from the breaking of the particle-particle bonds within the resin matrix once the applied stress overcomes the yield point, that is, the shear stress at which a material begins to flow [17].



Figure 2-5: Increased zero-shear viscosity with increased filler content [1]

2.2.2 Filler Materials

It is important to mention that, while it may be possible to extrude some Newtonian fluids, these fluids are incapable of maintaining their shape postextrusion. However, Newtonian materials can be printed, as can other materials with low stiffness, by using structural supports consisting of sacrificial materials [5]. Another method used to extrude

Newtonian fluids is to introduce filler particles into



Figure 2-6: Yield stress values increase with increased clay filler content [1]

the system to induce shear thinning [1]. Organo-modified clays and fumed silica are the most common filler materials used to modify the rheology DIW resins [1], where the clays tend to result in anisotropic mechanical properties due to their plate-like morphology compared to the isotropic properties of spherical silica. Many different types of clays have been utilized ranging from mixed mineral thixotropic clays, such as Garamite®, to surface modified montmorillonite clays such as Cloisite®. Garamite® is a mixture of bentonite and sepiolite clays that are specifically designed to alter the rheology of the medium they are dispersed in [26], while Cloisite® clays are designed to enable dispersion based upon a medium's polarity due to surface modification [27-29]. In addition to inducing shear thinning behavior and increasing zero shear viscosity of neat resin, the storage moduli of filled resins exceeds the loss modulus which results in the inks displaying solid-like behavior, as opposed to liquid-like behavior, at low stress. As filler content increases, the yield stress values increase, as seen in Figure **2-6** [1]. This is due to the addition of more solid-like material effectively thickening resin and making the material more solid-like in behavior.

Yet another approach used to print Newtonian fluids, that avoids sacrificial materials or relying on heavily-loaded systems, is to use UV-exposure or rapid thermal curing of reactive materials to maintain structure after extrusion. Such systems containing multiple reactive constituents are called dual-cure systems.

2.3 Dual-cure Systems in AM

Dual-cure systems are a way to synthesize thermosets via a combination of different but compatible polymerization reactions. The combination of such reactions allows the tailoring of the reaction chemistry, reaction rate, and resulting material properties. For example, the addition of flexible oligomers to neat acrylate resins overcomes the drawbacks of shrinkage and embrittlement caused by high amounts of crosslinking resulting from fast free radical polymerization [2, 24]. Dual-cure systems offer the benefit of combining different reactive stimuli (i.e. light exposure, temperature, kinetics) to create a network that is structurally stable after exposure to one type of stimulus and to enhance properties (mechanical, thermal, etc.) after exposure to the other reactive stimulus. In dual-cure systems, a stable network is produced *in situ*

during the first cure of the dual-mixture[2, 30]. This network holds the shape of the printed structure post-DIW printing. After the first-polymerization reaction, the second polymerization reaction is initiated which further cross-links the system to enhance the material properties [30, 31]. The network formations that result from dual-cure systems are called interpenetrating polymer networks.

2.3.1 Interpenetrating Networks

The development of interpenetrating polymer network (IPN) structures have been of interest to study they as improve mechanical and thermal properties within an epoxy composite[2]. The improvement is due to the micro-heterogenous morphology that is intrinsic to the formation of two or more intertwined polymer networks, which results in a broadening of the glass transition temperature Ink and increased range of damping behavior [32]. Homogeneous Several categories of IPNs exist, but the focus of this research involves the formation of

sequential IPNs where the formation of the first polymer network is then sequentially followed by the formation of the second network [30, 32]. The two networks are not covalently bound to each other but are instead formed

Mixture of Resin UV-exposure Heat exposure



around and within each other, so they cannot be separated unless chemical bonds are broken. Figure 2-7 represents the formation of sequential IPN, which can result from a UV curable and thermally curable dual-cure system. Within a dual-cure system, a UV-curable resin forms a network capable of maintaining the printed structure, via photopolymerization, after UV curing. The epoxy oligomer then creates an IPN composite after thermal curing, which results in enhanced mechanical properties relative to the neat UV-cured resin [2, 30, 33]. IPNs formed by miscible and compatible materials result in increased entanglement of networks, which then enhances the mechanical properties such as impact resistance, Young's moduli, and elongation [34].

A dual-cure formulation utilizing the formation of an IPN structure was utilized by Yu *et al.* [35] to make a 3D-printable epoxy-acrylate hybrid photopolymer. Preformed particles composed of polyacrylate-co-epoxy were dispersed within an epoxy matrix. A hybrid photopolymer consisting of epoxide and acrylate monomers enabled high curing rates while maintaining low volume shrinkage. During UV curing, the cross-linking bonded the acrylate and epoxide polymers amongst each other to form an IPN. This resulted in increased toughening effect and impact strength and increased elongation at break[35].

Invernizzi *et al.* [36] and Chen *et al.* [30] investigated the role of interlayer adhesion on mechanical properties of a dual-cure system for 3D printed structures. An IPN was formed from using photo-curable and thermal-curable resins. UV exposure enabled the curing of the photocure resin at room temperature to form a structurally stable cross-linked network. The partial UVcrosslinked resin allowed for partial interpenetration and merging between sequential deposited layers, which also enabled the network to maintain its shape prior to thermal cure. The interlayer adhesion was further enhanced upon heat treatment due to the promotion of crosslinks between the printed layers via thermal curing of the epoxy oligomer. The strong interfacial adhesion between the deposited layers led to improved mechanical properties.

The impact of resin formulation on crosslinking kinetics and mechanical properties of a dual-cure system was studied by Kuang *et al.* [2]. Using dual-cure polymer composites composed of a photo-cure resin and thermal-cure epoxy, the two resins were mixed in varying weight ratios and sequentially polymerized into networks through different mechanisms. Two separate
networks were formed via the two-stage curing process, which enabled the formation of an IPN. Similar to Yu *et al.*[35], the presence of the photo-cure resin increased the curing rate allowing the printed polymer to cure rapidly and hold its shape, while the incorporation of the thermal-cure epoxy oligomer reduced the volume shrinkage during UV and thermal curing. With increased thermal-cure epoxy, the gel fraction after only UV light exposure decreased, because the thermal epoxy oligomer is unable to be cured via UV light and is readily dissolved by the solvent. This also caused a decrease in tensile strength prior to thermal treatment due to the thermal-cure epoxy behaving as a plasticizer. However, upon subsequent thermal treatment, the gel fraction increased to 100% indicating a cross-linked network was formed. This was also evidenced by a significant increase in the Young's modulus.

2.4 Acrylate & Epoxy Chemistry

The acrylate and epoxy networks are formed by chain polymerization, where the network is formed by the continuous addition of monomers to the already growing chains. There are three kinetic steps involved with the network formation: initiation, propagation, and termination. During the initiation step, the initiators are dissociated by light (or heat) to react and form free radicals which react with the monomers to start the formation of a propagating chain. Propagation starts when the initiator fragments and/or propagating chains continue to add monomers to form growing polymer chains. Termination, for free-radical polymerization, then occurs by either combination or disproportionation.

The formation of the acrylate network discussed in this thesis occurs via free-radical polymerization upon exposure to UV light. The production of free radicals results from the decomposition of photoinitiators once they absorb light. Free-radicals can be uni- and bi-molecular where either one or two molecular species, respectively, interacts with light to produce a free-radical active center [37]. The structure and decomposition of one of the photoinitators used in this

thesis is diphenyl(2,4,6-trimethylbenzoyl) phosphine oxide (TPO), as seen in Figure **2-8**, and is an example of a unimolecular photoinitiator.



Figure 2-8: Decomposition of diphenyl(2,4,6-trimethylbenzoyl) phosphine oxide (TPO)

The free-radicals that are generated react with acrylate or methacrylate monomers to form initiation species which then transfer the radical to other monomers which form the acrylate network.



Methacrylate $R_1 = CH_3$

Figure 2-9: Structure of the acrylate monomer and acrylate network formation

This reaction is depicted in Figure **2-9**. The acrylate monomers are very reactive but also have several drawbacks ranging from health hazards, volatility, oxygen inhibition, and high shrinkage.

The oxygen inhibition and high shrinkage can be explained via chemical reactions. Molecular oxygen present in the air can react with the excited-state photoinitiator to quench the initiation reaction by forming peroxy radicals that are unable to react with acrylate double bonds. Thus, oxygen behaves as a chain terminator, decreasing the polymerization rate in free-radical reactions. Shrinkage occurs until the overall reaction is terminated, and results from volumetric decrease as the polymer network forms. This shrinkage is inherent of polymers that polymerize from carbon-carbon double bond monomers because of long-distance, weak Van der Waals bonds between monomers being replaced by shorter, stronger covalent bonds in the polymer [38-41]. Ways to combat or reduce shrinkage consist of changing the reaction temperature, reaction speed, and light intensity [38, 42].

The formation of the epoxy network discussed in this thesis occurs via ring-opening homopolymerization upon exposure to increased temperature. The latent curing agent delays the onset of epoxy network formation until the activation temperature is reached, which for 1-ethyl 3-methyl imidazolium dicyanamide (**Error! Reference source not found.** is between 120-180°C [43].



1-Ethyl-3-methylimidazolium Dicyanamide

Figure **2-10**:Structure of 1-ethyl 3-methyl imidazolium dicyanamide latent curing agent The epoxy monomer structure and epoxy polymer network formation is depicted in Figure **2-11**.



Figure 2-11: Structure of epoxide monomer and epoxy polymer repeat unit

Unlike the fast polymerization of acrylate network formation, the epoxy polymerization reaction and conversion are slower. However, unlike acrylates, shrinkage is not often an issue for epoxies or any polymer that forms by ring-opening polymerization. Instead, expansion often occurs [44, 45]. Another benefit of epoxy over acrylate is that epoxies tend to have higher glass transition temperatures, making them more versatile in high temperature applications.

2.5 Summary

DIW has been used in a vast array of applications due to the capability of using highly loaded composite materials to create specially designed porous or hollow structures that are otherwise unattainable using traditional fabrication methods [46-48]. Additionally, the versatility of print direction and filler orientation intrinsic to DIW enables control over the material properties of printed parts [15, 17, 49]. While DIW resins have traditionally consisted of metalloaded and ceramic-loaded polymers, thermoset polymers have also been investigated as a material choice in recent years. The extrusion and shape retention of thermoset polymers is possible through the addition of filler materials or via dual-cure.

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CHAPTER 3 : EXPERIMENTAL SETUP

In this chapter, I will describe the general experimental methods commonly used throughout chapters 4-7 of this dissertation. More specific experimental procedures are included in each individual chapter. First, a brief description is given of the particle functionalization procedure for both fumed silica and sodium montmorillonite, as well as the silanes that were utilized for the surface modification. This is followed by a walkthrough of the chemical reaction utilized for converting epoxy functional groups into acrylate functional groups. The characterization of the functionalized fillers is then explained and is followed by the procedures used for preparing the resin for printing, printing parameters, and finally the characterization of the resin and printed DIW parts.

3.1 Particle Functionalization

Silica nanoparticles and clay platelets are the most common filler materials used to modify rheological properties of DIW resins and to modify the mechanical and thermal properties of the printed nanocomposite. However due to the incompatible surface chemistry of these particles and the matrix material, they tend to agglomerate when mixed into organic materials which hinders the rheological and resulting mechanical properties[1, 2]. To prevent agglomeration, the surface polarity by forming organic-inorganic hybrid bonds which better enables homogeneous dispersion[3]. The most common group of materials utilized to alter surface chemistry are called silanes. The three silanes used in this research are glycidoxypropyltrimethoxysilane (Figure 3-1), hexyltrimethoxysilane (Figure 3-2), and methacryloxypropyltrimethoxysilane (Figure 3-3).



Figure 3-1: Glycidoxypropyltrimethoxysilane (GPS)



Figure 3-2: Hexyltrimethoxysilane (HMS)



Figure 3-3: Methacryloxypropyltrimethoxysilane (MPTS)

3.1.1 Silane Surface Modification of Silica Nanoparticles

The chemical properties of fumed silica are determined by the silanol and siloxane groups present on and within the nanoparticle. The hydroxyl groups on the surface of fumed silica nanoparticles can react with various organic compounds or polymers to alter the very hydrophilic surface chemistry[4]. Silanol groups, under the correct conditions, can react with the surface



hydroxyl groups and form covalently bonded polymer-functionalized nanoparticles (Figure 3-4).

Figure 3-4: Surface functionalization of silica nanoparticles

The epoxy functionalization procedure for the silica nanoparticles is modified from the procedure used by Chu *et al.* [5], where the nanosilica is dispersed in a 50:50 vol:vol ethanol:water solution and the pH is adjusted down to 4 using 1M HNO₃ solution. The silane is then added to the suspension under vigorous stirring at room temperature for 24 hours. For 7.26g of nanosilica, 98mL of water was used and 3.48g of silane were used. After the completion of the reaction, the silica suspension is then centrifuged at room temperature at 8000rpm for 10 minutes in 50mL polypropylene tubes. The pellet is then washed and centrifuged three more times using excess ethanol to remove unreacted silane coupling agents. The moist silica pellet is then left to air dry overnight in the hood to allow the ethanol to evaporate. The following day, the silica is dried under vacuum at 80°C for 24 hours. Finally, aggregates of the silylated-silica are ground using a mortar and pestle to make a fine powder with a particle size ~500nm. The remaining silica silylation reactions are discussed in further detail in **Chapter 6**.

3.1.2 Silane Surface Modification of Clay Platelets

The structure of clay consists of a regular arrangement of two silicon tetrahedral (SiO₄⁴⁻)

layers with one aluminum octahedral (Al(OH)₃⁶⁻) layer sandwiched in between Figure **3-5**. Oxygens form the corners and cations reside in the center to charge balance the otherwise negatively-charged structure. The deficit of positive charges usually results from an Al³⁺ cation substituting for a Si⁴⁺ cation [6]. The chemical properties of clay are dominated by the hydroxyl groups that result from broken bond at the edges of the platelets. The extremely reactive hydroxyl



groups can react in silulation reactions at the interlayer spaces, external surfaces, and at the platelet edges [7-11].

The epoxy functionalization procedure for the clay nanoparticles is adapted from Asgari *et al.*[12]. In a 300 mL lidded container, 2g of Cloisite[®] Na+ montmorillonite clay is dispersed in 200mL of deionized water and then sonicated at room temperature for 1 hour to break up clay tactoids within the solvent. The solution is then transferred to a 500 mL round bottomed flask where the pH of the solution is then adjusted to ~4 using a 1M solution of HCl, under stirring. 2g of the silane is then dissolved in 50mL of deionized water, stirred for 1 minute, then added dropwise to the clay-water suspension under constant stirring. The suspension is then stirred for 24 hours at 80°C to complete the silylation reaction. After 24 hours, the silane-modified clay was centrifuged at room temperature at 8000rpm for 10 minutes in 50mL polypropylene tubes. The pellet was then washed and centrifuged three more times using excess methanol to remove unreacted silane coupling agents. The moist clay pellet was left to air-dry overnight in the hood. The following day the clay was dried under vacuum at 80°C for 24 hours. Finally, aggregates of

the silvlated-clay were ground using a mortar and pestle to make a powder with a particle size ~700nm. The remaining clay silvlation reactions are discussed in further detail in **Chapter 6**.

3.2 Filler Characterization

Surface modified silica and clay particles have been extensively studied. The characterization studies enable the understanding of reaction mechanisms involved with the grafting, final properties of the modified particle, and help determine how these particles may be used in various applications. There are a few analytical techniques, repeatedly referenced in literature, that are used to characterize surface modified particles before, during, and after the surface modification has reached completion.

3.2.1 Thermogravimetric analysis

There are a handful of particle analysis techniques ranging from gravimetric, spectroscopy, to electrophoresis analysis. Gravimetric techniques determine the changes in weight before and after the surface modification. Thermal analysis, such as thermogravimetric analysis (TGA), gives an idea of grafting density as well as thermal degradation of the surface modified particle[1]. Bartholome *et al.*[2] calculated the amount of grafted silanes on silica nanoparticles via TGA analysis (Equation **3-2**) [3, 13]



Grafted amount
$$\left(\frac{mmol}{g}\right) = \frac{\frac{m_{60-730} - W_{silica}}{MW_{silane}}}{M_{silica}} \times 1000$$

Where m_{60-730} is the weight loss measured in grams between 60°C and 730°C, which corresponds to the decomposition of the silane. MW_{silane} (g/mol) is the molecular weight of the hydrolyzed silane, W_{silica} is the weight loss measured in grams of the silica, and M_{silica} is the mass of the silica sample being measured via TGA. The W_{silica} value used for MPTS SiO₂ is the weight loss of the 'no silane' MPTS control sample between 60-400°C, because this range is where the maximum weight loss occurs. For GPS SiO₂, the W_{silica} value is the weight loss of the 'no silane' GPS control sample taken between 60-500°C, because this is the range where the maximum weight loss occurs. The multiplication factor of 1000 is to convert the mass of the samples from grams to milligrams.

Asgari *et al.*[12] used TGA to calculate the amount of grafted (Equation **3-3**) and amount of intercalated (Equation **3-4**) silane on functionalized Cloisite[®] Na+ MMT. The mass loss between 200°C and 600°C, $m_{200-600}$, is caused by the evaporation of trapped solvent molecules and the debonding/removal of physically adsorbed, intercalated, and chemically grafted silane coupling agents. In both equations, M (g/mol) is the molecular weight of the hydrolyzed silane molecules. In Equation **3-3**, the grafting amount indicates the total amount of silane molecules attached physically and chemically to the surfaces of the clay. The intercalated amount, or physically adsorbed silanes, is taken as the mass loss between $m_{350-500}$. The multiplication of factor of 1000 is to convert grams to milligrams.

Equation 3-3: Silane Grafted Amount

Grafted amount
$$\left(\frac{mmol}{g \ clay}\right) = \frac{(m_{\ 200-600} \ x \ 1000)}{m_{600} \ x \ MW_{silane}}$$

Equation 3-4: Silane Intercalated Amount

Intercalated amount
$$\left(\frac{mmol}{g \ clay}\right) = \frac{m_{350-500} \ x \ 1000}{m_{500} \ x \ MW_{silane}}$$

The TGA procedure consists of a temperature ramp of 20°C/min from room temperature to 800°C. Platinum weight pans were used and were tared before analyzing the samples. Once tared, finely ground powder samples were loaded onto the pans. The pans were then placed on the autosampler and the test was started.

3.2.1.1 TGA-Mass Spectroscopy

TGA-Mass spectroscopy is a combination of two techniques that occur simultaneously. While a specimen is decomposed via TGA, the decomposition fragments are carried to a mass spectrometer which measures the mass of the fragment. By knowing the mass of each fragment, the chemical structure associated with that mass can be approximated.

3.2.3 Fourier Transform Infrared Spectroscopy

Fourier-transform infrared spectroscopy (FTIR) is technique used to analyze functional groups present in a sample. FTIR utilizes an infrared radiation of about 10,000 to 100cm⁻¹ to scan a sample that may or may not absorb some of the radiation. The radiation that is absorbed is converted into in rotational and/or vibrational energy that is characteristic to molecular or functional groups within the sample. For example, the characteristic peaks for acrylates are C=O at 1726cm⁻¹ and C=C at 1630cm⁻¹ [14], while the characteristic peak for an epoxy group ranges from 925-899cm⁻¹ [15] The resulting signal is collected by a detector and results in a spectrum ranging from ~4000cm⁻¹ to 400cm⁻¹. Attenuated total reflectance (ATR) is a type of FTIR that consists of using a perfectly polished crystal usually diamond or germanium that relies on total internal reflection which results in an evanescent wave to identify organic, polymeric, and sometimes inorganic materials. Total internal reflection is only achieved by using a crystal with a higher refractive index than the sample being analyzed, or else the beam is lost into the sample. One benefit of ATR-FTIR is that there is limited path length into the sample which decreases the attenuation for strong IR absorbing materials. Another benefit of ATR-FTIR is the ability to measure a wide variety of solid and liquid samples without needing complex sample preparation.

FTIR is used to compare the spectra of functionalized and unfunctionalized filler materials[3, 11, 16]. Figure **3-6** is the FTIR spectra collected by Shanmugharaj *et al.* comparing the spectra of unfunctionalized Na⁺ MMT and 3-aminotriethoxysilane functionalized Na⁺ MMT, where the clay was functionalized in different solvents[16]. The full spectrum is of the



Figure 3-6: FTIR spectra of silylated and unsilylated Na+ MMT

unfunctionalized Na⁺ MMT and the smaller spectra sections are characteristic to the grafted silane. The characteristic peaks of unfunctionalized Na⁺ MMT are at ~3636 cm⁻¹, 3440 cm⁻¹, 1640 cm⁻¹, 1045 cm⁻¹, 915 cm⁻¹, 800 cm⁻¹, and 620cm⁻¹ [11, 16]. It is apparent that changing the solvent used for the silylation reaction changes the intensity of the characteristic peaks associated with the grafted silane. This can be correlated to the amount of grafted silane.

3.2.4 Dynamic Light Scattering

Dynamic light scattering (DLS) is a technique used to analyze particle size distribution in a suspension. DLS operates by measuring the fluctuation in scattered light intensity due to diffusing particles [17]. The refractive index and absorbance values of both the dispersing medium and particles being analyzed must be known. The absorbance value for the silica and clay were 1, and the refractive index values used were 1.46 for the silica[18] and 1.43 for the clay [19]. The instrument used was Malvern Nano Zetasizer. The dispersing medium used was distilled water and the disposable cuvettes were composed of polystyrene. The samples consisted of three-quarters of a cuvette filled with a solution of 0.033g of functionalized or unfunctionalized particles dispersed in 10mL of distilled water that were sonicated for 15 minutes prior to analysis. The samples were analyzed using16 iterations and were analyzed 3 different times: immediately after sonication, 15 minutes after sonication, and 30 minutes after sonication to see if any particle settling had occurred. DLS was chosen as a straightforward way to determine how the particle size distribution of the functionalized particles compared to the distribution of the unfunctionalized particles[2, 3].

3.3 Resin Characterization

Once the components of the dual-cure network are combined, it is important to understand the properties of the resulting resin before the resin is printed. Thermal and rheological analysis are vital to understanding the kinetics of each network as it forms as well as understanding the viscosity profile. All of which impact the stability and printability of the resin. In addition, these tests can help determine how the system is altered as functionalized fillers are added to the resin

3.3.1 Isothermal cure

An isothermal cure measurement is typically done using differential scanning calorimetry (DSC) or dynamic mechanical analysis (DMA) to study the gel point of a thermoset material, i.e. the epoxy in my system, at a constant temperature. Understanding when the gel point occurs is important from a processing standpoint because before the gel point the material can flow, relax,

and be shaped into a desired form. Post gelation, the material has formed an irreversible network with increased stiffness and can no longer be processed or shaped [20]. The gel point designates the transition of a fluid, liquid, amorphous material into a solid 'gelled' material via the process of gelation. This liquid to solid transition results from the formation and further growth of a chemically or physically bonded network, where the network connectivity goes from zero to infinite. Similarly, the molecular weight distribution is infinitely broad as it ranges from the molecular weight of the unreacted monomer/polymer/oligomer before gelation, to the molecular weight of the infinite network post-gelation [20, 21]. Beyond gelation the molecular weight no longer increases, however the cross-link density increases while the un-bonded polymer chain length decreases. The main differences between chemically and physically bonded networks are the lifetime of the network formation, and the types of bonds involved in the network. Typically, chemical cross-linking polymers form a covalently bonded network with an infinite lifetime, whereas physical cross-linking polymers form a network that has a finite lifetime[22]. This thesis focuses on chemical cross-linking networks. There are multiple ways of defining the onset of gelation using dynamic mechanical analysis. Some declare the crossover of the storage and loss moduli [21-23] as the onset of gelation while others claim that the exponential increase of the storage modulus and resulting peak of the tan delta[20]. This thesis will define the onset of gelation as the latter and will investigate how the epoxy gel point changes via the addition of epoxy-functionalized filers in the epoxy-acrylate dual-cure resin.

While discussing the analysis of the gel point, it is worth discussing vitrification. The point at which a material in a rubbery state is no longer thermodynamically stable and transitions into a glassy state is known as the vitrification point [24]. This switch from a rubbery to glassy state is due to a molecular weight or cross-link density that is thermodynamically unstable, and results in dramatically slowed kinetics due to limited mobility of polymeric chains[20]. The vitrification point can be studied via isothermal cure measurements using both DSC and DMA and occurs in systems that are run at isothermal temperatures below the system's ultimate $T_g[24]$. Therefore, vitrification is a thermo-reversible process, unlike gelation. Thus, if the system ran at

Storage modulus G' (Pa) riangle

an isothermal cure temperature above T_g ultimate, then the system will never vitrify and will only gel. The vitrification point is very similar to the onset of gelation in that both will result in an increase in the storage modulus (2), but only the onset of gelation has a



Figure 3-7: Example of isothermal cure data

parallel increase of both storage and loss moduli (1) on Figure 3-7.

Figure **3-8** is an example of an isothermal procedure used in this thesis. The equipment used is an ARES G2 DMA and the equipment and analysis software is TRIOS. 8mm aluminum

disposable parallel plates were chosen as the geometry as they were re-usable and were sensitive enough. The isothermal test was conducted at three temperatures: 100°C, 150°C, and 200°C and the duration was 40 minutes. Initially

- Environmental Contr Temperature	rol	۰C	Inherit Set Point
Soak Time	0.0	s	Wait For Temperature
Test Parameters			
Duration	7200.0	s	
Sampling rate	1.0	pts/s	U
Strain %	1.0	%	~
Single point			Ŷ

Figure 3-8: Example of an isothermal cure procedure

the isothermal measurements ran for 4 hours, but 40 minutes was found to be enough time to capture the gel point. The strain percent and frequency were 1% and 1 Hz, respectively, where the strain percent was found to be in the linear elastic region of the samples. The fixtures and plates were held for 5 minutes at the chosen isothermal temperature to ensure uniform heating and were then zeroed. The oven was then opened, the sample was loaded onto the plates, and the gap was lowered to the standard 1mm. The furnace was then closed, and the analysis started once the oven temperature reached 150°C.

3.3.2 Viscosity

The viscosity behavior of a material is studied by conducting a viscosity versus shear rate measurement to see whether the material behaves in a Newtonian or non-Newtonian manner. Newtonian fluids, like unfilled epoxies, have a viscosity profile that is independent of shear rate. Non-Newtonian fluids have a viscosity profile that does vary with shear rate. Pseudoplastic or shear-thinning materials have a viscosity that decreases while the shear rate increases, while dilatant or shear thickening materials have a viscosity that increases with increasing shear rate. The viscosity profile gives an idea of the printability of a resin. For DIW, shear-thinning behavior is advantageous as it enables a material to easily extrude due to the deceased viscosity under the applied shear, but then is able to retain the printed shape post-extrusion due to the increased zero-shear viscosity. The addition of fillers has traditionally been the method of choice to achieve shear thinning behavior of an otherwise Newtonian system[25]. The printing of Newtonian fluids is possible via dual-cure systems where the extruded material can be partially cured to lock-in the structure during the print, then post-cured to obtain the desired mechanical properties.

The equipment used is an ARES G2 DMA and the equipment and analysis software is TRIOS. 25mm aluminum disposable parallel plates were chosen as the fixture geometry as they were re-usable and are most sensitive than the 8mm plates for this measurement. The plates had 80-grit sandpaper adhered to their surface to help prevent slippage of the resin from occurring.

Flow Sweep

The plates were zeroed once the sandpaper was adhered after which the sample was loaded, and the gap was lowered to the standard 1mm for testing. The shear rate test was conducted at room temperature and the rate was swept from 0.01 to 100 1/s, as shown in Figure **3-9**. Steady state sensing was utilized to ensure

- Environmental Control - Temperature	25	°C	Inherit Set Point Wait For Temperature		
Soak Time	0.0	s			
Test Parameters					
Logarithmic sweep			V		
Shear rate	0.01	to 100.0	1/s v		
Points per decade	10				
Steady state sensi	ng				
Max. equilibration time	180.0	S			
Sample period	5.0				
% tolerance	3.0				
Consecutive within	3				
Scaled time average	je				

Figure 3-9: Example of viscosity procedure

the most representative data. This feature enables the machine to compare the difference between three consecutive data points collected every 5 seconds to see if they're within 3% tolerance of each other. If not, then the system will not move onto the next data collection set until three collection points are within the tolerance OR until the maximum equilibrium time (180s) has been reached.

3.3.3 Ultraviolet Differential Scanning Calorimetry (UV-DSC)

DSC is an analytical technique used to measure the change in heat flow of a sample compared to a reference as temperature is applied. UV-DSC operates similarly, except UV light is applied to the system instead of temperature. The change in heat flow is a result of chemical reactions taking place within the sample that result in heat either being absorbed by an endothermic reaction (i.e. melting, or glass transition temperature), or heat being emitted during an exothermic reaction (i.e. cold crystallization).

The UV-DSC equipment is a TA Instruments Q200 DSC and TA universal analysis is the analysis software. An external TA Instrument photocalorimeter accessory (PCA) was attached to the DSC according to TA Instruments set-up guidelines [26] Once the DSC was in PCA mode, the sample and reference intensity were adjusted to the same intensity (+/- 0.5 mW/cm²) as measured by the equipment. The intensity of the light guides was measured using a radiometer and by mimicking the same set-up as within the UV-DSC cell. This data can be found in Appendix I. Standard aluminum pans were used for both reference and sample analysis. No lids were used as they would block the incoming UV light. The sample size ranged from 23.1-23.8mg. To accurately compare the UV-active species cure kinetics, it is important to keep the sample sizes small and consistent. Sample sizes that significantly vary (23mg vs 30mg) could cause possible UV-penetration issues as well as resulting in core-shell analysis where the top layer of the sample is cured but the rest of the sample is not. Figure **3-10** is an example of a pulsed UV-DSC procedure ran at room temperature, and is adapted from TA Instruments multipulse UV-DSC procedure [27]. The rapid cooling accessory maintains the temperature of the

oven at a programmed 30°C to prevent the sample chamber from heating up due to light exposure as well as to isolate the UV-only kinetics. An isothermal step is necessary pre-and post- UV

exposure to ensure a stable baseline is achieved both before and after light exposure. The shutter opening refers to the exposure of UV light, and the isothermal step for 0.04minutes (2.4s) is the duration of light exposure to the sample. Shutter close refers to the sample no

```
OrgMethod 1: Equilibrate at 30.00 °C
OrgMethod 2: Isothermal for 2.00 min
OrgMethod 3: Shutter state Open
OrgMethod 4: Isothermal for 0.04 min
OrgMethod 5: Shutter state Close
OrgMethod 6: Isothermal for 3.00 min
OrgMethod 7: Mark end of cycle 0
OrgMethod 8: Repeat segment 2 for 19 times
```

Figure 3-10: Example of UV-DSC pulsed procedure

longer being exposed to the light source. The post-exposure isotherm may need to be tailored based on how active the sample is to the UV light. Ideally, the isotherm before and after the shutter opening should be long enough that the sample reaches the same value pre and post UV exposure. This baseline is then used to integrate each heat flow peak to determine the relative amount of network formed during each UV light exposure. The number of exposures is 20 per sample.

The results of UV-DSC measurements are like the graph shown in Figure **3-11**. The peaks are representative of the heat released upon UV-light exposure as the acrylate network forms. As shown, the first 5-7 peaks are much taller than the last few peaks because this is when most of the network has formed. Once the sample is 'fully cured' the peaks present are the characteristic heat capacity of the fully cured material.



For pulsed exposures, the samples were held isothermally at 25 °C for 2 minutes, exposed to light for 2.4 seconds, then held isothermally for 5 minutes at 25°C under 50 mL/min nitrogen flow. A total of 20 pulses were conducted. A stable baseline was determined when the standard deviation value between the 3 sequential peaks was less than 0.1 J/g. The baseline was subtracted from each individual pulsed enthalpy value. The resulting DSC enthalpy values were used in the conversion calculation which is discussed below.

For continuous exposures, the samples were held isothermally at 25 °C for 2 minutes, exposed to light for 10 minutes, then held isothermally for 5 minutes at 25°C under 50 mL/min nitrogen flow. A total of two 10-minute exposures were conducted. The first 10-minute exposure measures the heat evolved during the cure reaction while the second captures the baseline differences in heat flow on UV exposure between the empty reference pan and the resin-filled sample pan due to the specific heat capacity of the reacted sample. Subtracting the total enthalpy of the second baseline peak from that of the first yields the heat of polymerization. To ensure that the second exposure was not measuring any additional cure reaction, three 10-minute exposures were conducted for a 30wt% acrylate sample. The difference between the 2nd and 3rd exposures was <1% of the total baseline heat flow indicating a stable baseline for use in calculating the heat of polymerization from the first continuous exposure (Figure **3-12**).



Figure **3-12**: UV-DSC plot of three 10-minute continuous exposures

The percent conversion was calculated using Equation **3-5** where 56.6 kJ/mol is the theoretical heat of polymerization for methacrylate and 86 kJ/mol for acrylate. The experimental enthalpy was calculated using Equation **3-6** where the DSC enthalpy values are the baseline corrected enthalpy values discussed above.

Equation 3-5: Acrylate percent conversion calculation

% conversion =
$$\left(\frac{Enthalpy_{exp}}{56.6 kJ_{mol}}\right) \ge 100$$





Figure **3-13**: Plot of relative conversion vs. UV light pulse graph

The percent conversion can then be plotted versus the pulse in order to investigate the kinetics of the reaction Figure **3-13**.

3.4. DIW of the resin and cure profiles

Once the resin has been characterized, the resin is placed in a disposable mixing container and heated to 80°C for 5 minutes. The container is mixed in a vacuum-assisted planetary mixer for 2 minutes at 2000 rpm and 0.7 kPa. The material is transferred to a 30-mL syringe and centrifuged for 3 minutes at 3000 RPM to remove entrapped air bubbles resulting from the transfer. The resin is extruded from the 30-mL syringe through a 0.84 mm (Nordson EFD SmoothFlow) tapered tip at a constant rate of 0.01 mL/s using a constant volume linear syringe pump equipped with an *in situ* UV light source Figure **3-14**. The printer was designed and built by Adam Cook and Derek Reinholtz of Sandia National Laboratories. An extrusion rate of 0.01 mL/s and printing speed of 15 mm/s were found to provide ideal Cartesian deposition conditions. Two, 3 mm diameter liquid light guides (Dymax MX-150) deliver UV light (365nm) direction to the point of extrusion for *in situ* curing of the printed material. A maximum intensity



Figure **3-14**: Home built DIW printer with UV attachment

of 24W/cm² as measured directly at the UV emitter is used for *in situ* curing of the dual-cure resins. [28]

Different UV light intensities are used to study and compare cure kinetics while printing the *in situ* print cure only samples. Two print directions are investigated to understand print direction effects on mechanical bar samples. The mechanical bar dimensions are 0.12 inches thick x 0.12 inches wide x 1.25 inch long.

An estimated dose of 504 mJ/cm² per transverse printed mechanical bar and 414 mJ/cm² per longitudinal printed bar was calculated based up on the time it takes to print a sample, the number of passes over the printed sample, and how much of the sample is repeatedly exposed to the light. For the printed bars, the intensity of the light during printing is 7 mW/cm² and the print time is

~73s per transverse-printed bar and ~60s per longitudinal-printed bar. This is an estimated value because ~6mm diameter of the bar is exposed to the light during the print. The exposure profile for 1 of 4 total layers is found in Figure **3-15**.



Figure 3-15: Exposure profile for transverse and longitudinal bars

"UV print-cure only" samples refer to printed samples that are UV-cured during printing and are characterized without any further UV or thermal cure. The intensity used during various print conditions ranged from 7 mW/cm² to 29 mW/cm², which corresponds to a UV dose of 504 mJ/cm² to 2,117 mJ/cm² per transverse printed mechanical bar and 414 mJ/cm² to 1,740 mJ/cm² per longitudinal printed mechanical bar. "UV print cure + flood cure" samples refer to print-cured samples that are UV flood cured after the *in situ* print cure. The UV print cure only samples are flood cured for 30 minutes using an ABM, INC 500W near/mid UV 2105C2 illumination controller with an intensity of 5.7 mW/cm². After the UV flood cure, a standard thermal cure procedure to form the epoxy network.

The standard thermal cure procedure starts by placing the samples in a room temperature oven that is then heated to 100°C at 1°C/min where it sits for 4 hours, then the oven temperature is increased to 150°C at 1°C/min where it sits for an additional 2 hours, then the oven is ramped back down to room temperature at 1°C/min. The samples are then removed. Post thermal treatments were also investigated, where the samples were subjected to additional higher temperature cures of varying lengths.

The storage and loss moduli and tan delta of print cure only, print + flood cure, standard cure and standard + additional thermal cure samples are measured to study the formation of the acrylate network and acrylate and epoxy network, and how these networks are influenced by unfunctionalized and functionalized fillers and heterobifunctional monomers. The flexural modulus and flexural strength of printed parts are measured to study the interlayer adhesion, particle dispersion, and particle orientation as a function of print direction and presence of functionalized and unfunctionalized fillers. The dispersion, orientation, and incorporation of the functionalized and unfunctionalized fillers is measured using electron microscopy techniques [25].

3.5 Thermomechanical Characterization

3.5.1 Torsional Dynamic Mechanical Analysis

Torsional DMA (TDMA) is a way to analyze the stiffness and network formation of printed parts. TDMA can measure the storage and loss modulus of both print cure only, print + flood cure, standard cure, and standard + additional thermal cure samples to investigate the acrylate-only network formation and acrylate-epoxy interpenetrating network formation. Temperature TDMA of print cure only and print + flood cure samples measures the evolution of the storage and loss modulus as the epoxy network forms around the already existing acrylate network. Temperature TDMA of standard cure and standard + additional thermal cure samples gives the T_g of the acrylate-epoxy IPN, where the T_g in this thesis is defined as the peak in the tan delta curve.

Oscillation Temperature Ramp			Oscillation Temperature Ramp				
Environmental Control			Environmental Control				
Start temperature	25	°C	Inherit set point	Start temperature	250	°C	Inherit set point
Soak time	0.0	S	Wait for temperature	Soak time	0.0	S	Wait for temperature
Ramp rate	3.0	°C/min		Ramp rate	3.0	°C/min	
End temperature	250	°C		End temperature	25	°C	
Soak time after ramp	0.0	S		Soak time after ramp	0.0	S	
Estimated time to complete	01:15:00	hh:mm:ss		Estimated time to complete	01:15:00	hh:mm:ss	
Test Parameters		Test Parameters					
Sampling interval	10.0	s/pt	\sim	Sampling interval	10.0	s/pt	~
Strain %	0.1	%	ų.	Strain %).1	%	U.
Single point v			Single point v				
Frequency	1.0	Hz 👻		Frequency 1	1.0	Hz 👻	

Figure 3-16:Example of temperature TDMA procedure: heat up (left), cool down (right)

Figure 3-16 is an example of a temperature TDMA procedure where the starting and ending temperature was 25°C and temperature sweep was up to 250°C. Room temperature TDMA followed the same procedure, except the sample was tested at room temperature instead of being placed into an oven and heated. The equipment used for torsional DMA analysis is an ARES G2 DMA and the equipment and analysis software is TRIOS. The rectangular torsion fixtures were chosen as the geometry and the testing area was adjusted using the 2mm blocks. The strain percent and frequency were 0.1% and 1 Hz, respectively, where the strain percent was found to be in the linear elastic region of the samples. The ramp rate of 3° C/min is commonly used and is the fastest rate before a significant thermal differential between fixtures and sample occurs. Before analysis the fixtures were zeroed so that the equipment calculated the exact testing area of each individual sample, which allowed samples to be varying sizes. The sample thickness and width were measured with calipers and that information was entered in the program. The sample was then loaded into the fixture, usually at a gap of 12.7mm, and fastened securely. The force was adjusted to a negative load, as per TA instruments instructions, and then the test was started. For samples experiencing temperature, the oven was closed before the test was started and the oven environment was set to house nitrogen.

3.5.2 Three-point Bend Test

Three-point bend tests are a type of mechanical test conducted to obtain the flexural strength, flexural modulus, and strain-to-failure of a sample [25, 29-31]. The flexural strength,

depicted by a red 'x' in Figure **3-17**, is taken as the maximum stress applied to a sample on the flexural stress-strain curve. The strength determines the amount of stress the material can handle before it fails. This value may or may not be equal to the stress at failure depending on whether the sample exhibits plastic deformation. The flexural elastic modulus is taken as the slope of the linear



region of the flexural stress-strain curve and this value represents how much the material deflects under a given load. This linear region is the elastic region, meaning the strain experienced by the sample as stress applied is 100% recoverable once the stress is removed. Some materials exhibit plastic deformation which is non-linear and not recoverable once the stress is removed. The strain-to-failure is measures how much of material is elongated to failure. This value is given as a percent of the ratio of the deflection at failure (distance traveled) to the initial deflection (zero if the equipment was zeroed at the start of the test).

The samples were tested using an Instron with a three-point bend attachment. The rate was 0.1 inch/minute, and the support span was 1 inch. The width and thickness of each sample were measured using calipers and the values were entered in the Bluehill 3 software. Before any measurements were made, the fixture load and strain were zeroed. The head was raised, and the sample was loaded in the middle of the support fixture. The head was then lowered until a 0.2lbf preload was achieved. This preload ensured the same starting position and immobility of the tested samples. At this preload, the strain was zeroed, and the test was then started.

3.5.3 Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) is used to measure the Young's modulus of printed samples. The DMA equipment used was a TA Instruments DMA Q800 and the procedure was a ramped force of 1 N/min to 18 N. The tested samples were print-cure only, and the objective was to study the impact of print direction on the resulting modulus. The machine was calibrated using the 15 mm three-point bend setup, then a rectangular sample ~2mm thick was loaded. Next, a preload of 0.2N was placed on the sample to ensure contact between the probe and sample, and then the test was started.

3.5.4 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is a technique used to analyze the surface topography and composition of a material [32]. SEM operates by scanning the surface of a sample with a focused beam of electrons that interacts with the atoms within the sample and results in escaped electrons are collected by detectors. The two main detectors of SEM are secondary electron (SE) and back-scattered electron (BSE), where SE gives information about topography while BSE gives compositional information. SE are low energy electrons that escape from the surface, while BSE are high energy electrons that interact more with the atomic shell and give compositional information. In a SE SEM micrograph, the bright areas correspond to hills while the dark areas correspond to valleys, and the bright sides correspond to the side where the detector is. In a BSE micrograph, the bright areas correspond to atoms that are heavier and have more electrons to excite and eject compared to the dark areas that correspond to lighter elements.

SEM can also be used to analyze particle dispersion and orientation within a sample in addition to particle-matrix interaction by investigating fractured surfaces [25, 33, 34]. The more chemically compatible the filler is with the matrix material, the debonding will be present on the fractured surface will be due to enhanced interfacial strength between the network and filler An





Figure **3-18**: Fractured surface SEM images of unfunctionalized (a) and functionalized (b) clay dispersed in an epoxy matrix

example of a fractured surface SEM micrograph of a fractured surface is shown in Figure **3-18** [34].where Ha *et al.* [34] investigated the intercalation and interfacial strength between unfunctionalized (a) and functionalized (b) clay dispersed in an epoxy matrix. Utilizing the SEM image, Ha *et al.* found that functionalized clay dispersed better and had increased interfacial strength compared to the unfunctionalized clay.

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CHAPTER 4 : COMPOSITIONAL EFFECTS ON CURE KINETICS, MECHANICAL PROPERTIES AND PRINTABILITY OF A DUAL-CURE RESIN FOR DIRECT INK WRITE ADDITIVE MANUFACTURING

Portions of this chapter come from: J. Kopatz, J. Unangst, A. Cook, L. Appelhans "Compositional Effects On Cure Kinetics, Mechanical Properties and Printability Of A Dual-Cure Epoxy/Acrylate Resin System For DIW Additive Manufacturing"

This chapter investigates the effect of acrylate weight percent and *in situ* UV intensity on the green strength, printability, and structural fidelity of dual-cure epoxy acrylate thermoset resins. It was hypothesized that the increased acrylate content in the resin formulation would increase green strength because there would be more acrylate present in the resin to form the acrylate network. Additionally, it was hypothesized that the increased print intensity would also increase the green strength by increasing the total conversion of the acrylate network. The goal was to investigate the minimum amount of acrylate necessary to form a structurally stable part while printing using DIW. This chapter demonstrates that there is a range of acrylate formulations where the acrylate conversion depends on the UV exposure profile. By optimizing the *in situ* cure conditions during the print profile, you can reach satisfactory levels of conversion and green strength for the different formulations.

4.1 Introduction:

Dual-cure resins are of interest due to their versatility, working time [1], and tailorability to produce a wide range of material properties[1-10]. Much like polymer blends, dual-cure resins can produce materials possessing tunable mechanical [2, 3, 11], thermal [12, 13], and electrical [12, 14, 15] properties and have been investigated for use as shape memory polymers [16-18], holographic materials [19, 20], and for additive manufacturing [5, 6, 16, 21, 22].

The term 'dual-cure' is used to describe a process where two curing mechanisms occur simultaneously or sequentially polymerize two different monomers. For AM applications dualcure resins are typically two-component resins which employ an *in situ* curable component, to maintain shape and structure during printing, while a post-print cure of the second component enhances the final thermal and mechanical properties. Mixed monomer dual-cure approaches can be used to advantageously combine the beneficial properties of multiple resins. Mixed monomer dual-cure approaches are also beneficial in systems where a rapid cure might negatively impact material properties, or where one of the neat resins exhibits an undesirable property, such as excessive cure shrinkage [23, 24]. This is especially useful in the realm of AM, where a mechanically and dimensionally stable green part can be constructed via rapid polymerization of one component followed by a post-print cure to polymerize the second component and impart the desired material properties [1, 5, 6, 8, 16, 21, 22, 25].

Most common thermoset dual-cure systems require external stimuli, typically heat or light, to initiate polymerization and cure the system. Rapidly polymerizing formulations used in AM applications often contain UV-curable acrylate resins. Their rapid polymerization via a freeradical chain-growth mechanism is initiated by photoactivated radical initiators. For AM applications, acrylates are often combined with epoxy resins because pure acrylate resins can suffer from shrinkage, oxygen sensitivity, and inferior mechanical properties, such as fracture toughness [5, 6, 16, 21, 22, 26]. The presence of the epoxy reduces the amount of shrinkage [4, 17], and also enhances the final thermomechanical properties once the part is thermally cured [16, 24, 27].

In dual-cure resins the green strength, which we define as the mechanical performance of a printed dual-cure material, after the initial *in situ* cure but before the final cure, is the main factor determining the complexity and size of parts that can be successfully printed with a specific resin system. The green strength is determined by the properties of the acrylate network,
which can be tailored by varying the acrylate functionality, acrylate content, and UV exposure [28, 29]. The green strength is extremely important because it determines the structural stability, dimensional fidelity, and load-bearing properties of the AM part, as it is being printed [30]. If the printed part has a low green strength, it may compress under its own weight after reaching a critical height, cave in on itself, or lose dimensional resolution, either during the print or during subsequent thermal cure. A high green strength also allows for easier handling of the printed part if post-print processing or handling prior to the final cure is necessary [31].

Dual-cure systems typically form interpenetrating polymer networks (IPNs) that are physically intertwined but chemically discrete, that is, not linked to each other by chemical bonds [2, 32]. IPN formation in dual-cure epoxy thermoset resins has been a topic of research for the past few decades [33], but has recently gained more interest due to applications in additive manufacturing. Common dual-cure resins used in additive manufacturing rely on forming sequential IPNs, where one polymer network is rapidly formed during the print, and the second network upon additional cure [5, 6, 21]. In addition to enabling the printing of complex geometries having high green strength and tailorable post-cure properties, the dual-cure approach to DIW printing can also can reduce or eliminate the anisotropy common in AM-printed parts, compared to both fused filament deposition of thermoplastics [34, 35] and stereolithography methods used for printing thermosets [36-39]. The anisotropy results from inhomogeneity at the interfaces between the printed filaments and layers and often leads to a reduction in strength in the build-direction [40]. Curing the materials in a two-stage approach allows for polymerization and crosslinking to occur across interfaces, effectively homogenizing the printed layers, and resulting in greater property isotropy [26]. Property anisotropy due to interlayer adhesion should be differentiated from anisotropy caused by alignment of high-aspect ratio fillers in the print direction, which is another phenomenon that can occur in filled thermoset and thermoplastic resins [41-45] that would not be affected by a dual-cure approach.

In this chapter, the link between resin compositions and the mechanical properties, cure kinetics, and printability of dual-cure epoxy/acrylate system consisting of varying amounts of trifunctional epoxy, difunctional epoxy, and difunctional methacrylate resins was explored. Varying amounts of dimethacrylate resin and the UV cure intensity and exposure profile impact the acrylate cure kinetics and the green strength of DIW printed parts. We find that the acrylate cure kinetics and extent of cure are greatly influenced by the dose profile, episodic versus continuous, in addition to the acrylate content and UV intensity, when measured by photocalorimeter differential scanning calorimetry. We demonstrated that the *in situ* print intensity significantly impacts the printability and structural integrity as well as the green strength of the resulting part, where printability is the ability to consistently extrude the resin and structural integrity is the ability to maintain shape during the print.

4.2 Experimental procedure

The chemical structures of the epoxy and acrylate monomers used in these formulations is presented in Figure **4-1**. The bisphenol-A ethoxylated dimethacrylate (Sartomer SR348) was supplied by Arkema with an n + m value ranging from 0 to 7. An acrylate equivalent molecular weight of 264 g was used to calculate photoinitiator loadings. The diglycidyl ether of bisphenol-A based epoxy resin (EPON 828) was supplied by Hexion with an epoxide equivalent weight of 188.5 g. The tri-functional epoxy (Tactix 742) has an epoxide equivalent weight of 150-170 g and was supplied by Huntsman. The photoinitiator used was 2,2-dimethoxy-1,2-diphenylethan-1-one and the latent curing agent used was 1-ethyl-3-methyl imidazolium dicyanamide, both purchased from Sigma-Aldrich. All chemicals were used as received. All formulations contained 5 wt % of a rheology modifier, hydrophilic fumed silica (Cab-O-Sil® M-5) with a surface area of 200 m²/g and a nominal particle size of 200-300nm [46], purchased from Cabot.



Figure 4-1: Components of the dual-cure epoxy/acrylate resin

4.2.1 Blend Nomenclature

Blends with varying acrylate weight percent are labeled as xx wt %, where xx corresponds to the wt % of dimethacrylate. The remaining wt % is composed of a constant 1:1 mol:mol ratio (moles epoxy functional groups) of trifunctional: difunctional epoxy, 5 wt % fumed silica, 5 mol % (relative to total epoxy functional groups) latent curing agent, and 2 mol % (relative to total acrylate functional groups) photoinitator. For example, the 10wt% formulation is 10 wt % acrylate, 40wt % triepoxy, 40 wt % diepoxy, 0.2 wt % (0.2 mol % vs. acrylate functional

groups) photoinitiator, 4 wt % (5 mol % vs. epoxy functional groups) latent curing agent, and 5 wt % fumed silica. The 'pure acrylate' formulation is composed of dimethacrylate, 5 wt % fumed silica, and 2 mol % photoinitator. The 'pure epoxy' formulation is composed of a 1:1 mol:mol ratio of trifunctional: difunctional epoxy, 5 wt % fumed silica, and 5 mol % (relative to total epoxy functional groups) latent curing agent. The formulations are found in Table 4-1. These formulations were chosen to test the influence of a printable range of acrylate content on green strength and printability. It was hypothesized that lower amounts of acrylate would result in better thermomechanical properties because the thermomechanical properties of pure acrylate are lower than that of the pure epoxy.

Table 4-1: Activate formulations							
Variation in Formulation	10 wt% acrylate	15 wt% acrylate	30 wt% acrylate	50 wt% acrylate			
Component	wt%	wt%	wt%	wt%			
Sartomer SR348	10	15	30	50			
Tactix 742	38	35	28	19			
EPON 828	42	41	34	23			
PI	0.2	0.3	0.6	1.0			
LCA	4	4	3	2			
Silica	5	5	5	5			

4.2.2 Preparation of resins

The trifunctional epoxy was heated to 70 °C for 1 hour prior to use to attain a workable viscosity. The dimethacrylate and diepoxy were combined in a 125 mL polypropylene centrifugal mixer container and hand mixed. The triepoxy was added to the dimethacrylate/diepoxy mixture, hand mixed, and placed back into an oven at 70 °C for 5 minutes. The combined resins were mixed for 60 seconds at 1800 RPM and 10.1 kPa in a Thinky ARV-310 planetary centrifugal mixer. The resin was cooled to room temperature where it remained visibly miscible and optically clear with a moderate viscosity. The photoinitiator, latent curing agent, and fumed silica were added to the resin and hand mixed before being placed back into the mixer for 60 seconds at 1800



RPM and 10.1 kPa. The resulting resins are highly viscous tacky pastes that are shear-thinning in behavior (Figure **4-2**).

Figure 4-2: Viscosity data for varying acrylate content

4.2.3 Cure conditions

As previously mentioned, there are three categories of samples based on the cure procedure. "UV print-cure only" samples refer to printed samples that are UV-cured during printing and are characterized without any further UV or thermal cure. The intensity used during various print conditions ranged from 7 mW/cm² to 54 mW/cm², which corresponds to a UV dose of 0.4 J/cm² to 1.9 J/cm² per printed mechanical bar. "UV print cure + flood cure" samples refer to print-cured samples that are UV flood cured after the *in situ* print cure. The UV print cure only

samples are flood cured for 30 minutes using an ABM, INC 500W near/mid UV 2105C2 illumination controller with an intensity of 5.7 mW/cm².

4.2.4 Characterization

Viscosity and photocalorimeter differential scanning calorimetry (UV-DSC) were conducted on the uncured resin while DMA and variable temperature DMA were used to analyze printed samples. Experimental details are included in Chapter 3.

4.3 Results & Discussion

4.3.1 Acrylate Cure Kinetics

Quantifying the UV cure kinetics provides a framework for understanding how different *in situ* UV cure profiles used while printing affect the cure state of the printed part. While some UV polymerizations obey the reciprocity law, which states that exposure duration and intensity are interchangeable, meaning that a short exposure at high intensity will have the same outcome as a long exposure at low intensity as long as the total dose is the same [47-49], many systems do not, including the resin systems used in this study. The lack of reciprocity means that the total conversion of the photopolymerization reaction depends on both exposure duration and intensity, and not only on total dose. Incomplete conversion is expected to impact the green strength of the printed parts and could also affect the long-term stability, due to the presence of unreacted acrylate monomer and trapped radicals [50-52]. Many factors can impact the extent of conversion, including the intrinsic reactivity of the acrylate monomers [53, 54], the type and concentration of the radical initiator [53, 55, 56], the UV intensity, dose, and exposure profile [53], that is, the duration, intensity, and order of sequential UV exposures, and factors that impact monomer mobility such as the presence of plasticizing non-reactive monomers or simultaneously growing polymer networks [24].

For additive manufacturing of dual-cure systems, the presence of a second monomer or growing polymer network and the UV exposure profile, which can vary depending on the print geometry and print path, are extremely important. There has been extensive previous work on the impact of irradiation intensity and dose on acrylate conversion [57-59], but researchers have reported varying outcomes. A limited number of studies have investigated the effect of intensity and dose on acrylate polymerization for AM applications. Some studies have found that the total extent of conversion depends only on the total dose, independent of exposure profile [60, 61], while others have found that the exposure profile greatly impacts the overall conversion [47, 62-65]

In this system the key factors affecting acrylate polymerization are the acrylate content, *in situ* intensity, exposure profile, and exposure duration. Each can have different effects on the kinetics and conversion depending on the interplay with the other variables. For example, oxygen inhibition is caused by molecular oxygen terminating or consuming free radicals that would otherwise initiate polymerization. This creates peroxy radicals that are more stable and less likely to reinitiate the polymerization of the acrylate network. If oxygen is present, an induction period occurs where the acrylate polymerization reaction does not proceed until the oxygen is much greater than the rate of reaction with monomer [66]. Therefore, sufficient free radicals must be generated to consume the residual dissolved oxygen within the resin before polymerization begins [66, 67]. The UV DSC experiments are performed under nitrogen so once oxygen inhibition due to residual oxygen is overcome, the polymerization reaction proceeds with further impact from oxygen inhibition. However, oxygen inhibition can have radically different impacts depending on the concentration of monomer, photoinitiator, and the UV intensity. At high radical concentrations, whether due to high PI concentration or high intensity, dissolved oxygen is

consumed quickly and little or no induction period is observed. In contrast, at low radical concentrations the induction period can be quite long, and the low initial rate of polymerization can affect the total conversion.

The UV intensity and exposure duration directly affect the concentration of radicals generated and this, in turn, affects not only the latency due to oxygen inhibition, but also, the reaction rate and radical efficiency. At low radical concentrations, the reaction rate is slower and propagation is favored over termination [47]. This results in each generated radical having a higher efficiency, that is, each radical reacts with more monomers before termination. As the radical concentration increases termination is favored over propagation, due to the increased frequency of radical recombination, and the radical efficiency is diminished. However, the high radical concentration also results in a high rate of polymerization, which results in higher conversions before the onset of deceleration [53]. Deceleration occurs when the diffusion of monomers becomes the rate-limiting factor for polymer chain propagation. As the mobility of the reactive acrylate monomers is reduced, the polymerization slows until the reaction vitrifies [53]. Faster reactions create more free volume, because the reaction rate exceeds the volume relaxation rate, and form more inhomogeneous networks [68] because the high rate of reaction depletes the local monomer concentration faster than diffusion can replenish it [69]. Both of these factors, faster reactions and free volume, can result in higher conversion by increasing monomer mobility at a specific extent of conversion [70].

The final factors effecting total conversion are dilution and vitrification. Vitrification occurs when the temperature during curing is exceeded by the glass transition temperature of the growing polymer network, which causes the network to freeze in a glassy-state [71]. Vitrification is common in many neat acrylate systems, particularly with multifunctional acrylates, that are photo-cured at room temperature and often results in low conversion [53]. Vitrification and

dilution both depend on the concentration of the reactive monomer. In dual-cure systems acrylate polymerization is often taking place in the presence of a second monomer that does not polymerize during the UV cure step. The unreactive monomer has two effects. First, prior to acrylate polymerization, it dilutes the reactive monomer, which can lower the radical efficiency and the rate of reaction, reducing the overall conversion. Second, the unreactive monomer can act as a plasticizer for the acrylate network. This plasticizing effect can delay the onset of deceleration and vitrification and enable the acrylate network to reach a higher conversion than it would in the absence of unreactive monomer [24, 50, 51].

Vitrification is common in many neat acrylate systems, particularly with multifunctional acrylates, and results in low conversion due to the formation of a highly crosslinked network [53]. The role of vitrification in inhibiting conversion in the neat dimethacrylate system was confirmed by comparing pulsed exposure experiments on the neat dimethacrylate at 30 °C and at an elevated temperature of 70 °C Figure **4-3**. At 70 °C, the conversion reached is 85% compared to 65% conversion at 30 °C.



Figure **4-3**: Percent conversion vs UV exposure at 30°C vs 70°C pulsed UV-DSC at 80mW/cm² for 100 wt% acrylate. The percent conversion was calculated using methods explained in Chapter 3.

At 30 °C 64% conversion was reached while at 70 °C 85 % conversion was reached. Both reactions proceeded rapidly and reached maximum conversion after the first pulse. However, the higher temperature delays vitrification of the network and allows for increased mobility of the monomers due to a lower viscosity resin. This results in a higher conversion reached before the material converts into a glassy state due to the glass transition temperature of the growing polymer. In contrast to neat acrylate resins, the uncured epoxy resin in these epoxy/acrylate systems is expected to plasticize the acrylate network, allowing for greater conversion [24, 50, 51].

We investigated the impact of UV intensity and exposure profile on varying epoxy/acrylate formulations with UV-DSC. The UV-DSC experiments are run under nitrogen flow, with a 2-minute nitrogen purge prior to irradiation, however, it is assumed that there remains some residual dissolved oxygen in the resin at the start of the test [72]. Pulsed experiments, consisting of short UV exposures followed by a dark period, are designed to mimic the episodic *in situ* UV irradiation that a printed part might be exposed to during printing. Depending on the print geometry and print path, a specific area of the print will be irradiated at different intensities and durations, and with varying dark intervals, over the course of the print. The pulsed UV-DSC experiments do not perfectly mimic the UV exposure during printing, because they are performed at a single intensity, whereas, during printing, the intensity of UV exposure will vary depending on the distance from the actively printing bead where the UV light is focused. Nevertheless, the experiments do give insight into how cure evolves during an episodic UV exposure profile. For comparison a continuous UV exposure profile was examined to determine what impact the episodic UV exposure profile has on the extent of acrylate conversion. A continuous exposure profile might be experienced during printing of small parts or for printers using an *in situ* flood cure UV source with a large irradiation area.

The pulsed exposure experiments consisted of twenty 2.4 second UV pulses, with a 5 min dark time between pulses, and was tested at varying intensities for each resin composition. With this pulsed exposure profile, the overall percent conversion for a given resin composition increases as the UV intensity increases from 5, to 80, to 160 mW/cm², as shown in Figure **4-4**. The increase in conversion is due to the increase in free radical concentration with increasing intensity [47, 53, 60, 61]. The increased free radical concentration causes the reaction rate to increase such that, at the highest intensity (160 mW/cm²), the reactions have nearly reached maximum conversion after the first 2.4 second pulse. The lower conversions of the 50wt% acrylate, at higher intensities (80 and 160 mW/cm²), are due to vitrification, due to the high percentage of acrylate present in the resin and the lower amount of epoxy resin to act as a plasticizer.



Figure 4-4 Percent conversion of dimethacrylate by UV-DSC at 5 mW/cm² (top), 80 mW/cm²(middle), 160 mW/cm² (bottom)

At low intensity (5mW/cm²), the total conversion for pulsed exposures increases with increasing acrylate wt%, due to a higher concentration of acrylate monomers, which increases radical efficiency [47]. The overall conversion at 5mW/cm² is lower than the conversion at higher intensities due the decreased generation of free radicals at low intensity. The longer induction period and slow initial rate of polymerization contribute to an overall lower conversion than seen at higher intensities [67].

For pulsed exposures at 80 mW/cm², the total conversion for each formulation is greater than the total conversion achieved at 5 mW/cm². The greater radical concentration generated by the higher intensity can more quickly consume residual oxygen which results in a negligible induction period [66] and the higher radical concentration also results in faster reaction rates [47]. Both these factors lead to higher conversions before the onset of deceleration. As at 5mW/cm², as the acrylate content is increased, the total conversion tends to increase, except for the 50 and 100 wt% acrylate formulations. In these formulations the lower conversions are caused by vitrification.

Finally, at 160 mW/cm², the reaction rates are fast enough that most of the formulations reach maximum, or near-maximum, conversion after the first pulse, with the exception of 10wt% acrylate. The slower kinetics in the 10wt% system, even at the higher radical concentrations generated at high intensity, are due to the large amount of epoxy in the system acting as a non-reactive diluent [73]. For the other formulations the higher radical concentration results in faster reaction rates, than at lower intensities, and higher conversion before the onset of deceleration [53, 66].

All the formulations reach a similar total conversion at 80 and 160mW/cm^2 intensities except the 50 wt% acrylate formulation. The 50 wt% formulation reaches a higher conversion before vitrification at 160 mW/cm² versus 80 mW/cm². We hypothesize this is due to the increased reaction rate at the higher intensity. This highlights the role of the epoxy resin in facilitating higher conversion in the acrylate polymerization. Without unreactive epoxy resin to act as a plasticizer in the 100wt% acrylate system the higher reaction rate caused by higher intensity does not overcome vitrification, and the neat acrylate reaches a similar total conversion at both 80 and 160 mW/cm² intensities. When epoxy is present to plasticize the growing acrylate network in the 50 wt% acrylate formulation the higher reaction rate combined with delayed vitrification results in greater conversion.

At the highest intensities local resin temperature rise due to the UV exposure and reaction exotherms might also be expected to play a role in increasing conversion. However, for the pulsed exposure profiles, we believe the contribution from local resin heating is minimal, even at high intensities, due to the intermittent UV exposures. This is supported by the by the similarity in extent of conversion for the 100wt% acrylate system at 80 and 160 mW/cm² intensities.



Figure 4-5: Continuous exposure UV-DSC comparing 5 mW/cm² and 80 mW/cm² for varying acrylate wt. %.

To determine if the episodic exposure profiles experienced during printing result in significantly different conversions than continuous exposures, we next conducted UV-DSC experiments using longer exposures. We found that for a 10-minute exposure length, the

measured enthalpy in the second and third exposures were equivalent, indicating that no further measurable reaction was occurring after the first 10-minute exposure (SI Figure 1). Having established that 10 minutes was a sufficient duration to reach maximum conversion, all subsequent experiments consisted of two 10-minute exposures. The first exposure measures the enthalpy of the reaction, while the second exposure measures the specific heat capacity, under UV-irradiation, of the reacted polymer, and is used as the baseline.

In pulsed exposures the free radical concentration varies cyclically, reaching a maximum during or shortly after the UV pulse and then diminishing due to reaction with monomer or termination reactions until the next pulse. In contrast, in a continuous exposure, radicals will be constantly generated, at a rate that is generally proportional to intensity, until the photoinitiator is consumed. This means that for any time greater than the first pulse length, the radical concentration in a continuous experiment will be higher than that in a pulsed experiment at the same intensity.

Figure **4-5** shows the total conversion at two different UV intensities for different weight percent acrylate formulations after a 10-minute continuous exposure. The effects of intensity and acrylate weight percent on conversion with continuous UV exposures are quite different than with pulsed exposures. First, the total conversion is equivalent or higher at low intensity vs high intensity. Secondly, the trends in total conversion with acrylate weight percent are opposite at low and high intensities. These differences show the complexity of the interplay between reaction kinetics, radical efficiency, and acrylate concentration.

With low intensity continuous irradiation, the total percent conversion decreases with increasing acrylate content. At low intensity the radical concentration, and therefore the reaction rate, is slower, and the radical efficiency is high. The slower reaction rate results in a more homogeneous acrylate network [74] and allows more time for free volume relaxation relative to polymer propagation. Both these factors reduce monomer and chain mobility. Under these

conditions, as the acrylate weight percent increases the conversion prior to deceleration decreases because there is less epoxy present to plasticize the system and retard deceleration or vitrification [70].

In contrast, at higher intensity the percent conversion increases with increasing acrylate content. The higher radical concentration leads to more rapid reaction rates, resulting in an inhomogeneous network [68]. At low acrylate weight percent the inhomogeneous network formation, in combination with the diluent effect of the epoxy, leads to a sparse/dense morphology that lowers the radical efficiency and decreases the total conversion reached before the photoinitiator is consumed. At higher weight percent acrylate the higher concentration of acrylate monomer results in higher radical efficiency, and the network inhomogeneity actually increases monomer mobility enabling the network to reach a greater extent of conversion before deceleration [47, 53].

In contrast to the pulsed exposures, for the continuous exposures the total conversions at 5mW/cm² are higher than at 80 mW/cm² except for 50 and 100wt% acrylate which reach slightly higher conversions at the higher intensity. In the lower weight percent acrylate formulations, the negative effects of dilution and inhomogeneous network formation on radical efficiency play a bigger role at high intensity, when a higher concentration of radicals are generated initially. The total conversion under these conditions may be limited by the PI consumption, so the decrease in radical efficiency with higher UV intensity leads to a lower overall conversion at high intensities. At 50 and 100wt% acrylate, radical efficiency is higher due to the higher concentrations of reactive monomers, and the limiting factor becomes vitrification. For this reason, the conversion for the higher weight percent acrylate compositions is similar at both low and high intensity.



Figure **4-6**: Comparing pulsed exposure versus continuous exposure of varying acrylate wt% at 5mW/cm² (left) and 80mW/cm² (right)

Finally, we consider the differences in total conversion in pulsed versus continuous exposures at both low and high intensities. Figure **4-6** compares the total percent conversion reached with pulsed UV exposure to that reached with continuous exposure at 5 and 80 mW/cm² intensities.

At low intensity (5mW/cm²), the conversion is much higher for continuous versus pulsed exposures. For short pulses and low intensities, a lower concentration of free radicals are generated [47] with relatively long dark times in between bursts of radical generation. The long induction periods with pulsed exposure result in more consumption of free radicals by termination processes during the induction period, reducing radical efficiency, and lowering the overall conversion reached before the PI is consumed [66]. This results in lower conversion rates and incomplete consumption of the acrylate monomers for pulsed exposure at low intensity. However, for continuous exposures at low intensity, the low radical concentrations favor propagation over termination, increase radical efficiency, and a higher total conversion is reached, as discussed above [47].

At high intensity (80mW/cm²) the opposite trend is observed, conversion is higher for pulsed exposures than for continuous exposures. At high intensities the high concentration of

radicals generated increase the rate of polymerization before the onset of deceleration. For any given intensity, a higher concentration of free radicals are generated during continuous exposure versus pulsed exposures. However, in the high intensity continuous exposures the radical concentration is high enough that termination through radical recombination competes with propagation [47]. This results in a lower propagation efficiency per radical and lower conversions for continuous versus pulsed exposures at high intensities for the 10, 15, and 30wt% acrylate formulations. The maximum conversion of 50 and 100 wt% acrylate formulations at higher intensities is limited by vitrification rather than radical efficiency and therefore slightly higher conversions are reached for continuous exposure, where the local temperature increase due both to continued UV exposure and to the ongoing polymerization reaction, drives conversion slightly higher before vitrification occurs.

4.3.2 Mechanical Properties of UV-only Cured Composites

The mechanical stability of the resins during printing, and during the subsequent thermal cure, is a function of the green strength arising from the acrylate network formed during the UV cure. The storage moduli as a function of temperature were compared for different formulations and print conditions. The room temperature storage modulus was measured after UV cure at three different intensities during printing, "UV print cure only", and then again following a 30-minute post-print UV flood cure, "UV Print Cure + Flood Cure", to compare differences in the green strength with varying intensity and after the final flood UV cure step. The UV intensities and exposure times are detailed in the methods section. The flood cure was utilized to push the acrylate reaction to reach maximum conversion.

For the "UV print cure only" samples the storage modulus increases with increasing acrylate weight percent. This is because there is more acrylate network formed as the acrylate content increases, and less unreacted epoxy acting as a plasticizer (Figure **4-7**). The green

strength also increases with increased print UV intensity, indicating that, at the higher intensities, the acrylate network is reaching higher conversion. This is consistent with the findings from UV-DSC for the lowest intensity of 5 mW/cm² exposures, which are the most representative of the intensities used during printing. There are no consistent print direction effects on the mechanical properties of the UV-print cure only samples except in the 50 wt % where there is a print direction effect for the samples cured at the highest intensity. However, this is due to the printability differences where the longitudinal samples result in back-cure during the print compared to transverse samples. The 10 wt % acrylate UV print-cure only samples did not have a sufficient green strength to be measured in our experimental setup.



Figure 4-7: Room temperature storage modulus values of UV print-cure only and UV print-cure + flood-cure samples measured by DMA. UV-print cure only longitudinal- and transverse printed bars are also compared. Error bars indicate the standard deviation in the measured values

UV print-cure only samples were then flood cured in order to investigate the impact of flood cure on the network formation and green strength. For samples print-cured at a UV intensity of 7mW/cm² and then flood cured (black bars in Figure **4-7**) we found that the storage modulus increases significantly after the flood cure due to additional acrylate conversion. In contrast, for

samples printed with higher *in situ* UV intensity no change in storage modulus with the additional UV flood cure was observed (Figure **4-8**).



Figure **4-8**: print cure only and print + flood cure of samples printed with 29 mW/cm² *in situ* UV intensity. Longitudinal and transverse samples

The increase in the storage modulus values after the UV flood cure, indicates that the UV print-cure only samples do not reach full conversion during the *in situ* UV print cure. This could be beneficial because full conversion during print could lead to poor interlayer adhesion, especially in the higher weight percent acrylate formulations, but it could also be disadvantage in more complex parts with non-planar geometries where irradiation penetration during the flood cure could vary for different areas resulting in varied extents of cure [75].

The impact of *in situ* print intensity on print direction effects was further investigated using a TA Q800 DMA with a 15mm gap 3-point bend fixture. The method used was a force ramp of 1 N/minute from a pre-load of 0.2N to 18N at room temperature in air. Printing at an *in situ* print intensity of 7 mW/cm² does not result in print direction effects for 50 wt% acrylate print-cure only samples, however printing at 29 mW/cm² does result in print direction effects for print-cure only samples (Figure **4-9**). This is likely due to the greater extent of acrylate

conversion reached when printing at the higher intensity. Longitudinal samples result in a single extruded bead reaching a high conversion before encountering the next printed bead, which creates low bead-to-bead adhesion in each layer and poor layer-to-layer adhesion. Conversely, transverse samples allow for the beads within each layer to fuse to each other during the print allowing for better bead-to-bead adhesion, but possibly poor layer-to-layer adhesion.



Figure 4-9: DMA modulus differences of 50 wt% acrylate transverse and longitudinal samples printed at 7 mW/cm² and 29 mW/cm²

4.3.3 Print Fidelity

A qualitative evaluation of the structural stability of the resins while printing and curing was performed by printing 25-layer single-bead walls (25.4 mm long x 0.85 mm wide x 15mm tall) using varying *in situ* print UV intensities and acrylate weight percents. The high aspect ratio geometry was selected to determine what print condition and resin combinations could print challenging geometries without deviations like sagging or leaning, and if the green strength was sufficient to maintain the geometry during thermal cure. Both printability and structural stability were investigated, where printability means that the resin could be extruded without clogging or back cure and structural stability means that the printed part maintained the intended shape during the print.

Each formulation requires a different optmized print intensity in order to retain structural integrity and print without clogging or back cure. Figure **4-10**, Figure **4-11**, and Figure **4-12** show examples of different compositions printed at the same print inteisty and demosntrate the cooperative effect of acryalte content and intenisty.



Figure 4-10: 15wt% (left) 30wt% (right) acrylate single-bead wall printed at 106 mW/cm² intensity



Figure 4-11: 15wt% (left) 30wt% (right) acrylate single-bead wall printed at 29 mW/cm²



Figure 4-12: 30wt% (left) and 50wt% (right) acrylate single-bead wall printed at 14 mW/cm²

The printability and structural integrity of all formulations at varying print intensities are found in Table **4-2**. As the acrylate weight percent increases, the printed part becomes structurally stable at lower *in situ* print intensities. However, the printability of the resin at higher UV intensities decreases with increased acrylate content due to back-cure into the tip of the nozzle resulting in clogging. Therefore, there is a window of intensity values for each resin where printability and structural integrity are both achievable. This information offers the ability to streamline printing process conditions while correlating to resulting mechanical properties. Additionally, by utilizing UV-DSC to mimic the print conditions resulting in printability and

structural integrity for a given resin, the extent of conversion can be determined and correlated to the structural integrity, printability, and green strength of printed parts.

P = printable $S = structural integrity$							
Acrylate Content (wt%)	15	30	50				
UV intensity (mW/cm ²)							
0	Р	Р	Р				
7	Р	Р	P, S				
14	Р	P, S	P, S				
29	Р	P, S	P, S				
57	P, S	S	S				
106	P, S	S	S				

Table **4-2**: Printability and Structural integrity of 25-layer single bead walls

Finally, to determine how well the varying print conditions and resin formulation maintained print fidelity the "UV print-cure only" walls were thermally cured, without being exposed to an additional UV flood cure. As UV/thermal dual-cure compositions require a postprint thermal cure to polymerize the second polymer component, structural stability during the thermal cure is necessary to maintain good dimensional fidelity of the fully cured part, and may vary significantly from structural stability at room temperature due to the significant decreases in modulus with increasing temperature (see Chapter 5 Section 5.3.1) The dimensions of the walls post thermal cure are presented Table **4-3**: Dimensions of 25-layer single bead walls post thermal treatment as well as the designed wall dimensions. The designed width of the wall was the nominal width of one bead (0.85mm), however the width of an actual printed bead is closer to 1.5 mm. The '-' symbols in indicate conditions where the printed geometry was no longer wall-like enough to measure a length, width, and height.

With no UV irradiation, the prints do not maintain the target geometry regardless of the composition. While the resins are shear thinning, the zero-shear viscosity is not sufficient to maintain a structure after extrusion. As the UV intensity is increased the dimensions begin to

match the originally designed dimensions. The heights increase and the widths decrease due to each layer being able to support the weight of the subsequent layers. However, for 30 and 50 wt% acrylate compositions printed at intensities of 57 mW/cm² and higher, the height begins to decrease and the width increases. This is the result of several factors. At higher print intensities and weight percent acrylates the acrylate conversion during printing is sufficient to cause poor interlayer adhesion, as described in the previous section. This causes subsequent beads to roll off the bead underneath, leading to an offset geometry as shown in the left image in Figure **4-12**. At even higher intensities printability is impacted and clogging of the nozzle due to back-cure can cause missing layers in the print, decreasing the height, and increasing the width due to structural collapse. The increase in width can also result from the syringe passing clogs, which causes subsequent over extrusion, that can lead to greater bead width.

Acrylate Content (wt %)		15			30			50	
UV intensity (mW/cm ²)	L	W	Η	L	W	Н	L	W	Η
0	-	-	-	-	-	-	-	-	-
7	-	-	-	16.7	2.3	16.1	25.4	1.4	17.1
14	27.4	4.2	10.8	23.3	1.9	16.8	22.2	1.4	18.4
29	24.6	4.2	14.1	23.2	1.5	17.3	22.6	1.4	17.5
57	25.4	1.8	16.4	24.1	2	16.6	25.8	2.3	17.3
106	25.4	1.8	16.6	23.8	3	14.8	23.4	2.7	8.7
Target Wall Dimensions	25.4	0.9	18	25.4	0.9	18	25.4	0.9	18

Table 4-3: Dimensions of 25-layer single bead walls post thermal treatment

Finally, to determine how well the varying print conditions and resin formulation maintained print fidelity the "UV print-cure only" walls were thermally cured, without being exposed to an additional UV flood cure. As UV/thermal dual-cure compositions require a postprint thermal cure to polymerize the second polymer component, structural stability during the thermal cure is necessary to maintain good dimensional fidelity of the fully cured part, and may vary significantly from structural stability at room temperature due to the significant decreases in modulus with increasing temperature (see Chapter 5 Section 5.3.1) The dimensions of the walls post thermal cure are presented Table 4-3: Dimensions of 25-layer single bead walls post thermal treatment as well as the designed wall dimensions. The designed width of the wall was the nominal width of one bead (0.85mm), however the width of an actual printed bead is closer to 1.5 mm. The '-' symbols in indicate conditions where the printed geometry was no longer wall-like enough to measure a length, width, and height.

With no UV irradiation, the prints do not maintain the target geometry regardless of the composition. While the resins are shear thinning, the zero-shear viscosity is not sufficient to maintain a structure after extrusion. As the UV intensity is increased the dimensions begin to match the originally designed dimensions. The heights increase and the widths decrease due to each layer being able to support the weight of the subsequent layers. However, for 30 and 50 wt% acrylate compositions printed at intensities of 57 mW/cm2 and higher, the height begins to decrease and the width increases. This is the result of several factors. At higher print intensities and weight percent acrylates the acrylate conversion during printing is sufficient to cause poor interlayer adhesion, as described in the previous section. This causes subsequent beads to roll off the bead underneath, leading to an offset geometry as shown in the left image in Figure **4-12.** At even higher intensities printability is impacted and clogging of the nozzle due to back-cure can cause missing layers in the print, decreasing the height, and increasing the width due to structural collapse. The increase in width can also result from the syringe passing clogs, which causes subsequent over extrusion, that can lead to greater bead width.

Table **4-3**Comparing Table **4-2** to Table **4-3**, it is apparent that the conditions leading to printability and structural integrity more closely matched the designed wall dimensions. For example, 15 wt % acrylate printed using 57 and 106 mW/cm² had wall dimensions that were similar to the designed wall dimensions compared to walls printed at lower intensities. These

results demonstrate that dual-cure systems allow for tailoring of print conditions and resin formulation in order to achieve the desired geometry and green strength of printed parts

4.4 Conclusion

The effect of acrylate content and *in situ* UV intensity on the cure kinetics, green strength, printability and structural stability of dual-cure epoxy/acrylate DIW resins was investigated. During DIW printing, the UV exposure profile varies with the print path which may influence the acrylate conversion and green strength of the printed part. To investigate the influence of varying UV exposure profiles on the cure kinetics and total acrylate conversion, UV-DSC was performed. We found that both the irradiation intensity and the exposure profile significantly impact the total acrylate conversion. At low intensities, the conversion was higher for continuous exposure compared to pulsed exposure. In contrast, at higher intensities the acrylate conversion are due primarily to the variations in radical efficiency under varying combinations of acrylate concentration and UV intensity.

The effect of *in situ* UV intensity and acrylate content on the green strength of printed parts was investigated and increasing both acrylate content and print intensity were found to increase the green strength of transverse and longitudinal printed parts. Print direction effects were only observed for the highest print intensity (29 mW/cm²) and highest weight percent acrylate (50 wt%) formulation, due to the poor bead-to-bead adhesion of the longitudinal print compared to the transverse print, further illustrating the impact that different UV exposure profiles can have on printed parts. This difference in print direction is due to diminished interbead adhesion in the longitudinal parts caused by high acrylate conversion and the increased time between printing adjacent beads for the longitudinal prints.

An additional post-print flood cure results in additional acrylate cure and increases the green strength for parts printed at low UV intensities, but does not significantly impact green

strength for parts printed at higher UV intensities, consistent with UV-DSC results, showing that maximum conversion is reached quickly with high light intensity. After both UV and thermal cure, the mechanical properties further improve but are largely independent of composition as detailed in Chapter 5.

The most important finding of this work is that the print conditions which optimize printability, structural stability, and print fidelity do not, in most cases, match the UV exposure profiles and intensities that maximize acrylate conversion. This is important because incomplete acrylate conversion can lead to various adverse material qualities that can be detrimental to the structural integrity and long-term stability of the printed part, e.g. reduced green strength or lower chemical stability due to the presence of unreacted acrylate monomer. Issues like unreacted monomers or trapped free radicals that cause these instabilities are commonly solved in planar parts via an additional uniform UV flood exposure. However, this solution is not viable for complex and non-planar structures that are commonly created using additive manufacturing. This non-uniform curing issue should drive the development of tunable and novel resin chemistries that can promote maximum conversion of the acrylate network while optimizing print quality. By utilizing alternative radical initiation mechanisms, e.g. that enable dark or thermal cure, such novel resin chemistries could optimize additive manufacturing print quality for acrylate-based materials.

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CHAPTER 5 : COMPOSITIONAL AND CURE PROFILE IMPACTS ON INTERPENETRATING POLYMER NETWORK FORMATION AND MECHANICAL PROPERTIES OF A DUAL-CURE EPOXY/ACRYLATE RESIN

This chapter expands on the results found in **Chapter 4** and investigates the effect of thermal cure profiles and acrylate weight percent on the IPN network formation, epoxy cure kinetics, and thermomechanical properties of dual-cure epoxy-acrylate thermoset resins. Greater amounts of acrylate were found to result in phase separated interpenetrating polymer networks during the standard thermal cure profile. Higher thermal cure temperatures were found to result in a single glass transition temperature. This is hypothesized to result from the increased thermal temperature aiding in epoxy monomer mobility and diffusion and allowing for greater amounts of interpenetration. Exotherms were present in the standard cure DSC thermographs, which indicates that further cure was happening at increased temperatures. However, as post cure temperatures increased, the exotherms minimized until none were present, indicating that the samples were fully cured. The mechanical properties were analyzed using three-point bend which showed that the flexural modulus, flexural strength, flexural strain, and modulus increased with increasing acrylate content. Additional post-cure conditions at higher temperatures decreased the room temperature modulus, flexural modulus and glass transition temperature. Scanning electron microscopy (SEM) of the three-point bend fracture surfaces show mirror, mist, hackle, and river patterns indicate brittle failure mechanisms occurred.

5.1 Introduction

Polymer blends are widely used to tune material performance and properties in everyday applications [1-4]. Their low cost, toughness, elasticity, transparency, and processability make them desirable for modern technology [5]. In this thesis, polymer blends are defined as mixtures of two or more polymers that have been physically mixed together to create a new material [6-8].

Three main categories of polymer blends are: miscible, immiscible, and compatible polymer blends [7, 9, 10]. Miscible polymer blends have a microstructure that is dominated by one homogenous phase, because the polymers involved have an affinity for each other. In contrast, immiscible polymer blends consist of multiple phases and result in a heterogeneous micro and macrostructure, since the polymers involved do not have an affinity for each other and cause phase separation. Compatible polymer blends have an apparently homogeneous phase and properties at the macroscale, but often possess a heterogeneous microstructure consisting of small phases of the individual polymers [11, 12].

A special type of polymer blends are interpenetrating polymer networks (IPNs) [13], which are defined as two networks that are interwoven at the molecular level, but not chemically bonded to each other [14]. IPNs form from a blend of monomers which polymerize in the presence of each other and form two independent but interlaced polymer networks. IPNs offer the ability to alter bulk properties by changing the sizes of the microscale phase domains of the interwoven networks [15, 16]. In contrast to typical polymer blends where phase separation is largely determined by miscibility [17], IPNs enable control over phase separation [18] by changing the concentration of polymers, altering the cure order, varying the cure kinetics, modifying the crosslink density, tailoring the polymer miscibility, etc. [14, 17, 19]. IPNs have been used in the automobile industry for sound and vibration damping and protective coatings of plastic components [20], in dentistry to make resilient yet formable artificial teeth [14], and in biomedical fields for wound, scar, or skin care products [21]. IPNs have also been used to control undesirable properties in mixed resin systems, such as acrylate shrinkage. This was investigated by Sangermano *et al.* who discovered that increasing the amount of epoxy resin from 0 to 50wt% led to a decrease from 13 to 10% in shrinkage experienced during the simultaneous photoinitiated cure of an epoxy/acrylate system [22]. Additionally, Kuang et al. found that increasing the epoxy content from 0 to 80wt% in a sequentially cured dual-cure epoxy-acrylate system

decreased the acrylate-epoxy blend shrinkage from ~27% to 12% [23]. Shrinkage in pure acrylates results from the van der Waals to covalent bond conversion that occurs during cure. Having increased amounts of epoxy in the system minimizes the acrylate shrinkage during cure due to the slight expansion of the epoxy from the ring opening during the epoxy cure.

All IPN's, by definition, are comprised of at least one crosslinked polymer network [14, 24-26], meaning that IPNs are formed either from only thermoset polymers or thermoset and thermoplastic polymers. Therefore, the two networks cannot be separated from each other without breaking chemical bonds. IPN networks are often formed between miscible or compatible thermoset materials that are cured using different stimuli, such as heat or light. The resulting IPN structures are then defined as being a 'full-IPN' or 'semi-IPN'. A full IPN is one in which two separate 3-D polymer networks have formed. In a semi-IPN, one component forms a linear polymer, which is entangled within the 3-D crosslinked network formed by the second component[9, 27-30]. These structures are depicted in Figure **5-1**.



Figure 5-1: Full-IPN vs Semi-IPN
Full-IPNs are formed from thermoset polymers which each form their own networks, while semi-IPNs consist of both thermoset and thermoplastic polymers. Due to the structural differences between full- and semi- IPNs, the bulk properties are also different. For example, Lin *et al.* investigated the differences of semi and full-IPNs on the mechanical properties and specifically damping. The breadth of the tan delta peak was used to measure damping properties, where a broad peak indicates greater energy absorbing capability compared to a narrow peak. In comparison to semi-IPNs, full-IPNs were found to have a higher storage moduli and better damping properties due to greater entanglement of the networks and less chain mobility [31]. Full-IPNs may also mitigate macroscale phase separation, relative to semi-IPNs, due to the complete network entanglement of both 3-D networks. This can result in heterogeneity at a microscale with different phase domains ranging from nanometers to microns in size, but homogeneity at the macroscale where properties, such as the Tg, have a single value. The phase separation and microstructure of full-IPN's strongly depends on the miscibility of the monomer and polymer components and the polymerization kinetics of each system, [26]. This thesis is focused on full-IPNs.

Another classification of IPNs involves the order of initiation and polymer network formation. Simultaneous IPNs result from the simultaneous initiation of network formation of the two polymer networks, whereas sequential IPNs result from the formation of the individual networks in sequential order [30, 32]. These IPNs are depicted in Figure **5-2**.



Figure 5-2: Simultaneous-IPN vs Sequential-IPN

Regardless of the type of IPN formed, it is well known that phase separation can occurs during the reactions [24, 25, 30, 31, 33]. However, the detection of phase separation can be difficult, depending on the size of the phase domains and the similarity of the two polymer systems. A combination of characterization techniques is necessary to determine the homogeneity or heterogeneity of IPNs. The glass transition temperature (T_g) measured via variable temperature dynamic mechanical analysis (DMA) can be correlated with IPN homogeneity. If an IPN material is phase separated with a sufficient domain size, there will be two distinct glass transitions associated with the two components of the resin system. There will only be one glass transition for a completely miscible polymer blend, acting as a single phase [34]. The glass transition temperature is often found between the glass transition temperatures of the pure polymers, depending on the polymer ratios. For compatible but not completely miscible systems, the breadth of the T_g peak provides information as to the homogeneity of the IPN formed and is a direct consequence of the extent of mixing and/or volume fraction of the interphases [17]. A broad T_g peak indicates a distribution of phase compositions [35] within the interphase material [17, 19]. In contrast, a narrower T_g peak indicates a more homogeneous morphology due to either increased miscibility or kinetic trapping where the network crosslinking precedes phase separation [17, 32, 34, 36].

The extent and timing of phase separation are determined by monomer and polymer miscibility and the rates of the polymerization reactions [22, 37]. Unfortunately, it is very difficult to predict miscibility based on composition because phase separation occurs simultaneously with IPN formation [19]. Network fragment composition and molecular mass evolve during cure which affects thermodynamic miscibility that depends on extent of cure. The changing miscibility between monomer-monomer, monomer-polymer, and polymer-polymer compositions can lead to phase separation, and the varying composition throughout the cure makes creating phase diagrams difficult. Rocco *et al.* investigated how the miscibility of a polybutadiene dimethacrylate and dicyclohexylepoxide IPN changed when the compositions were varied. They found that ratios above 40wt% methacrylate were miscible, and the DMA exhibited 3 T_g's: one corresponding to the pure methacrylate, one for the IPN interphase, and one for the epoxy. Ratios under 20wt% methacrylate were immiscible and caused complete phase separation in the IPN as evidenced by two T_g's representing each homopolymer. [37]. Using atomic force microscopy, the phase separation for the 20wt% methacrylate composition was further confirmed by the presence of methacrylate nodules dispersed within an epoxy matrix.

The mechanism of phase separation is dependent on the type of IPN formed. Domain growth during sequential IPN formation is believed to follow a nucleation and growth mechanism, while the phase separation mechanism in simultaneous IPN formation is spinodal decomposition [38]. For sequential IPNs, Sperling *et al.* assumed there are four separate states of polymer A and polymer B leading to phase separation. In state 1, the network of polymer A is completely separated from monomer B. In state 2, the network of polymer A has gelled, and is swollen by monomer B. State 3 is a 'mutually mixed state' where both polymer A and B are mixed and diluted by each other. State 4 is when phase separation proceeds with the formation of spherical domains of polymer B surrounded by polymer A [19]. The spherical domains formed are the nucleation sites of polymer B. These nucleation sites then grow (or coalesce) during with time and result in domains that ranging from nanometers to microns in size. The growth rate of the nucleating sites varies during the cure with particularly large variation due to the abrupt increase in viscosity near the gel point. Near the gel point of each polymer, the increase in viscosity results in small nucleation sites.

For sequential IPN's, phase separation occurs as a result of the polymerization and crosslinking of the second network within the first network [39]. For both sequential and simultaneous IPNs , the reaction rates of each of the two polymer networks and cross-linking reactions influence the phase separation and the degree of interpenetration. During fast reactions there is not enough time for phase separation to occur and the degree of interpenetration is high, whereas for low reaction rates the microphase separation ends before the gel point and the degree of interpenetration is low [38]. Additionally, by controlling the volumetric ratio [24, 40, 41] and the degree of crosslinking of the polymer components [42], the size of the phase domains can also be altered, allowing for a gradient of properties to be achieved. For systems where gelation precedes phase separation, crosslinks can often restrict phase separation and consequently results in smaller domain sizes.

While simultaneous IPNs usually have significantly less phase separation compared to sequential IPNs, in some simultaneous systems phase separation still occurs, and the rates of phase separation versus gelation play a key role in determining domain size [24]. For example, Touhsaent *et al.*[43], found that the gel time and morphology of epoxy/acrylate simultaneous IPNs depends on when the phase separation occurred during the cure reaction. If phase separation

occurred before gelation, then the gel time of the epoxy was delayed due to a dilution effect of the acrylate network forming faster than the epoxy network. This resulted in large phase domains in the IPN as evidenced by the transition from a transparent to opaque material upon curing and two distinct T_g transitions. This is typical of sequential IPNs. In contrast, if phase separation occurred near or after the gel point, then the gel time was much longer due to simultaneous reactions of the epoxy and acrylate networks increasing the viscosity of the resin. The resulting IPN morphology is a result of the competition between the rate of phase separation and rate of gelation.

For simultaneous IPNs, the closer the reaction rates are to each other, the greater the IPN homogeneity [43]. For example, by closely matching the reaction rates in the simultaneous IPN formation of an epoxy and bismaleimide allylester, Iisak *et al.* [44] found that the extent of molecular mixing was increased, which was evidenced by a maximum glass transition temperature and tensile strength. Similarly, Zhou *et al.* reported that a closely-matched gelation time between polyurethane and PMMA yielded an IPN exhibiting a single glass transition temperature with no observable phase separation [45].

The most common approach to simultaneous IPNs use curing agents or catalyst, one for each network, that are activated by the same stimulus (e.g. heat). While it has been shown that simultaneous IPNs can have better mechanical properties compared to sequential IPNs, [33] due to minimizing phase separation, it is rare to achieve truly simultaneous IPNs because of the difficulty of identically matching the polymerization reaction kinetics. For instance, Dean *et al.* and others have found that in simultaneously-initiated IPNs consisting of an acrylate and an epoxy, the rate of the acrylate network formation is generally much faster than that of the epoxy network formation, which then impacts the overall conversion of the epoxy network [26, 43, 46, 47]. A similar effect was found to occur in other simultaneously-initiated IPN epoxy/acrylate systems. Though both polymerization reactions are initiated at the same time, the acrylate network will crosslink and gel faster than the epoxy network and will be the limiting factor of

epoxy conversion. Once the acrylate network gels, the viscosity exponentially increases, which then limits the diffusion of epoxy molecules. This results in a lower conversion of the epoxy network due to limited mobility, while the opposite is true for the acrylate network. The unreacted epoxy acts as a plasticizer and enables a higher conversion of acrylate in comparison to the neat acrylate resin [26, 48, 49]. Thus, in this system a two-phase IPN is formed, as determined by the presence of two glass transitions [26], despite the simultaneous initiation of polymerization. However, Cook and coworkers found that if reactions with near-identical rates are used, the final conversion for both networks are similar and the morphology is homogeneous due to the early interlocking of the networks [50].

This thesis focuses on sequential IPNs which warrants a more detailed discussion about different sequential IPN systems. Unlike simultaneous IPNs, sequential IPNs typically utilize two different types of stimuli (e.g. heat, light, etc.), to independently crosslink each network [9, 23]. The order of polymerization greatly impacts the morphology and resulting mechanical properties. For example, in an epoxy/acrylate sequential-IPN, Dean *et al.* found that thermally curing the epoxy before photocuring the acrylate resulted in a homogeneous morphology with a single T_g, however when the cure order was reversed, phase separation occurred, as evidenced by two glass transition temperatures [25]. However, the storage modulus was closer to that of the pure thermally-cured epoxy when the resin was thermally cured before being photo cured, as opposed to when the system was photo cured first followed by a thermal cure. When the resin was photo cured then thermally cured, the modulus was like that of the UV-cured pure acrylate. This indicates that the cure profile influences the conversion of each network which then dominates the value of the storage modulus. When the epoxy is cured first, the dual-cure system remains miscible for a longer period of time because the decrease in entropy of mixing and increase in free energy as the epoxy slowly approaches the gel point is counterbalanced by the unreacted dimethacrylate molecules that swell the epoxy gel. The subsequent rapid polymerization of the

dimethacrylate locks the two networks together resulting in a single T_g . The final conversion of the acrylate is limited by vitrification or topological constraint of the IPN, resulting in a storage modulus close to that of the pure epoxy. Conversely, when the acrylate is cured first, the acrylate gelation occurs at a lower conversion [51] compared to the epoxy conversion, and the entropy of mixing is reduced. The subsequent slower cure rate of the epoxy further decreases the entropy of mixing and further increase the free energy of mixing. Since the epoxy does not gel until a high conversion, the slow cure reaction allows for the diffusion of epoxy monomers out of the acrylate gel which allows for further phase separation [25].

While phase separation during polymerization controls domain size in simultaneous IPNs, the domain size in sequential IPNs is often controlled by the crosslink density. Shorter chains generally result in smaller domains due to forming network with a high crosslink density, while longer chains result in larger domains. For sequential IPNs, the domain size generally decreases with increasing crosslink density of the networks and the domain sizes can range between 10-100nm [14]. Yang et al. reported that in a polyurethane/polyacrylate sequential IPN, when polyurethane is polymerized before polyacrylate, the greatest extent of phase mixing occurs resulting in nanometer sized phase domains and a single Tg. In contrast, when polyacrylate is polymerized first, severe phase separation occurred resulting in larger phase domains and two separate Tg's close to the Tg's of individual components resulted [33]. For bisphenol A diglycidyl ether and polyethylene glycol dimethacrylate IPNs Chen et al. found phase separation occurred in nearly all fully cured sequential and simultaneous IPNs [52], The domain sizes of the IPNs were less than 500nm when both polymer networks were simultaneously photo-cured but micron sized for samples where the epoxy was thermo-cured followed by photocuring of the acrylate [52]. This thesis will focus on dual-cured sequential IPNs, where the first network is formed via photoinitiated free radical polymerization and the second network is sequentially formed via thermal initiated cure.

5.1.1 Epoxy/Acrylate systems

There have been a number of studies investigating epoxy-acrylate IPNs specifically, and how the order of polymerization impacts the morphology and resulting material properties [53, 54]. Baidak *et al.* studied the effect of increasing weight percent of epoxy on acrylate conversion and gel time of simultaneous IPNs composed of poly(n-butyl acrylate), diethylene glycol dimethacrylate, and diglycidyl ether of bisphenol A (DGEBA). Greater than 70 weight percent of epoxy resulted in decreased conversion rates and increased gel times of the poly(n-butyl acrylate) because of the unreacted epoxy acting as a diluent. Similarly, increasing the amount of acrylate also decreased the epoxy polymerization rate due to the same dilution effect from the unreacted acrylate. Additionally, the ester groups on the acrylate were thought to weaken the epoxy hydroxyl reactivity with the anhydride curing agent and further diminish the rate of reaction [24]. Similar effects on conversion were found by Dean *et al.* for the simultaneous IPN of diglycidyl ether of bisphenol A and bisphenol A diglycidyl ether dimethacrylate [26, 46, 47].

Nowers *et al.* investigated the effects of temperature and cure order on the reaction kinetics of polyethylene glycol diacrylate and DGEBA sequential-IPNs and simultaneous IPNs. In sequential IPNs, the presence of the first polymer decreases the polymerization rate of the subsequent polymer. The mobility of the propagating monomer is reduced due to the presence of the pre-formed gel. The pre-formed epoxy network decreased the acrylate reaction rate and final conversion more so than vice versa due to decreased mobility of the acrylate in the highly viscous resin [49]. For simultaneous IPNs where the monomers are polymerized together, the overall reaction rate is reduced as the viscosity increases and the dilution effect on both polymerization reactions declines.

Dean *et al.* further explained the impact of network formation kinetics and entropy of mixing on the resulting morphology of a 50:50 wt:wt DGEBA/ bisphenol A dimethacrylate sequential IPN. When the epoxy is cured first, the large acrylate molecules swell the gel and

counterbalance the decrease in the entropy of mixing. Following the epoxy cure the rapid photopolymerization then locks the networks together and prevents phase separation. Conversely, when the acrylate is polymerized first the fast polymerization of the acrylate results in gelation at low acrylate conversion and a steep reduction in the entropy of mixing. Because the epoxy does not gel until high conversion, the slow epoxy polymerization allows for the diffusion of the growing epoxy network out of the acrylate network resulting in phase separation [25].

Although Kuang *et al.* did not explicitly study polymerization kinetics and phase separation in their use of an epoxy/acrylate system for 3D printing, they reported a single broad T_g for systems that were cured sequentially via photo-curing then thermo-curing [23]. Other groups have also used similar dual-cure epoxy/acrylate systems but did not explore microstructure and did not provide any information to indicate if systems were homogeneous or heterogeneous [55-57].

This chapter focuses on sequential IPNs where first the acrylate network is cured via UV initiated free-radical polymerization, and the epoxy network is cured sequentially via thermally initiated homopolymerization catalyzed by a latent curing agent. Sequential IPNs require the sequential initiation of the cure reactions and generally assumes a complete reaction of the first network before the initiation of the second [14, 32, 43, 45]. While the properties of the sequential IPNs are highly dependent on the intrinsic miscibility of the polymers involved, cure kinetics, cure order, acrylate content and resin formulation also play a role on the IPN homogenization and thermomechanical properties.

5.2 Experimental procedure

The chemical structures of the epoxy and acrylate monomers used in these formulations is presented in Figure **5-3**. The bisphenol-A ethoxylated dimethacrylate (Sartomer SR348) was supplied by Arkema with an n + m value ranging from 0 to 7. An acrylate equivalent molecular weight of 264 g was used to calculate photoinitiator loadings. The diglycidyl ether of bisphenol-A

based epoxy resin (EPON 828) was supplied by Hexion with an epoxide equivalent weight of 188.5 g. The tri-functional epoxy (Tactix 742) has an epoxide equivalent weight of 153.5 g and was supplied by Huntsman. The photoinitiator used was 2,2-dimethoxy-1,2-diphenylethan-1-one and the latent curing agent used was 1-ethyl-3-methyl imidazolium dicyanamide, both purchased from Sigma-Aldrich. All chemicals were used as received. All formulations contained 5 wt % of a rheology modifier, hydrophilic fumed silica (Cab-O-Sil® M-5) with a surface area of 200 m²/g and a nominal particle size of 200-300nm [58], purchased from Cabot.



Figure 5-3: Components of the dual-cure epoxy/acrylate resin

5.2.1 Blend Nomenclature

Blends with varying acrylate weight percent are labeled as xx wt %, where xx corresponds to the wt % of dimethacrylate resin. The remaining wt % is composed of a constant 1:1 mol:mol ratio (moles epoxy functional groups) of trifunctional: difunctional epoxy, 5 wt % fumed silica, 5 mol % (relative to total epoxy functional groups) latent curing agent, and 2 mol % (relative to total acrylate functional groups) photoinitator. For example, the 10wt% formulation is

10 wt % acrylate, 40wt % triepoxy, 40 wt % diepoxy, 0.2 wt % (0.2 mol % vs. acrylate functional groups) photoinitiator, 4 wt % (5 mol % vs. epoxy functional groups) latent curing agent, and 5 wt % fumed silica. The formulations are found in Table **5-1**Table **4-1**.

	· · · · · · · · · · · · · · · · · · ·			
Variation in Formulation	10 wt% acrylate	15 wt% acrylate	30 wt% acrylate	50 wt% acrylate
Component	wt%	wt%	wt%	wt%
Sartomer SR348	10	15	30	50
Tactix 742	38	35	28	19
EPON 828	42	41	34	23
PI	0.2	0.3	0.6	1.0
LCA	4	4	3	2
Silica	5	5	5	5

Table 5-1:	Acrylate	formu	lations
	,		

5.2.2 Preparation of resins

The trifunctional epoxy was heated to 70 °C for 1 hour prior to use to attain a workable viscosity. The dimethacrylate and diepoxy were combined in a 125 mL polypropylene centrifugal mixer container and hand mixed. The triepoxy was added to the dimethacrylate/diepoxy mixture, hand mixed, and placed back into an oven at 70 °C for 5 minutes. The combined resins were mixed for 60 seconds at 1800 RPM and 10.1 kPa in a Thinky ARV-310 planetary centrifugal mixer. The resin was cooled to room temperature where it remained visibly miscible and optically clear with a moderate viscosity. The photoinitiator, latent curing agent, and fumed silica were added to the resin and hand mixed before being placed back into the mixer for 60 seconds at 1800 RPM and 10.1 kPa.

5.2.3 Cure conditions

'UV print + flood cure' refer to samples that were *in situ* UV print cured at 7 mW/cm^2 and then UV flood cured after the *in situ* print cure. The *in situ* print cure corresponds to a UV dose of 0.5 J/cm² per transverse printed mechanical bar and 0.42 mJ/cm² per longitudinal printed mechanical bar. The post-print flood cure lasts 30 minutes using an ABM, INC 500W near/mid UV 2105C2 illumination controller with an intensity of 5.7 mW/cm². 'Standard thermal cure' samples refer to UV cure samples that are then thermally cured in a Memmert programmable oven (model UF30plus). The standard thermal cure profile is as follows: ramp from 25 °C to 100 °C at 1 °C/min, isothermal for 4 hours, ramp to 150 °C at 1 °C/min, isothermal for 2 hours, cool down at 1 °C/min to 25 °C. These samples are referred to as 'standard thermal cure' (SC). Five Additional thermal profiles were explored and are listed in Table 5-2.

Table 5-2: Additional thermal cure profiles explored
SC = 4hrs 100°C + 2hrs 150°C
SC + 6hrs 150°C
SC + 2hrs 200°C
SC + 2hrs 250°C
UV cure + 4hrs 100°C + 2hrs 250°C
UV cure + 2hrs 250°C

5.2.4 Characterization

Isothermal measurements were conducted on the uncured resin while 3-point bend,

DMA, and variable temperature DMA were used to analyze printed samples. All parameters investigated are explained in Chapter 3.

5.3 Results & Discussion

5.3.1 Epoxy Cure Kinetics

The bulk mechanical strength and thermal stability of the printed parts rely on the full conversion of the epoxy network when thermally cured. Epoxy homopolymerization is expected to result in a slower conversion than amine and anhydride mediated epoxy polymerization [59-61], but homopolymerized epoxy has been shown to have higher glass transition temperatures, storage moduli, and thermal stability [62]. In dual-cure resins, the polymerization of the epoxy network is impacted by the presence of the polymerized acrylate network [25]. This can significantly impact the kinetics of the epoxy polymerization by reducing monomer diffusion and chain mobility in the growing epoxy network [25]. To investigate the impact of the pre-formed acrylate network on the rate of epoxy polymerization the onset of gelation of the epoxy network in UV-cured 'UV print cure + flood cure' samples was measured using variable temperature DMA.

In these experiments (Figure 5-4), the second peak in tan delta, where storage and loss moduli slopes are parallel, is used to determine the onset of gelation as the first peak in tan delta corresponds to the T_g of the acrylate network plasticized by epoxy monomer.



Figure **5-4**:VT DMA of 'UV print cure + flood cure' 15wt% (top) 30wt% (middle) and 50wt% (bottom) acrylate. hollow = heat up, solid = cool down



Figure 5-5:Onset of gelation of the epoxy network as a function of acrylate wt % in 'UV print + flood cure' samples

As expected, with increasing acrylate content the onset of gelation of the epoxy is delayed (Figure **5-5**) [25, 47]. The presence of the polymerized acrylate network decreases the rate of epoxy polymerization due to vitrification or topological constraint [25, 48]. The mobility of epoxy molecules is constrained and the diffusion of the monomer and oligomers through the pre-formed acrylate network is limited. The deceleration of epoxy cure in the presence of the pre-formed acrylate network is an important consideration when optimizing the cure profile for dual-cure printed parts as the kinetics may be much slower than in analogous epoxy-only systems. The presence of the acrylate network can also decrease the final conversion of the epoxy [25, 48] although I did not investigate the epoxy extent of cure in this study.



Figure 5-6: Onset of gelation for unreacted epoxy and unreacted acrylate

Isothermal cure measurements of unreacted resin offer insight regarding the time required for the epoxy network to form at a specific temperature. Additionally, isothermal cure measurements indicate if and when vitrification occurs during cure [63]. In this work, varying compositions of acrylate/epoxy dual-cure resins were prepared as described in the Methods section. Isothermal cure measurements were conducted at 150 °C in order to investigate the impact of uncured acrylate content on the gelation of the epoxy resin. The initiation temperature of the latent curing agent is around 130 °C [64], therefore a temperature of 150 °C was chosen for isothermal cure measurements. Figure **5-6** shows the onset of gelation time of the unreacted epoxy resin for the varying wt% of unreacted acrylate. As the wt% of unreacted acrylate increases, the onset of gelation time for the epoxy increases. This is because there is less epoxy to form the network as the acrylate wt% increases.

5.3.3 Mechanical properties of standard thermal cure composites

After investigating the effects of acrylate content and *in situ* UV print intensity on the cure kinetics and mechanical properties of printed samples, the samples were then subjected to a thermal cure to study the changes in mechanical properties during and after the formation of the epoxy network. Once the epoxy network is formed, modulus, T_g , and strength increase. However, as the 'UV print cure + flood cure' samples are exposed to temperature during thermal cure, the uncured epoxy resin decreases in viscosity until it begins to cure. This can result in large changes to the modulus and strength and impact the structural integrity of the print. Therefore, in order to optimize cure profiles and maintain print fidelity during thermal cure it is important to understand the material property changes that occur with thermal exposure.

To investigate the evolution of modulus during the epoxy cure, variable temperature DMA measurements, ranging from 20-250°C, with a 3°C/min ramp rate, were conducted on 'UV print cure + flood cure' samples. Table **5-3** lists the room temperature modulus and the lowest storage modulus with corresponding temperature, which shows the maximum softening point of the printed sample. The lower weight percent acrylate samples were difficult to measure with variable temperature DMA in our experimental setup, due to the low modulus and the softening during thermal cure, therefore, 10 wt % acrylate formulations are not included.

The modulus decreases 1-2 orders of magnitude from the room temperature modulus value as the temperature increases. The modulus decreases until activation of the latent curing agent and epoxy gelation occurs. Increased acrylate content results in both a higher minimum storage modulus and higher temperature where the minimum storage modulus is reached, due to the greater amount of acrylate network present and the presence of less unreacted epoxy to plasticize the acrylate network. Although epoxy gelation is slower for higher acrylate content, the

modulus, T_g, and mechanical performance improve from the increased acrylate network that is formed.

23°C Storage Modulus Acrylate Content Minmium Storage Modulus Temperature MPa °C wt% MPa 15wt% 0.1 (0.1) 104(2)5.0(2)30wt% 36.9 (4) 1.1(0.1)124 (13) 50wt% 211.9 (58) 6.6 (0.9) 134 (3)

 Table 5-3:Room temperature (23°C) modulus and minimum storage modulus of 'UV print-cure + flood-cure' samples during variable temperature DMA up to 250°C.

Understanding the evolution of modulus with temperature is important in order to design thermal cure profiles for dual-cure formulations that will minimize deformation of the UV cured parts due to softening during the thermal cure. However, as demonstrated in **Chapter 4**, the 15 wt% acrylate printed vertical walls maintained their structural integrity during our standard thermal cure profile (100°C for 4 hrs, 150°C for 2 hrs, 1°C/min ramps).

The room temperature storage modulus values of epoxy/acrylate formulations printed at 7 mW/cm² UV intensity were measured after the thermal cure in order to probe the network formation. The modulus values shown in Figure 5-7 are orders of magnitude higher than the 23°C (room temperature) storage modulus values in Table 5-3. This is because the composite is moving from an acrylate dominated regime to a cured epoxy dominated regime. Unlike the storage moduli of the UV-cured samples, there is no trend in storage modulus with acrylate weight percent for the thermally cured samples (Figure 5-7). This is likely due to the similarity in the 'pure epoxy' and 'pure 100 wt% acrylate moduli values. It is important to note that the 'pure epoxy' and 'pure 100 wt% acrylate' samples used are molded samples, not printed samples.





Glass transition (T_g) temperatures were measured with VT DMA after the 'standard

thermal cure' for samples of varying acrylate weight percent, and the values are shown in Table

5-4. The glass transition temperature increases with greater epoxy content because the T_g of the

mixed diepoxy/triepoxy polymer (215°C) is greater than the $T_{\rm g}$ of the pure acrylate network

(165°C).

Acrylate Content	Tg	
wt%	°C	
0	215	
5	215 (2)	
10	221 (1)	
15	210 (6)	
30	189 (6)	
50	121 (4), 186 (5)	
100	165	

Table 5-4: Glass transition temperatures for 'standard thermal cure' samples

The 50wt% acrylate system forms a phase-separated IPN, as evidenced by the appearance of two T_g transitions, a lower temperature T_g for the acrylate-rich phase and a higher T_g for the epoxy-rich phase Figure **5-8**.



Figure 5-8: Variable temperature DMA of 50 wt% acrylate after 'standard thermal cure'

This phase separation is likely why the T_g does not vary significantly between the 30wt% formulation and the epoxy-rich phase of the 50 wt% formulations. The T_g decreases with increasing acrylate content, where the single T_g of the 50 wt% acrylate would be expected to be lower than the single T_g of 30 wt% acrylate had phase separation not occurred. Both variable temperature DMA measurements (Figure 5-9) and thermal DSC measurements (Figure 5-10) show that the epoxy networks are not fully cured after the 'SC', as evidenced by shifts in the T_g after the first VT DMA temperature ramp (Figure 5-9) and measurable exotherms in the first

thermal cycle of DSC (Figure 5-10).



Figure 5-9: Variable temperature DMA glass transition shifts for 15 and 30 wt% acrylate after 'standard thermal cure'



Figure 5-10: Thermal DSC extent of cure for 15wt%, 30wt%, and 50wt% Acrylate

The exotherms present in the DSC for the 'SC' samples indicate that the epoxy was not fully cured. Therefore, higher temperature cure steps were investigated to determine the impact of fully cured epoxy on the IPN homogenization and mechanical properties.

5.3.4 Mechanical properties of additional thermal cure composites

Additional thermal cure profiles were explored for 15, 30, and 50 wt% acrylate formulations to observe IPN homogeneity and thermomechanical properties. The higher cure temperatures were expected to increase epoxy conversion and increase the room temperature modulus, compared to the 'SC' moduli values.



Figure 5-11: Room temperature storage modulus measurements for longitudinal print samples for different thermal cure profiles

Room temperature storage modulus values were measured for the various thermal cure profiles (Figure 5-11). Note that the room temperature modulus values for 0 wt% and 100 wt% acrylate were measured on molded samples, not printed samples. There is no consistent statistically significant trend in moduli with increasing acrylate wt% regardless of the cure profile. However, there is a slight decrease in the moduli values for all acrylate wt% samples with the 'UV + 2hrs 250°C' cure profile, where the 30 wt% acrylate is within standard deviation. This decrease indicates that the post-cured samples have a decrease in crosslinking relative to 'SC' samples This decrease may be because there is not a low temperature cure step to enable slow epoxy network formation, there is only a high temperature cure step which results in a rapidly formed epoxy network which may be less dense [65] and therefore have a lower storage modulus.



Figure 5-12: Glass transition temperatures for longitudinal print samples for different thermal cure profiles. The double purple bar indicates the two glass transition temperatures for the 50 wt% Acrylate 'SC' sample

Glass transition measurements were taken of all thermal cure profiles and the values are shown in Figure 5-12. As previously stated, the 'SC' 50 wt% acrylate sample had phase separation, as evidenced by the two glass transition temperatures (Figure 5-13). Aside from the 'SC' 50 wt% acrylate sample, the other formulations had a single T_g value. Additionally, as the thermal cure temperature increased, the breadth of the T_g peak narrows (Figure 5-13) which indicates greater interpenetration of the acrylate and epoxy networks within the IPN [31]. In samples with higher cure temperatures, there is also less shifting of the T_g between the heat and cool cycles of the VT DMA.

The T_g decreases slightly with greater acrylate content, as previously stated, because the T_g of the mixed diepoxy/triepoxy polymer (215°C) is greater than the T_g of the pure acrylate network (165°C) (Appendix I). For all formulations, the glass transition temperatures stay the

same or decrease slightly after thermal cure at 250°C. This was originally assumed to result from either further homogenization of the IPN microstructure or coalescence of the epoxy and acrylate phase T_{gs} due to exposure to a high temperature [66, 67].



Figure 5-13:Variable temperature DMA glass transition measurements for 15, 30, and 50 wt% acrylate after 'standard thermal cure' (top), 'SC + 2hrs 200°C' (left) and 'SC + 2hrs 250°C' (right). Data below 80°C is ignored due to slipping of the sample. Hollow = heat up, solid = cool down

To help identify whether degradation or coalescence was responsible for the decreased T_g values in the IPNs for the varying thermal cure profiles, DSC extent of cure measurements (Figure 5-14) and isothermal TGA measurements (Figure 5-15) were taken for 5wt% SiO₂ filled 100% and 0% acrylate molded samples.



Figure 5-14: DSC extent of cure measurements for 'SC' and 'SC + 2hrs 250°C' 0 wt% Acrylate molded samples

DSC extent of cure measurements were utilized to investigate if the 'SC' profile resulted in unreacted resin, and if so, whether a higher temperature thermal cure profile would push the epoxy to full conversion. The 'SC' 0 wt% acrylate (black) has an exotherm indicating that there is residual unreacted epoxy present in the system. This exotherm disappears for the 'SC + 2hrs 250°C' sample, which indicates that the residual epoxy has all reacted.



Figure 5-15: 6-hour 250°C isothermal TGA measurements for 100 wt% Acrylate (left) and 0 wt% Acrylate (right) to investigate whether significant degradation occurs during the 250°C cure step.

Isothermal TGA measurements indicate that minimal weight loss (8% and 3%) occurs during the 6-hour isothermal for the 100 wt% and 0 wt% acrylate samples, respectively. These experiments used a 10°C/min ramp rate from room temperature to 150°C, which is the maximum temperature used in the 'SC' thermal cure profile, and then used a 1°C/min ramp to 250°C where they were isothermally held for 6 hours. The 1°C/min ramp rate is to mimic the rate used in the 'SC + 2hrs 250°C' cure profile. Though the thermal cure profile only holds the samples at 250°C for 2 hours, a longer duration was of interest to investigate the material stability at this temperature. These results indicate that minimal weight loss due to degradation occurs during the high temperature exposure, but oxidative degradation could occur without significant weight loss, and could lead to a reduction in crosslink density due to oxidative scission [68].

The next step was to investigate how this weight loss, and the presence of a small amount of unreacted epoxy in the 'SC' samples, indicated by the exotherm in the DSC measurements, influences the glass transition temperature of the 0 wt% and 100 wt% acrylate samples. The T_g for the 'SC + 2hrs 250°C' 0 wt% acrylate sample was found to be 171°C, while that of the 100 wt% acrylate sample was 120°C (Appendix I). These T_g values are lower than the T_g values of the

'SC' samples (215°C for 0 wt% and 165°C for 100 wt%). This was unexpected, because it was hypothesized that the higher temperature thermal cure for the 'SC + 250°C' samples would have increased the crosslink density and increased the T_g . However, this is not the case and the decrease in thermomechanical properties with additional thermal exposure has been found to occur in epoxy-amine systems [66, 67].

There is an approximately 50 °C difference in the glass transition temperatures of the 100wt% and 0 wt% acrylate formulations in both the standard cure (phase separated) and higher temperature (single T_g) cured samples. This suggests that the single glass transition values observed in the 50 wt% acrylate samples cured at higher temperatures are not due to the acrylate T_g and epoxy T_g coalescence because there would still be a significant separation in the T_g values of the pure phases. However, the significant decrease in modulus values in the IPNs suggest that there has been some change to the crosslink density and network structure with the higher temperature thermal cure which could indicate IPN homogenization.

In contrast, there is no significant change in the T_g after an additional post cure of 2 hrs at 200 °C for any of the acrylate formulations, which suggests that 200 °C is not a high enough temperature to allow for thermal diffusion and complete cure of the epoxy. This is confirmed by the presence of an exotherm in the DSC thermograph found in Figure 5-16 for the 15 and 30wt% 'SC + 2hrs 200°C' samples, and the lack of an exotherm in Figure 5-17 for the 'SC + 2hrs 250°C' samples. There is not a measurable exotherm present for 50 wt% acrylate for either 'SC + 2hrs 200°C' or the 'SC + 2hrs 250°C' exotherm, possibly due to sensitivity of the DSC and the minimal amount of epoxy present in the system to react.



Figure 5-16:Thermal DSC exotherms for 15, 30, and 50 wt% acrylate after 'UV+2hrs 200°C'



Figure 5-17:Thermal DSC exotherms for 15, 30, and 50 wt% acrylate after 'UV+2hrs 250°C'



Figure **5-18**: Flexural modulus, flexural strength, flexural strain, and toughness for varying acrylate wt% and after various cure profiles

Three-point bend measurements were conducted on samples after various cure profiles, as shown in Figure **5-18**. The flexural moduli increase with increased acrylate content. This is because the modulus of the filled acrylate ("Filled Sartomer") is greater than that of the filled epoxy ("50:50 T:E") (Figure **5-19**Figure **5-19**). Even though the standard deviations overlap for some samples, the flexural strength, flexural strain, and toughness show an increasing trend with increasing acrylate wt% for each cure condition. This is also likely due to the filled acrylate having a greater flexural strength and flexural strain than the filled epoxy network. The decreased strain-to-failure of the epoxy network is likely a result of the highly crosslinked diepoxy and triepoxy network.



Figure **5-19**: Three-point bend results for 5wt% silica filled and unfilled pure acrylate and pure epoxy samples after 'SC + 2hrs 250°C'

It is interesting to note that the filled acrylate and filled epoxy samples have lower flexural modulus values, flexural strength values, strain, and toughness values than the unfiled resins. The silica filler was expected to increase the modulus and flexural strength; however, this is not the case for these resins. The unexpected results could be caused by the filler agglomerating within the resin or due to difficulty degassing the casted samples. This would result in differing part quality for mechanical testing. Additionally, the pure filled resins have much lower flexural properties than the mixed epoxy/acrylate formulations. The difference is believed to result from vitrification of the pure components since there is not an unreactive resin to behave as a plasticizer or diluent during the network formation. This was confirmed by DSC (Appendix I).

To further investigate the differences in three-point bend samples for the different cure profiles, SEM was performed on the fractured surfaces.





Figure 5-20: SEM of 15 wt% acrylate 3-point bend fracture surfaces after various cure profiles



Figure 5-21: SEM of 30 wt% acrylate 3-point bend fracture surfaces after various cure profiles



Figure 5-22: SEM of 50 wt% acrylate 3-point bend fracture surfaces after various cure profiles

SEM images of three-point bend fracture surfaces of 15 wt%, 30 wt%, and 50 wt% acrylate are found in Figure **5-20**, Figure **5-21**, and Figure **5-22** respectively. The fracture surfaces show that brittle failure occurred. River patterns, mirror/mist/hackle patterns, and glassy surfaces are all evidence of brittle failure, which commonly occur in epoxies [69]. Similar to the three-point bend mechanical data, there are no obvious trends in failure mechanisms based on acrylate content or cure profile. The glassy surfaces of the 15 wt% 'UV + 250°C', 30 wt% '4hrs 100°C + 2hrs 250°C', and 50 wt% acrylate 'SC' samples fractured in a way where the initiation point is not able to be determined. The three-point bend samples were not notched, which could

explain the difficulty in determining the initiation point in some of the samples. However, even in samples where the initiation point is obvious, brittle failure still occurred.

5.4 Conclusions:

The impact of acrylate content and thermal cure profile on the epoxy cure kinetics, IPN formation, and resulting thermomechanical properties was investigated. The influence of acrylate content on the epoxy cure kinetics was explored to determine whether the presence of the acrylate network impacted the onset of gelation for the epoxy. As expected, it was found that the pre-formed acrylate network significantly delays the onset of gelation, and increased acrylate content has more of an impact compared to lower acrylate content. A similar trend occurs for the onset of epoxy gelation in the presence of unreacted acrylate resin, where increased acrylate monomer behaves as a diluent and delays the onset of gelation.

The glass transition temperatures were found to slightly increase with greater epoxy content. However, within a particular wt% acrylate formulation there were minimal changes in the glass transition temperature for the different thermal cure profiles, except in the 15wt% acrylate formulation, which decreased moderately with increased cure temperature. However, the T_g transition in DMA narrowed as the maximum thermal cure temperature increased, suggesting increased homogeneity of the epoxy and acrylate networks within the IPN or coalescence of the T_g transitions of the acrylate and epoxy phases.

There were no consistent statistically significant trends in room temperature storage moduli with increasing acrylate wt%, regardless of the cure profile. There was a slight increase in flexural modulus with increased acrylate content, which is because the modulus of the filled acrylate is greater than the modulus of the filled epoxy. Although the standard deviations overlap, the flexural strength, flexural strain, and toughness show an increasing trend for increasing acrylate wt% for each cure condition. It was hypothesized that increased thermal cure temperatures would mitigate phase separation as acrylate content increased because the epoxy monomers would require increased energy to diffuse through the dense acrylate network. These findings indicate that IPN homogenization or T_g coalescence may be controlled for this class of dual-cure formulations by manipulating the cure profile. While Dean *et al.* [25] and others [37, 52, 70] have found that phase separation occurs in acrylate-epoxy sequential IPNs that are first photo-cured then thermally cured, we have found that cure conditions can mitigate phase separation.

The most important finding of this work is that the T_g and flexural strength, strain-tofailure, and toughness values were not significantly altered by varying the acrylate content in the resin formulation. This highlights the versatility of a wide range of resin formulations that can be optimized in order to achieve the desired print properties, i.e. green strength, but reliably give similar mechanical properties after the final thermal cure. This is extremely valuable in AM where the same printed part can be printed using varying compositions and print conditions without the fear of sacrificing ultimate thermomechanical properties. For example, a complex part requiring a high green strength to maintain print fidelity would require a high acrylate composition, while a less-detailed, simple part could be printed using a low acrylate composition. However, both the complex and simple part would have similar thermomechanical properties after the sequential thermal cure profile.

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CHAPTER 6 : INTERPENETRATING POLYMER NETWORKS WITH FUNCTIONALIZED FILLERS

Having investigated the influence of resin formulation and cure parameters on the formation and properties of independent IPNs, the next step was to investigate the influence of functionalized fillers on IPN network formation. Filler materials are typically added to resins for rheological purposes, but the goal of this work was to go one step further and give the fillers a dual purpose. Functionalizing the surface of the fillers with epoxy or acrylate functional groups would enable the fillers to crosslink within the acrylate or epoxy network while also modifying rheology. We were interested in understanding how the functionalized fillers would impact the formation of the independent IPN after being integrated into either the acrylate or epoxy network. Due to the complexity of phase behavior in the previous system, we wanted to switch to a simpler resin system consisting of one epoxy and acrylate, and a more efficient photoinitiator at 365nm since the printing occurs using a monochromatic wavelength. The BPA backbones in the epoxy and acrylate were expected to result in miscibility and minimal phase separation between the two components [1]. Additionally, TPO was chosen as the photoinitiator as it has greater absorbance at a wavelength of 365nm compared to Irgacure 651 [2], making TPO more efficient at forming free radicals. Two fillers were chosen, sodium montmorillonite and fused silica, in order to investigate the influence of particle anisotropy on material properties. Sodium montmorillonite was chosen specifically because the surface is unfunctionalized which makes the surface functionalization process more straight-forward.

This chapter discusses the influence of functionalized filler materials on the rheology, cure kinetics, network formation, and thermomechanical properties of independent interpenetrating polymer networks. The fillers were functionalized via various silylation processes in order to graft acrylate and epoxy functional groups to the surface of the filler. The addition of acrylate functionalized fillers and epoxy functionalized fillers were expected to improve the mechanical properties by forming parts of the acrylate network and epoxy network, respectively. It was anticipated that the functionalized fumed silica would result in shear-thinning behavior and the functionalized montmorillonite would display Newtonian behavior. However, the montmorillonite formulations were still expected to be printable due to the dual-cure aspect of the formulation and by using formulations with enough acrylate content to form a structurally stable part. It was also hypothesized that the addition of acrylate-functionalized fillers would enhance the green strength and require less acrylate resin to maintain print fidelity due to the fillers aiding in the formation of the acrylate network. The epoxy-functionalized fillers were expected to aid in the epoxy network formation, which would result in a faster onset of gelation time. Additionally, the thermomechanical properties of the composites were expected to increase, compared to unfunctionalized fillers, because the epoxy surface functionalization was expected to improve the adhesion between the particle and the matrix.

However, in the dual-cure system studied we found that the addition of functionalized fillers did not significantly increase the rates of network formation of the acrylate or epoxy network. This was determined to be due to the fillers having insufficient functional groups capable of participating in the polymerization reactions as well as the agglomeration of the fillers, where agglomeration could also lead to insufficient available functional groups. Additionally, the rheology of the surface functionalized filler formulations was Newtonian due to particle agglomeration and/or the similar surface polarities of the matrix and filler surface.

6.1 Introduction

Fillers can be used to enhance mechanical [3, 4] and rheological properties [5, 6] of 3D printed materials. In direct ink write specifically, fillers are added to modify rheology [5, 7], tune the thermal and mechanical properties of the printed parts [6, 8], and control spatial gradients and generate shape memory composites [9, 10]. Among the various types of fillers utilized, silica and clay are two of the most common for rheology and mechanical property modification [5, 7, 11].

Not only does the filler composition alter properties, but the size [12, 13] and shape [14, 15] of the filler used also plays a role. In addition, filler effectiveness is dependent upon their compatibility with the dispersing medium, such as epoxy or acrylate resin [16-20]. Often, the differences in polarity between the filler and dispersing medium result in aggregation or settling of the filler, which degrades the resulting properties of the composite [21-26]. Rheological properties, such as shear thinning or shear thickening behavior, also depend on the polarity differences between the filler and dispersing medium.

Shear thinning behavior is when a material or system has a higher viscosity at rest or at zero shear rate but, once shear stress is applied, the viscosity begins to decrease [27]. This behavior is generally attributed to the microstructural rearrangement when a shear stress is applied [28]. Some examples of microstructures that undergo rearrangement are entangled polymer chains that disentangle and elongate, aggregated structures that break down into primary particles, and randomly oriented high aspect ratio particles that align with the flow [28]. At shear rates or stresses able to disrupt the existing microstructure, polymers and particles can rearrange, which increases the free space between dispersed components and deceases viscosity. Once the stress is reduced or removed, the network begins to reform which causes the viscosity to increase. The shear history of the material is also an important factor, because if viscosity measurements are taken before the structure has time to rebuild, then lower viscosity values will be measured. Similarly, if the viscosity measurements are taken as shear rates increase, then again as shear rates are decreased, the viscosity values will be lower for the decreasing-shear rate measurements as the structure has not had time to rebuild [29].

Fumed silica is one of the most common additives used to modify the rheology of a given system [29, 30]. It is often used as a shear-thinning promotor for polymeric composites, given its ability to form chain-like agglomerates that are easily broken and reformed under the application and removal of stress [7, 29, 31]. Fumed silica is just one example of an additive where the

production methods can easily be manipulated to achieve a desired particle size, surface area, and purity. The effectiveness of rheology modification depends on the wetting relationship between the silica and dispersing medium, which is a function of both the surface properties of the silica and the polarity of the dispersing medium. The silica surface is covered with polar silanol groups which creates a surface with high surface energy. When dispersed, the silica particles adsorb molecules from the dispersing medium (usually a liquid), until the surface energy of the particle is minimized relative to their environment [30]. This creates solvent-covered particles that interact with each other to form aggregates that create a larger viscoelastic three-dimensional network [29]. This viscoelastic network is what then results in increased viscosity at zero/low shear and shear-thinning behavior. In addition to surface charge, the dispersion of the silica also impacts the degree of rheology modification. Good dispersion results in a strong internal network formation, which results in ideal thixotropic properties [32]. When the silica internal network is broken down, the driving force to rebuild the network is Brownian motion. This motion increases with decreasing particle size, so the smaller the particle size, or thefewer agglomerates that are present, the faster the viscosity recovery will be.

For example, the surface of untreated silica particles is covered with hydroxyl groups which makes the silica very polar and therefore very hydrophilic. If the untreated silica particles are then dispersed in polar solvents, depending on the particle size and density of the solvent, the particles can eventually settle due to the charge similarity of the solvent and the particles' surface [30, 33]. The charge similarity between the particles and solvent interferes with the specific formation of hydrogen bonds between silica particles that is necessary to form an inter-particle network. The result is a very minor increase of viscosity because the polar dispersing medium interferes with and decreases the inter-particle network formation [29]. Therefore, hydrophilic silica is best used in nonpolar systems where the dispersing medium minimally interacts with the particle, which results in inter-particle network formation. However, a significant draw-back of

adding a polar filler to a nonpolar system, or vice versa, is that particle dispersion becomes increasingly difficult and agglomeration is more likely to occur. A common example of the use of silica as a rheology modifier would be the dispersion of hydrophilic silica in a nonpolar silicone polymer. The silica offers good shear-thinning behavior and an increase in the zero-shear viscosity due to the hydrogen bonding of the surface silanol groups forming a three-dimensional inter-particle network. This inter-particle network increases the zero-shear viscosity, and then gets destroyed when shear rate or stress is applied resulting in shear thinning behavior.

Depending on the dispersing medium used and the desired rheological characteristics, the hydrophilic surface of the silica may need to be altered. This modification can be achieved by grafting the silica with a silane or polymeric material [29, 34-38]. In the case of modification with an organosilane, most of the polar surface silanol groups are replaced with nonpolar organosilicon groups and the surface energy is lowered. This results in a more hydrophobic silica. The internal network formation of hydrophobic silica is both different and more complex than that of hydrophilic silica. While network formation of hydrophilic silica depends primarily on intraparticle hydrogen bonding, network formation of hydrophobic silica depends on the grafting density and chemical structure of the surface modifier and van der Waals forces between surface functional groups [39].

Another common filler material used to modify rheological properties is clay. There are many types of clay which give drastically different rheological properties. For example, montmorillonite is a type of clay that consists of two tetrahedral sheets of silica that sandwich an octahedral sheet of alumina. Unlike fumed silica, most of the surface hydroxyls are found on the edges of the platelets, not the platelet surface, resulting in a much lower hydroxyl concentration. Therefore, shear thinning behavior is not found to occur for un-modified montmorillonite clays. Contrastingly, the shear thinning behavior of many of the organo-clays is attributed to their exfoliation. The exfoliated platelets form a house-of-cards arrangement (Figure **6-1**) within the polymer which results in a high zero shear viscosity and shear thinning behavior under shear.



Static State (edge-to-face) "House of card structure"

Dynamic State

Figure 6-1: House-of-cards arrangement of montmorillonite [40]

The house-of-cards arrangement is due to the interactions between various electrostatic charges present on the clay platelets. The Newtonian behavior of the Na⁺ MMT is attributed to poor exfoliation of the clay particles within the polymer matrix. In order to increase the exfoliation of clay, minimize particle aggregation, and tune the interactions between fillers and the dispersing medium, the surfaces of fillers can be modified by functionalization. Silylation is just one of the many functionalization methods used to alter the surface of the filler to enhance the interaction between filler and dispersing medium [41-44]. However, silylation reactions are not always straightforward.

During the silylation of a particle, two bonding mechanisms can occur, physisorption and chemisorption [45]. Physisorption consists of weak electrostatic interactions between the adsorbate and surface that include van der Waals interactions, dipole-dipole interactions, and London forces, whereas chemisorption consists of covalent bonds formed between the adsorbate and substrate. These two types of mechanisms can be differentiated by the strength of the interactions. The bond strength typically ranges between 0.2-4 kJ/mol for physisorbed molecules,

while the strength is 12-30 kJ/mol for chemisorbed molecules [46]. Due to the difference in bond strengths, the type of interaction can be broadly determined by the temperature at which the species are removed from the surface. Additionally, the temperatures associated with desorption or debonding of the species are filler-dependent. Two common silylated fillers, silica particles and clay particles [24, 25, 47, 48], have different weight loss regimes for physisorbed and chemisorbed species, where the physisorbed species is anticipated to be only water. This assumption is based upon the washing procedure typically used following the silylation reaction. For silica, the convention is that the weight loss between 40-200°C is due to physisorbed water, while weight loss from 200-650°C is due to the decomposition of the chemisorbed/grafted silane [49]. In contrast, for montmorillonite clay the weight loss below 130°C is attributed to the loss of surface adsorbed water, while the weight loss between $\sim 130^{\circ}$ C and 600°C is attributed to the removal of structural hydroxyl groups and intercalated and grafted silane [50-53]. Major weight loss above 600°C is caused by the dehydroxylation of aluminosilicate [51, 52, 54]. If there is physisorbed silane still on the surface of a filler after the washing steps, there would be additional weight loss between ~100-250°C for silica [55] and up to 200°C for montmorillonite, which is associated with physisorbed monomeric silanes and physisorbed polycondensed silanes [56].

When silylating the surface of a filler, there are many factors to consider. The first factor to consider is the purpose for needing the silylation reaction, e.g. homogeneous dispersion. The second factor is the concentration of reactive surface hydroxyls which is controlled by particle morphology and surface chemistry. Montmorillonite, for example, has hydroxyls on the broken edges of the platelets or at surface defects on the platelet [57-59], which limits the density of reactive sites for the silane reaction. In contrast, fumed silica has a high density of surface hydroxyls which gives it a high degree of chemical reactivity [60]. In order for the particles to achieve the same silane grafting density, it is necessary that the surface of the filler has the same number of reactive silanol groups One way to achieve consistent grafting density on silica is

through surface treatments, such as hydrothermal treatment in boiling water [36]. This method also leads to increased grafting density due to the maximization of surface hydroxylation.

The third factor is determining what functionality will provide the desired properties. Silanes have the chemical formula X₃SiR, where R is the organic functional group that reacts with the polymer matrix, and X are the hydrolyzable group(s), such as alkoxy, amine, or chlorine, that are intermediates in the formation of the silanol groups that bond with the surface of the substrate. Alkoxysilanes are often used preferentially to chlorosilanes due to their greater stability and generation of less reactive by-products, *i.e.* the HCl that results from the reaction of chlorosilanes. Different functionalities of the hydrolyzable groups, i.e. mono/di/tri functional [61] or methoxy vs ethoxy [62], result in different reaction kinetics, surface coverage and required reaction conditions [63-66]. For example, comparing the reactivity of methoxy or ethoxy functionalities, methoxy-silanes hydrolyze 6-10 times faster than ethoxy-silanes [67]. This is because the ethoxy group is bulky relative to the methoxy and results in steric hindrance which slows down the reaction [63]. Likewise, while trialkoxy-silanes are more stable than monoalkoxy-silanes, they have a lower intrinsic reactivity and lower solubility in aqueous solutions.

The fourth consideration is to determine the reaction conditions to optimize the functionalization of the surface [68]. The mechanisms for the grafting of silanes are shown in Figure **6-2**.



Figure 6-2: Mechanisms involved with surface silylation [65]

Hydrolysis is generally performed in the presence of water and a catalyst, where the catalyst is generally an acid or a base [69]. In acidic conditions, the hydrolysis of the silane is favored over condensation of the silane, whereas in basic conditions the opposite is true [65, 70]. This is because in acidic conditions the hydrolysis is preceded by protonation of the hydrolyzable group (OMe in Figure **6-2**), whereas the rate of hydrolysis in basic conditions decreases as the electron density at the silicon atom increases or as steric bulk of the silane increases [63, 71, 72].

Acidic conditions can produce linearly polymerized silanes on silica nanoparticles, resulting in larger steric repulsive forces between silica nanoparticles causing lower viscosities when the particles were dispersed in methylethylketone compared to basic conditions that result in branched structures [72, 73]. The branched structures result from the favoring of condensation reactions over hydrolysis. Depending on the silane, acidic conditions can also result in core-shell silica particles [74-77]. Typical acidic reactions consist of 25:75 vol:vol water/ethanol mixtures where the pH is adjusted to 4 which enhances the formation of hydrolyzed alkoxy-silanes; the ethanol in the mixture solvates the silane and the water hinders self-condensation reactions [52, 78]. While water/ethanol mixtures are commonly used for silvlation reactions, these conditions do not always work for every silane. For example with methacryl silanes, an increased water content results in a loss of hydrolyzed species and an increase in condensed structures for silica [65]. Another example is glycidoxypropyltrimethoxysilane (Figure 6-3) where acidic conditions resulted in all or most of the epoxy-silane being adsorbed onto the silica surface, while basic conditions resulted in the epoxy-silane reacting with itself and not adsorbing onto the silica surface [70]. The difference is due to acidic conditions favoring hydrolysis while basic conditions favor condensation.



Figure 6-3: Glycidoxypropyltrimethoxysilane structure



For montmorillonite (MMT) clay, the silulation reaction can result in both exfoliation and intercalation of the clay layers Figure **6-4**.

Figure 6-4: Illustration of montmorillonite clay and intercalated and exfoliated montmorillonite[79]

Exfoliation of the clay results in individual 1nm-thick layers dispersed within a polymer matrix, while intercalation consists of a silane or polymer intercalating into the interlayer space of the clay and expanding the individual sheets while maintaining the overall layered structure [80]. During the silylation reaction, the solvent used impacts whether exfoliation, intercalation, or a mixture of both occurs. Shanmugharaj *et al.* found that the degree of exfoliation & intercalation depends on total surface energy of the solvents used [54]. For example, the silylation reaction for methacryl-silane has a higher grafting density when using a mixture of ethanol/water as opposed to just water or just ethanol. This is because solvents with a surface energy similar or lower than MMT can easily wet MMT, allowing the silane to interact with the surface hydroxyl groups present on the edges of the clay [54]. However, solvents with a high surface energy, such as water, have poor wetting capabilities and poor surface adsorption. This results in less interaction with the edges and instead allows silanes to diffuse between the clay layers [31].

After determining the goal of the overall silvlation reaction and choosing which silane and reaction conditions will help achieve that goal, it is important to think about which filler is the best to use. There are plenty of filler materials available that have various aspect ratios, morphologies, surface hydroxyl concentration, etc. Some common fillers are sol-gel silica, fumed silica, and montmorillonite clay.

6.1.1 Fumed silica

Fumed silica is a type of silica that is an attractive filler because of its isotropic morphology, large surface area to volume ratio, high mechanical strength, thermal and chemical stability, and high concentration of reactive surface hydroxyl groups [29, 36, 37]. However, fumed silica has a tendency to aggregate due to the formation of hydrogen bonds between the silica nanoparticles, which can form anisotropic aggregates [81, 82]. Therefore, silylating the silica surface can help to reduce aggregation [41]. For example, methacryloxy propyl trimethoxy silane (Figure **6-5**) is commonly used to improve the compatibility between fumed silica and acrylic monomers [83, 84]. Additionally, this silane can provide sites for other acrylate monomers [85-87] to be polymerized from the surface of the silica.



Figure 6-5: Methacryloxypropyltrimethoxysilane structure

Similarly, to improve the compatibility between fumed silica and epoxy monomers and enhance the materials properties of the resulting composites, glycidoxypropyltrimethoxysilane (Figure **6-3**) is commonly used [17, 43, 47, 70, 88-90].

In silica-epoxy composites, the increase in mechanical properties is attributed to the nanoparticles occupying small voids in the epoxy resin, and acting as a bridges between the molecules [20]. Zheng *et al.* found that treated 15nm nano-silica capable of bonding with the epoxy matrix acted as stress concentrators, resulting in increased tensile strength, tensile modulus, and impact strength [91]. This is also evidenced by SEM of fracture surfaces conducted by Rosso *et al.* [92] and Mahrholz *et al.* [24] using ~50nm nano-silica, where a high deflection of crack growth and rougher surfaces are present compared to the smooth brittle fracture surface of

neat epoxies. The impact of silica fillers on the T_g and other mechanical properties of the composites can vary significantly depending on the size, morphology, dispersion, and surface functionality of the filler. In some systems, the addition of nanoparticles limit polymer chain motion which results in an increased glass transition temperature and reduced flexibility of the composite [90, 93]. In other systems, surface functionalized nanoparticles ranging from 25nm-100nm at >10wt% loading have a plasticizer effect and decrease crosslinking density which reduces the T_g [22, 94]. Finally, in some systems the particles are not found to have any impact on the T_g [95-97].

When comparing the type and size of large silica fillers, Linec *et al.* found that the T_g and peak temperature of the cure exotherm were the same regardless of the type and size of silica used as a filler in a silica/epoxy composite [98] (50 micron glass beads, 50-200 micron foundry sand, 30 micron crystalline silica, and <50 micron fused silica). In contrast, when investigating the impact of fillers on the gel point of an epoxy system, Altmann *et al.* found that the gelation times, vitrification times, and conversion decreased with increased amounts of unfunctionalized 10 micron crystalline silica flour when the cure temperature was below 90 °C [99, 100]. When the cure temperature was above 100 °C, fillers had no impact on the gel time or vitrification time, but the samples showed a higher conversion at gelation. The idea of autocatalytic effects from the silica surface were suggested, where the hydrogen donor species present on the silica surface were believed to be catalyzing the amine-epoxy reaction, as has also been reported in other work [101].

6.1.1.1 Silylated fumed SiO₂

Fumed silica has been used as a filler to alter rheological, mechanical, thermal, electrical, and various other properties [17, 47, 70, 88, 102, 103]. Many researchers have functionalized the surface of fumed silica with various silanes in order to improve properties and aid in dispersion.

For example, Shirono *et al.* [38] investigated the rheological impact of different alkyl-length silanes grafted on fumed silica with a surface area of 130 m²/g in a bisphenol-A diepoxy matrix. At 5 and 7 wt% silica, longer alkyl-length (C=16 and 18) silanes resulted in higher stability and two orders of magnitude shear thinning behavior due to the increased hydrophobicity of the silica surface. The increased zero shear viscosity and increased shear thinning exponent were caused by the formation of a 3-D network of silica particles within the epoxy matrix that was disrupted under shear. The most interesting finding relevant to this work was that suspensions of untreated and hexyl-silylated fumed silica showed Newtonian behavior, up to the maximum loading tested (7 wt %) [38]. In other work done by Ji *et al.*, increasing the alkyl-length of the silane changes the surface polarity of the fumed silica from hydrophilic to hydrophobic and increasing the grafting density decreased the surface energy [49].

6.1.1.2 Epoxy-silylated SiO₂

Other researchers have investigated the impact of epoxy-grafted silica on the kinetics and properties of epoxy/silica composites [17, 43, 47, 70, 88, 90, 103]. The idea is that the epoxy-functionalized silica will not only disperse well within the polymer matrix, but will further improve thermomechanical properties by forming inter-crosslinked networks [47, 89]. For example, Haitao *et al.* found that the addition of epoxy-grafted (glycidoxy propyl trimethoxy silane) nano-silica increased the viscosity, flexural modulus and strength, and T_g of an SLA epoxy resin [90]. The viscosity increase is correlated to the dispersion of the functionalized silica, where greater than 3 wt% silica resulted in the formation and growth of agglomerates and thus a significant increase in viscosity [90]. The increased flexural modulus and strength are attributed to the interfacial bonding between the epoxy groups on the silica and the epoxy monomers [90]. The increase in the T_g is due to the decreased mobility of polymer chains that are crosslinked between the functionalized silica and the resin [88, 90]. The gel time was delayed with increasing

filler content due to increased light scattering and increased UV absorption [90]. Similar to the findings of Li *et al.*, the thermal stability of the epoxy-coated silica composites was better than the unfilled resin due to the inter-crosslinking of the epoxy-functionalized silica and the epoxy matrix [47, 90]. Going one step further and investigating the mechanical properties of epoxy functionalized silica, Afzal *et al.* investigated the fracture surfaces of epoxy-functionalized nano-silica and found that they appear rougher than the brittle fracture surfaces of neat epoxy. This suggests increased toughness and strength of the functionalized silica composites, which agrees with other findings [47, 70, 88]. Furthermore, the adhesive strength was found to increase by using epoxy-silylated silica, and the epoxy groups on the silica were found to react with the epoxy resin as well as with the hardener [103].

6.1.1.3 Acrylate-silylated SiO₂

Like epoxy-functionalized silica, acrylate-functionalized silica has been investigated to determine the impact on polymerization kinetics and the thermomechanical properties of the resulting composites [18, 20, 74-76, 84, 104-109]. Varvarin *et al.* explored whether a solid phase hydrosilylation reaction could convert Si-H groups into Si-C bonds directly on the surface by reacting silica with acrylic acid. Only at temperatures above 300 °C in acrylic acid vapor did a C=O band appear in FTIR [105]. Gläsel *et al.* reported a 50 K shift in Tg and a two-fold increase in storage modulus due to the crosslinking and incorporation of methacryl-silylated silica into a polyacrylate matrix [18, 74]. A different study was conducted by Rajan *et al.*, where interfacial bonding between silica and poly(methyl acrylate) was intentionally suppressed, with the expectation that the lack of interfacial interaction between the resin and the silica filler would decrease mechanical properties [20]. As expected, the Young's Modulus, strain at break, and toughness values of the samples with no interfacial bonding were all lower than the composites that had a silane bonding agent.

In summary, silica and functionalized silica have been extensively studied for the modification of rheological and thermomechanical properties of nanocomposites. The presence of the silica has varying effects on the T_g , flexural modulus, tensile, modulus, and dispersion based on the surface chemistry, morphology, and particle size of the silica. In some cases, epoxy-functionalized silica fillers have increased the flexural modulus, T_g and thermal stability by crosslinking the epoxy network in epoxy composites. Similar results have been found for acrylate-functionalized silica that has been crosslinked within the acrylate network.

6.1.2 Montmorillonite

Montmorillonite clay is often chosen as a filler due to its high aspect ratio, stiffness, and variable degree of intercalation and exfoliation within a dispersing medium [23, 110, 111]. Montmorillonite has a unique structure consisting of one alumina octahedral layer sandwiched between two silicon tetrahedral layers [59, 110, 112, 113]. Negative charges are generated on the surfaces of the layers due to isomorphic substitutions of lower valence ions (i.e. Mg^{2+} or Fe^{2+}) for the central atoms of Al^{3+} and Si^{4+} [111]. These charges are neutralized by hydrated cations such as Na⁺ or Ca²⁺ that are electrostatically adsorbed inside the interlayer space and on the surface of the layers [111]. These hydrated cations are what cause the clay to be hydrophilic. One single tetrahedral-octahedral-tetrahedral layer has a thickness of about 1 nm, while the length and width are typically about 200 nm [48, 50, 56]. Typical polymer/clay composites are a mixture of exfoliated and intercalated clay (see Figure 6-4). In intercalated composites the polymer chains insert between the clay platelets and increase the basal spacing [11, 48]. Exfoliated composites are when single platelets are separate and homogeneously dispersed throughout the matrix [48, 114]. When clay exfoliates, the clay volume decreases due to the loss of interplanar spacing, but the interaction area with the polymer increases greatly [115]. The extent of mechanical reinforcement within the polymer matrix is highly dependent upon the interaction of the polymer

chains with the clay particles and the degree of exfoliation and intercalation. The best mechanical properties reportedly result from fully exfoliated and homogeneously dispersed clay [116-119]. However, a greater degree of intercalation has been found to result in a more effective load transfer of stress and a higher storage modulus [120]. Ngo *et al.* investigated the effect of mixing temperature, duration, and mixing speed on the dispersion of clay in clay/epoxy nanocomposites. They found that higher temperatures and speeds cause greater breakdown of the clay platelets which allows for better dispersion and infiltration of epoxy monomers in the composite [121].

Organo-modified (not silvlated) MMT is a treated clay that is coated and exfoliated by quaternary ammonium ions or salts [116, 122]. This results in better dispersion of the clay within some polymer matrices. However, there are negative impacts of using organo-modified clay. One big drawback is that quaternary alkylammonium salts decompose around 200 °C, which is bad for composites where thermal stability is of interest [123]. Another drawback, discovered by Garcia del Cid *et al.*, is that organo-modified MMT have plasticizing effects on epoxies due to the alkyl ammonium chains and also can cause a stoichiometric imbalance between the epoxy resin and the curatives in amine-cured epoxies [120]. Additionally, lower Tg temperatures in epoxy-clay composites have been reported, resulting from a lower crosslinking density of the epoxy, which was attributed to preferential intercalation of the epoxy monomers within the clay, which also creates an imbalance in the epoxy/curative stoichiometry [116, 124]. Acidic alkyl ammonium cations were also found to catalyze the homopolymerization of epoxy and epoxy-amine systems, which shifted the cure reaction temperature to lower temperatures [57, 116, 120, 124]. Uhl et al. investigated the impact of clay on UV-curable epoxy-acrylate nanocomposites and found that the results contrast the results found in urethane-acrylate films [125, 126]. For instance, the unmodified Na+ MMT resulted in the greatest Tg, thermal stability, Young's modulus and hardness for the epoxy-acrylate system, but this system had the worst properties in the urethaneacrylate system [126]. The difference was attributed to the clay interacting an a nanoscopic level

with the epoxy-acrylate system compared to the high interfacial tension and poor interaction between the clay and urethane-acrylate system [125]. Additionally, the clay was found to hinder the UV cure process [126]. Specially designed thixotropic clay (Garamite 7305) was found to increase the storage modulus, viscosity, and mechanical properties of epoxy composites, but the anisotropy of the filler, which was aligned by an extrusion-based printing process, resulted in anisotropic properties [5].

In contrast to the detrimental effects on T_g in epoxy composites, Na⁺ MMT and organomodified MMT resulted in an increased T_g when dispersed in poly(methyl methacrylate) [127]. Additionally, the organo-modified clays exhibited shear thinning behavior while the unmodified Na+ MMT did not, and all clays led to a reduction in gelation time. Further investigation of how organo-clays impact the thermomechanical properties of acrylates was conducted by Sangermano *et al.* who found that the T_g was unaltered, but the thermal stability increased with the addition of clays [128]. Interestingly, the addition of organo-modified clay resulted in reaching a higher acrylate conversion than in the pure acrylate system [128].

6.1.2.1 Silylated MMT

Apart from organo-MMT, functionalized silanes have also been grafted to the surface of clays to aid in dispersion, exfoliation and intercalation, and to facilitate in 'grafting from' polymerization reactions [25, 129]. One common silane used is aminopropyltrimethoxysilane (APTMS) where the amino group can react with an epoxy polymer. Silva *et al.* and Choi *et al.* found that increasing the wt% of APTMS-MMT caused an increase in the T_g and an increased gel time due to confinement of the epoxy molecules [57, 130, 131]. This is explained by the slower diffusion and chemical reaction of the epoxy chains connected to the exfoliated amino-clay compared to the untethered epoxy molecules [57]. Choi *et al.* also discovered an increased strain at break and toughness occurred for the APTMS MMT [130]. The degree of silvlation of Na⁺

MMT was found to increase with increased aminosilane chain length, concentration, and temperature [132]. The impact of mixing method on dispersion and mechanical properties was investigated by Piscitelli *et al.*, who found that sonicated composites had a greater T_g than ballmilled composites, but that the addition of clay led to a lower crosslink density in the DGEBAclay composites [133]. The lower crosslink density was attributed to the homopolymerization promoted by the APTMS MMT. Wang *et al.* found that the storage modulus of epoxy-clay composites increased with the addition of the APTMS MMT, but the T_g did not change [134]. Another common silane used in epoxy-clay nanocomposites is aminopropyltriethoxysilane (APTES), where Shanmugharaj *et al.* found a higher degree of epoxy conversion in composites with the APTES-MMT compared to in composites with the untreated Na⁺ MMT [135]. Additionally, Ha *et al.* found that epoxy/APTES-MMT composites had increased fracture toughness due to improved interfacial strength between the epoxy and APTES-MMT [25].

6.1.2.2 Epoxy-MMT

Unlike silica, grafting an epoxy-functional group to the surface of MMT to determine the impact on the morphology and thermomechanical properties of epoxy-MMT polymer composites has been minimally investigated. Most of research has investigated using epoxy-functionalized MMT in non-epoxy resins. Chen *et al.* found that epoxy groups on the clay surface chemically react with the poly(l-lactide) matrix, leading to a greater degree of exfoliation and better mechanical properties [58]. The strong polymer-clay interaction was believed to lead to intercalation and dispersion of the clay layers, whereas weak polymer-clay interactions would have preserved the layered structure [136].

6.1.2.3 Acrylate-MMT

The effect of methacryl-silylated MMT on the cure kinetics and thermomechanical properties of clay-acrylate composites has also been investigated. It has been suggested that high surface area clays can reduce radical concentrations by surface collisions or by the aluminum ions at the edges acting as electron accepting sites and causing oxidation of free radicals [137]. Landry et al. found that increased amounts of methacryloxypropyl trimethoxysilane (MPTS) MMT led to a decrease in percent acrylate conversion and a decreased rate of reaction in various types of acrylate resins [113]. Contrasting results were found by Dean et al. in a polyurethane-acrylate system, where neither unfunctionalized MMT nor MPTS MMT impacted conversion [138]. In fact, both unfunctionalized MMT and MPTS-MMT increased the crosslink density in the polyurethane-acrylate composite. The increased crosslink density for the unfunctionalized MMT was due to physical aggregation of polymer chains onto the clay surface, which has been shown in other polymer composite systems [125]. The modified clays did not improve the modulus or yield stress, but did improve the strain at break [138]. In a PMMA matrix, the mechanical properties and Tg were found to increase with the addition of MPTS MMT [139] because the methacryl groups of the MPTS MMT behave as crosslinkers with the methyl methacrylate monomers, increasing the overall crosslink density.

6.1.3 Summary

Fillers are used in various applications, so it is important to understand what properties are looking to be improved within the composite. Material composition, size, and shape of the particle filler are just a few factors that affect the degree of silylation. The degree of silylation in turn impacts the effectiveness of the filler in modifying the rheology and mechanical properties. Additionally, depending on the resin system being investigated, different surface modifications may be required in order to enable compatibility between the filler and the polymer matrix. For silane functionalized fillers based upon the silane utilized for surface modification, the reaction conditions also have to be optimized in order to achieve the optimal grafting density. Surface functionalized fillers have been demonstrated to improve dispersion and the mechanical and thermal properties of the resulting composites in some cases, while showing no impact in others.

Functionalizing silica and clay with active epoxy and methacryl groups are expected to modify the cure kinetics, network formation, and thermomechanical properties of the functionalized nanocomposites. Based on previous acrylate-functionalized filler research, the MPTS-fillers are expected to increase the glass transition temperature by increasing the crosslink density. Similar results were expected for the epoxy-functionalized fillers. The increased interactions are also expected to increase the toughness and strain at failure. In this work we investigated the addition of acrylate functionalized fillers and epoxy functionalized fillers to see if the functionalized fillers would aid in the formation of the acrylate network and epoxy network, respectively. We studied the influence of acrylate functionalized fillers on the acrylate cure kinetics and the resulting mechanical properties of UV-cured only printed parts, while also studying the influence of epoxy functionalized fillers on the epoxy cure kinetics. Finally, the thermomechanical properties of the thermally cured parts were examined using three-point bend, DMA, and variable temperature DMA.

6.2 Experimental procedure

The chemical structures of the of the materials used in these formulations are shown in Figure **6-6**. The bisphenol-A glycerolate dimethacrylate was supplied by Arkema with acrylate equivalent weight of 256.3. The diglycidyl ether of bisphenol-A based epoxy resin (EPON 828) was supplied by Hexion having an epoxide equivalent weight of 188.5. The photo initiator used was TPO (diphenyl(2,4,6-trimethylbenzoyl) phosphine oxide)) and the latent curing agent used was 1-ethyl 3-methyl imidazolium dicyanamide, which were both purchased from Sigma-Aldrich and used as-received. The rheology modifiers used were hydrophilic fumed silica (Cab-O-Sil®

M-5) with a surface area of 200 m²/g and sodium montmorillonite with a surface area of 700m²/g [140]. The fumed silica was purchased from Cabot, while the montmorillonite was purchased from BYK. The glycidoxypropyltrimethoxysilane (GPS), methacryloxypropyltrimethoxysilane (MPTS), and hexyltrimethoxysilane (HMS) were all purchased from Gelest Inc. and used without further purification.



(EPON 828)

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Figure 6-6: Components of the functionalized filler resins

6.2.1 Silylation Procedures

There are multiple silylation procedures used for each reaction based on the silane and filler used. The silane reactions used are detailed below. After the silylation reaction, the silylated filler is rinsed and centrifuged at least three times with solvent. This is expected to remove any physisorbed silanes or silanols from the surface. Therefore, after this rinse treatment, the remaining silane species on the substrate surface are covalently bound [141].

6.2.1.1 GPS MMT: GPS MMT was made following the procedure used by Asgari *et al.* [142]. In a 500 mL round bottom flask, 2 g of MMT was added to 200 mL DI H₂O and the solution was sonicated for 1 hour. The pH of the solution was adjusted to 4 using 1N HCl solution. Next, 2 g (8.5 mmol) of GPS silane was mixed with 50 mL of DI H₂O, and the solution as added dropwise to the clay suspension. The solution was heated to 80°C and left to react overnight with a reflux condenser attached. The clay suspension was centrifuged to remove the excess solvent. The clay was then rinsed with methanol and centrifuged, this was repeated a total of 3 times to remove excess silane. The clay was left in the centrifuge tube, covered with a kimwipe, and placed in the hood to dry overnight. The following day the clay was placed in a vacuum oven at ~ -0.8 Bar and 80°C to dry overnight.

6.2.1.2 GPS SiO₂: GPS SiO₂ were made following the procedure used by Chu *et al.* [70]. Fumed silica 7.2 g (0.12 mol) was slowly stirred into a mixture of 98.2 mL EtOH and 98.2 mL DI H₂O in a 500 mL flask. After the SiO₂ was dispersed, the pH was adjusted to 4 using 1M HNO₃. Next, 3.48 g (14.7 mmol) of GPS silane were added dropwise to the SiO₂ solution. The solution was then covered and stirred at RT overnight. The SiO₂ solution was centrifuged to remove the excess solvent. The SiO₂ was rinsed with acetone and centrifuged three times to remove excess silane. The SiO₂ was left in the centrifuge tube, covered with a kimwipe, and placed in the hood to dry overnight. The following day the SiO₂ was placed in a vacuum oven at ~ -0.8 Bar and 80°C to dry overnight.

6.2.1.3 HMS MMT <u>:</u> HMS MMT was made following the procedure used by Gianni *et al.* [114]. First, 1.5 g of MMT was combined with 400 mL of a 75:25 vol:vol EtOH:H₂O mixture in a 1000 mL flask. Next, 5 g (24.2 mmol) of HMS silane was added dropwise to the clay solution and the mixture was heated to 80C, with a reflux condenser attached, and left to react for 4 hours. After four hours, the solution was left to cool down and the clay solution was centrifuged to removed excess solvent. The clay was rinsed with ethanol and centrifuged three times to remove excess silane. The clay was left in the centrifuge tube, covered with a kimwipe, and placed in the hood to dry overnight. The following day the clay was placed in a vacuum oven at ~ -0.8 Bar and 80° C to dry overnight.

6.2.1.4 HMS SiO₂: HMS SiO₂ was synthesized by the same procedure as GPS SiO₂ using
7.2 g (120 mmol) of SiO₂ and 3.48 g (16.9 mmol) of HMS silane.

6.2.1.5 MPTS MMT: MPTS MMT was made following the procedure used by Romanzini *et al.* [59]. In a 1000 mL round bottom flask, 10 g of MMT was dispersed in 150 mL EtOH and 150 mL DI H₂O. MTPS 5 g (20.1 mmol) , was added to a 250 mL beaker with 200 mL EtOH and stirred for an hour. After an hour the silane solution was added dropwise to the clay solution and the solution was stirred at 60°C overnight using a reflux condenser. The clay solution was centrifuged to remove the excess solvent. The clay was rinsed with EtOH and centrifuged three times to remove excess silane. The clay was left in the centrifuge tube, covered with a kimwipe, and placed in the hood to dry overnight. The following day the clay was placed in a vacuum oven at ~ -0.8 Bar and 80°C to dry overnight.

6.2.1.6 MPTS SiO_2 : MPTS SiO_2 was made following the procedure used by Pardal *et al.* [104]. In a 250 mL round bottom flask, 2 g (33.3 mmol) of SiO_2 was stirred in 48 g of toluene until the solution became transparent. Next, 2.1 g (8.5 mmol) of MPTS was added dropwise and the solution was mixed at room temperature for 30 minutes. The solution was the heated to 110° C overnight with a reflux condenser attached. The SiO₂ solution was centrifuged to remove the excess solvent. The SiO₂ was rinsed with acetone and centrifuged three times to remove excess silane. The SiO₂ was left in the centrifuge tube, covered with a kimwipe, and placed in the hood to dry overnight. The following day the SiO₂ was placed in a vacuum oven at ~ -0.8 Bar and 80°C to dry overnight.

The no-silane control reactions followed the same epoxy and acrylate grafting procedures explained above, but the silane was not added to the reaction. After drying the filler materials in the oven, the fillers were ground up using a mortar and pestle until they became fine powders. DLS measurements were taken of a dilute solution of 3 mg of filler dispersed by sonication in 10 mL DI H₂O in a cuvette. The results of the particle size measurements are found in Table **6-1**. DLS measurements were attempted in epoxy, but were unsuccessful due to the inability to completely degas and remove the air bubbles in the cuvette.

Filler Material	Z-average	Filler Material	Z-average
	(nm)		(nm)
SiO ₂	~550	MMT	~740
No silane 'GPS' SiO ₂	~550	No silane 'GPS' MMT	~530
No silane 'MPTS' SiO ₂	~290	No silane 'MPTS' MMT	~300
HMS-SiO ₂	~450	HMS-MMT	~820
GPS-SiO ₂	~340	GPS-MMT	~730
MPTS-SiO ₂	~210	MPTS-MMT	~700

Table 6-1: DLS results of unfunctionalized and functionalized SiO₂ and MMT

6.2.2 Blend Nomenclature

Formulations with different filler weight percent's and different surface modifications are labeled as x wt% 'GPS', 'MPTS', or 'HMS' filler. Where x is either 5 or 10 wt% and the filler is either 'MMT' for clay or 'SiO₂' for fumed silica. The total acrylate functional groups to epoxy functional groups are kept constant in a 1:2 mol:mol for every formulation. The remaining wt % is composed of EPON 828, BPA glycerolate dimethacrylate, 5 or 10 wt% filler, 5 mol% (relative to total epoxy functional groups) latent curing agent, and 1.2 mol% (relative to total acrylate functional groups) TPO as the photoinitator.

6.2.3 Preparation of resins

The diacrylate and diepoxy were combined in a 125 mL polypropylene centrifugal mixer container and hand mixed. The combined resins were mixed for 60 seconds at 1800 RPM and 10.1 kPa in a Thinky ARV-310 planetary centrifugal mixer. The photoinitiator, latent curing agent, and fumed silica were added to the resin and hand mixed before being placed back into the mixer for 60 seconds at 1800 RPM and 10.1 kPa.

6.2.4 Cure conditions

There are three categories of samples based on the cure procedure followed. All printed samples are exposed to *in situ* UV during printing. "UV print-cure only" samples refer to printed samples that are UV-cured during printing and are characterized without any further UV or thermal cure. The UV intensity used during printing is 7 mW/cm², which corresponds to a UV dose of 414 mJ/cm² per longitudinal printed mechanical bar. 'UV print cure + flood cure' samples refer to printed samples that are UV flood cured after the *in situ* print cure. The printed samples are flood cured for 30 minutes using an ABM, INC 500W near/mid UV 2105C2 illumination controller with an intensity of 5.7 mW/cm². Finally, samples that have been through the entire UV cure process (print + flood) and thermal cure are referred to as standard cure 'SC' samples. The standard thermal cure procedure starts by placing the samples in a room temperature oven that is then heated to 100°C at 1°C/min, and held for 4 hours, then the oven temperature is increased to 150°C at 1°C/min held for an additional 2 hours, and finally the oven is ramped back down to room temperature at 1°C/min. The 'SC' results are in an Appendix I. An additional

thermal post-cure procedure was also investigated, and these samples are identified as 'SC + 220°C'. After undergoing the standard thermal cure above samples are placed in a room temperature oven that is heated to 220°C at 1°C/min, held for 2 hours, then ramps down at 1°C/min back to room temperature.

6.2.5 Characterization

Dynamic light scattering measurements, TGA, TGA-MS, and ATR-FTIR measurements were conducted on filler materials. Viscosity, photocalorimeter differential scanning calorimetry (UV-DSC), and isothermal cure measurements were conducted on the uncured resins. DSC, three-point bend, DMA, and variable temperature DMA were used to analyze printed samples. All experimental and instrument details are described in CHAPTER 3: EXPERIMENTAL PROCEDURES

6.3 Results & Discussion

6.3.1 Characterization of the Silylated Fillers

When silylating the surface of filler materials it is important to measure the silane grafting density because this value gives an idea of how many functional groups are grafted to the surface and the amount of surface coverage. To measure the silane grafting density, the unfunctionalized and functionalized fumed silica and montmorillonite were subjected to TGA, TGA-MS, and FTIR measurements. The 'untreated' fillers are samples pulled directly from the original container given by the supplier. The 'no-silane' control fillers are samples that were subjected to the same silane grafting reaction conditions but without using the silane itself. The 'no-silane' control samples were used to investigate how the silylation reaction, without the silane, impacted the surface modification and change in surface polarity of the filler. This would inform whether the solvents in addition to the silane were responsible for modifying the surface of the filler.



The TGA mass loss of unfunctionalized and functionalized SiO_2 and MMT are shown in Figure 6-7 and Figure 6-8, and measurements are done in N_2 .

Figure 6-7: TGA weight loss for unfunctionalized and functionalized fumed silica

In Figure 6-7, the 'no silane' SiO₂ samples have minimal weight loss of less than 1%, which is expected because the SiO₂ samples were dried in an oven after the 'no-silane' reactions. This drying process would remove all adsorbed water. The 'untreated SiO₂' was a sample taken directly from the container of fumed silica. It has more weight loss than the 'no silane SiO₂' because silica is hygroscopic which means it readily absorbs moisture. The weight loss results from the absorbed water molecules on the surface being removed up until 200°C. The cause of the increased weight of the 'no silane' control samples and the 'untreated SiO₂' sample after 300°C is unknown. The TGA was repeated three times and the same outcome was found to occur for each sample. The difference in the weight loss curves and overall weight loss seen in the 'no

silane SiO₂' compared to the weight loss in 'HMS SiO₂', 'GPS SiO₂', and 'MPTS SiO₂'is evidence that the silane successfully grafted to the surface of the silica.



Figure 6-8:TGA weight loss for unfunctionalized and functionalized montmorillonite

The TGA curves for untreated and functionalized MMT are found in Figure **6-8**. The 'untreated' MMT sample was taken directly from the container of MMT. The 'no silane' MMT samples and 'untreated MMT' sample have similar weight loss because montmorillonite clay is not hygroscopic and does not readily absorb moisture. Therefore, the drying for 'no silane MMT' samples does not significantly impact the water content present in the sample. The weight loss that occurs at temperatures greater than 600°C results from water molecules that are trapped within the clay sheets themselves. The difference and increase in the weight loss curve and overall weight loss seen in the 'no silane' MMT samples compared to the weight loss in 'HMS

MMT', 'GPS MMT', and 'MPTS MMT' is evidence that the silane successfully grafted to the surface of the silica.

Using the weight loss values obtained from TGA in combination with Equation 3-7, Equation 3-8, and Equation 3-9 the grafted and intercalated silane amounts were calculated. The detailed discussion of these equations can be found in Chapter 3: Experimental Setup. It is important to note that the W_{silica} value used for the MPTS grafted SiO₂ samples is the weight loss of the 'no silane' MPTS control sample between 60-400°C because this range is where the maximum weight loss occurs. For the GPS SiO2 samples, the W_{silica} value is the weight loss of the 'no control' sample taken between 60-500°C because this is where the maximum weight loss occurs. The grafted and intercalated silane amounts are shown in Table 6-2, where intercalation only occurs in the montmorillonite samples.

Equation 3-7: amount of silane grafted onto silica nanoparticles [89, 143, 144]

- - -

Grafted amount
$$\left(\frac{mmol}{g}\right) = \frac{\frac{m_{60-730} - W_{silica}}{MW_{silane}}}{M_{silica}} \times 1000$$

Equation 3-8: Silane Grafted Amount Calculation for MMT [59, 142, 145]

Grafted amount
$$\left(\frac{mmol}{g \ clay}\right) = \frac{(m_{200-600} \ x \ 1000)}{m_{600} \ x \ MW_{silane}}$$

Equation 3-9: Silane Intercalated Amount [59, 142, 145]

Intercalated amount
$$\left(\frac{mmol}{g \ clay}\right) = \frac{m_{350-500} \ x \ 1000}{m_{500} \ x \ MW_{silane}}$$

Filler	Silane	Grafted + Intercalated amount (mmol/g)	Intrcalated amount (mmol/g)
SiO ₂	Glycidoxypropyltrimethoxysilane	0.268 (0.01)	-
SiO ₂	Hexyltrimethoxysilane	0.189 (0.02)	-
SiO ₂	Methacryloxypropyltrimethoxysilane	0.295 (0.03)	-
MMT	Glycidoxypropyltrimethoxysilane	0.595 (0.09)	0.333 (0.01)
MMT	Hexyltrimethoxysilane	2.942 (N/A)	1.478 (N/A)
MMT	Methacryloxypropyltrimethoxysilane	0.262 (0.04)	0.119 (0.03)

 Table 6-2: Silane grafted and intercalated amount (MMT only) found for functionalized fumed silica and montmorillonite

Based on the TGA results, all the filler materials were successfully grafted with the various silanes. This is evidenced by the increased weight loss for the silylated fillers compared to the untreated fillers and control fillers. The HMS-MMT had a greater grafting density than the GPS-MMT or MPTS-MMT. The silane grafting density on MMT and SiO₂ was very similar for the acrylate-functionalized fillers, while the GPS- and HMS- functionalized fillers had differing grafting densities.

The surface concentration of hydroxyl groups present on the fumed silica were estimated using the following equation:

$$\propto_{OH=\delta_{OH}N_A 10^{-21}S^{-1}}$$

where α_{OH} is the silanol number which is a constant value of 4.6 ± 0.5 OH/nm², N_A is Avogadro's number, S is the specific surface area (m²/g), and δ_{OH} is the concentration of hydroxyl groups (mmol/g). The silanol number is claimed to be independent of the origin and structural characteristics such as specific surface area. δ_{OH} is calculated to be 1.5 mmol/g for a surface area of 200 m²/g. According to this calculation, the silane grafted amounts are less than the available surface concentration of hydroxyls. This means that the grafted silanes have formed islands/ligands (Figure 6-9) as opposed to a coating which would have resulted if the grafted silane amount equaled or exceeded 1.5 mmol/g.



Figure 6-9: Diagram of silane-coated surface and silane ligand/island surfaces

TGA showed differences in weight loss between the unfunctionalized and functionalized filler samples, indicated that there was grafted material presence on the surface of the fillers after the silylation reaction. TGA-MS was conducted to confirm that the specific silane species were on the surface by analyzing the fragment pattern during the decomposition of the grafted silane. Eric Coker at Sandia National Laboratories (Department 1865, Applied Optical/Plasma Science) conducted the TGA-MS. Analysis was jointly conducted with Eric Coker and the author. The MS fragment patterns were obtained from the NIST database, and the chemical species associated with the m/z values were estimated using CFM-ID software. The spectra and species associated with the fragments for each silane are found in Figure **6-10**.


Figure 6-10: Predicted MS spectra of silanes from NIST [146-148] and structures of fragments from CFM-ID

The major m/z values for each silane and the fragments associated with each m/z value are highlighted.



Figure 6-11: TGA-MS data on the GPS-SiO2

An example TGA-MS results for the GPS-SiO₂ is included in Figure **6-11**. Other results are in Appendix I. The species that correlate with the significant weight loss are water (blue line) and the fragments associated with the epoxy functionalization groups (green and orange lines). As the temperature increases, the ion current for m/z 43 and 57 increases. This means that as more heat is added to the system, the decomposition reaction happens faster and to a greater extent, which results in increased ion concentration. Isothermal TGA/MS was performed to confirm that the increase in ion current was due to true species evolution and not background noise (Appendix I). These results confirm that SiO₂ was successful functionalized with the GPS silane.

TGA-MS for MPTS and HMS functionalized SiO_2 and MMT (Appendix I) also showed characteristic fragmentation patterns of the corresponding functional groups. This confirms that the additional weight loss of the silylated fillers in the TGA measurements were from the grafted silane. ATR-FTIR was attempted in order to quantify the presence of grafted silanes, however, due to the low amount of functionalization, the signal of the functional groups was not strong enough to exceed the background noise.

6.3.2 Rheology

Fillers are commonly added to resin systems to tailor the rheology. For DIW specifically, shear thinning behavior is generally desired [5]. We wanted to give the fillers in this system a dual-purpose: rheology modification and network formation.



Figure **6-12**: Viscosity of formulations with functionalized SiO₂ (left) and functionalized MMT (right) as a function of shear rate. Note: The scale for the MMT samples is from 10 to 500 Pa*s.

The viscosity of the unfunctionalized and functionalized formulations are shown in Figure 6-12. The addition of unfunctionalized SiO_2 imparts shear thinning behavior, and a higher weight percent lading impacts greater shear thinning behavior compared to the lower weight

percent. However, when the surface of silica is modified with any silane, the resins were found to have Newtonian rheological behavior. This is likely due to a combination of particle agglomeration in the functionalized silica and to the replacement of surface hydroxyls with organosilane functional groups. This changes the surface polarity of the silica, which disrupts the formation of the silica microstructure. Similar results were found by Sun *et al.* where untreated silica displayed shear thinning behavior within EPON 828, but GPS SiO₂ and pure EPON 828 were Newtonian [43]. The Newtonian behavior of the GPS SiO₂ resulted from the enhanced compatibility of the filler surface and epoxy resin which increased the wetting of the epoxy resin on the SiO₂ and reduced the filler-filler interaction [43]. All the montmorillonite formulations are Newtonian, which is commonly found for dispersions of MMT in epoxy resins [149].

The Newtonian behavior of the functionalized fillers results from the surface polarity of the fillers. The shear thinning behavior of the unfunctionalized silica is caused by the dispersion of the highly polar silica within a less polar matrix. The polar surface of the fumed silica results from a high concentration of surface hydroxyls. In contrast, the montmorillonite has a lower surface hydroxyl concentration and is less polar compared to the fumed silica, which is why it does not exhibit shear thinning behavior at these filler loadings. While the surface functionalization of the fillers results in Newtonian behavior, the formulations are still printable via DIW because they are in a dual-cure resin. During the print, as the resin is extruded from the nozzle, the bead maintains shape by partially curing the acrylate via *in situ* UV exposure. However, this loss of shear thinning behavior does diminish the utility of functionalized silica fillers to serve a dual role as both rheology modifiers and network modifiers.

While shear thinning resins are generally desired for direct ink write printing, dual-cure systems can enable the printing of Newtonian fluids. Future work investigating methods to enhance the silane grafting density and better disperse the particles in nonpolar resins after functionalization might improve shear thinning behavior. Sonication could aid in dispersion of

the particles after they are added to the resin [43]. If the fillers are miscible within the resin then they will stay dispersed, as long as the viscosity does not allow them to settle. If the fillers are immiscible with the resin matrix, then they will eventually agglomerate again.

6.3.3 Acrylate Cure Kinetics

Having understood how the functionalized fillers altered the rheology, the acrylate cure kinetics were investigated. Understanding the acrylate cure kinetics of Newtonian systems is extremely important because the green strength is reliant on the acrylate network conversion. The impact of functionalized fillers on the acrylate cure kinetics and final acrylate conversion of the epoxy/acrylate dual-cure formulations was investigated using UV-DSC. The pulsed experiments consisted of short UV exposures followed by a dark period, which was chosen to mimic the episodic *in situ* UV irradiation during printing. The pulsed UV-DSC results are shown in Figure **6-13**.



Figure 6-13: Percent conversion of different functionalized filler formulations by pulsed exposure UV-DSC at 80 mW/cm². Standard deviation values are taken between three separate experiments except for GPS and HMS functionalized SiO₂ and MMT. 0 wt% MPTS SiO₂ standard deviation values are too small to be visible in the graph.

There appears to be a trend that the methacrylate (MPTS)_ functionalized fillers, both clay and silica, have slower initial reaction rates compared to other formulations, where the first few pulses have a lower conversion compared to the remaining formulations. The presence of the fillers could reduce the mobility of the acrylate monomer or reduce the mobility of the propagating chain after the acrylate is grafted to the surface of the filler. In order to react with rest of the acrylate network, the propagating chain now must diffuse through the network while attached to a bulky particle. Similar results were found by Landry *et al.* where MPTS-MMT slowed the acrylate conversion in different acrylate systems [113]. It is unknown how significant of an effect this would have on the reaction rate because the concentration of grafted methacrylate

functional groups on the surface of fillers makes up a low portion of the total methacrylate functional groups resent in the resin. However, this could be the cause of the decreased reaction rate for formulations with MPTS functionalized fillers.

In the MMT system, the MPTS MMT formulations also reach a lower final conversion than the unfunctionalized fillers or the fillers functionalized with different hexyl- or glycidylgroups. In contrast, the MPTS SiO₂ formulations reach a similar final conversion to the other functionalized and unfunctionalized SiO₂ formulations. Clay has been known to act as a free radical scavenger, which would decrease photoinitiator concentration and cause lower network conversion [137]. However, this effect would be expected to lower the overall conversion in all clay systems, not just MPTS clay.

Although the methacrylate-functionalized fillers did not increase the rates of the polymerization reaction, it is possible that the functionalized fillers might have an effect on the gel point of the acrylate. This could be beneficial for printing by providing greater stability at a lower acrylate conversion. The UV-DSC measurements only investigate conversion of the acrylate functional group and cannot interrogate mechanical properties such as the onset of gelation. The gel point is extremely important because it dictates when the formation of the macro-network occurs, and ideally, this would happen after the sample has been printed. The effect of fillers on the onset of gelation of the acrylate network could be investigated with UV-rheometry, but this capability was not available at the time of this work.

As shown in **Chapter 4**, the UV exposure profile and duration could have significant effects on the extent of acrylate conversion. To investigate the impact of these variables in the filled systems, UV-DSC experiments were conducted using continuous exposures. The exposure time was long enough to allow the reaction to reach maximum conversion before the end of the exposure. The continuous UV-DSC exposures consisted of two 10-minute exposures where the



first exposure measures the enthalpy of the reaction and the second exposure measures the specific heat capacity under UV-irradiation of the reacted polymer and is used as the baseline.

Figure 6-14: Comparing pulsed exposure versus continuous exposure of varying functionalized SiO₂ (left) and MMT (right) at 80 mW/cm²

The continuous and pulsed UV-DSC results are shown in Figure **6-14**. Tables of the values are in Appendix I. The continuous exposure results in a greater conversion than the pulsed exposure due to the higher concentration of free radicals generated and the constant versus cyclic generation of free radicals. This is explained in detail in **Chapter 4 Section 4.3.1 Acrylate Cure Kinetics**. However, the type of surface functionalization does not have an impact on the total conversion for continuous exposures for either filler. For continuous exposure, the total conversion is greater for filled formulations compared to the unfilled formulation, except for the 10wt% GPS MMT which is an outlier. Mohsen *et al.* [150] found that the addition of 1.5 micron MPTS silylated zirconia-silica increased the conversion of urethane dimethacrylate. In contrast, surface functionalization does not appear to play a role in our system. This could be due to the functionalized fillers forming large dispersed agglomerates that impede the acrylate network formation less, or from mitigating the vitrification of the acrylate network [151].

The total acrylate conversion for the continuous exposures is greater for these filler formulations compared to the formulations used in **Chapter 4**. This is likely due to the BPA

glycerolate dimethacrylate having greater mobility than the longer ethoxylated BPA dimethacrylate used in **Chapter 4** formulations (See Appendix I).

6.3.4 Epoxy Cure Kinetics

Acrylate functionalized fillers were investigated to determine the impact of acrylate surface functionalization on the acrylate cure kinetics. Epoxy functionalized fillers were also of interest to determine if they impacted the epoxy network formation because the mechanical strength and thermal stability of printed dual-cure parts also relies on the epoxy conversion. To investigate the impact of epoxy-functionalized fillers on the epoxy cure kinetics of the unreacted resin, isothermal cure DMA measurements were conducted at 150°C.



Figure 6-15: Onset of gelation times for various filler formulations at a 150°C isotherm

Figure **6-15** shows the onset of gelation times for the various unfunctionalized and functionalized filler formulations. Note that in these tests the acrylate resins have not been polymerized so results will differ versus when the acrylate network is formed. The presence of the fillers delays the onset of gelation. This deceleration is likely due to the fillers constraining the mobility of the epoxy molecules. Increasing the filler loading further decreases the onset of gelation due to decreasing the epoxy monomer mobility. It was hypothesized that the GPS-fillers (epoxy functionalized) would result in faster epoxy gel times due to the presence of the additional epoxy functional groups on the silica surface, however the GPS-fillers behave the same as the unfunctionalized fillers. There is an increase in the gel time with the addition of fillers, but there are no consistent changes to the epoxy gel time dependent on the presence or type of surface functionalization. In particular, the lack of difference in onset of gelation between the MPTS-functionalized and GPS-functionalized fillers suggests that the type of functional group on the filler surface did not affect the onset of gelation time of the epoxy polymerization.

6.3.5 Mechanical Properties

After investigating the effects of functionalized fillers and varying weight percent of fillers on the cure kinetics of the dual-cure epoxy-acrylate IPN, mechanical properties were investigated. One finding of interest was to determine if functionalized fillers influenced the mechanical properties at any stage of the cure. The first steps were to measure the room temperature storage modulus of 'print cure only', 'UV print + flood cure', and 'SC + 2hrs 220°C' samples, shown in Figure **6-16**.



Figure **6-16**:Room temperature storage modulus values of 'Print Cure Only', 'UV Print + Flood Cure', and 'SC + 2hrs 220°C' samples measured by DMA of longitudinal printed bars. Standard deviation is between 4 samples

After thermally curing the 'UV print + flood cure', the epoxy network was formed and the room temperature modulus was measured again. The thermal cure profile was the standard cure profile + 2hrs at 220°C (see Experimental). As expected, the room temperature storage modulus of the 'SC + 2hrs 220°C' samples increased after the thermal cure due to the epoxy network formation and the IPN formation. Increasing the filler loading increases the modulus. This is due to the fillers acting as reinforcement particles in the matrix. The modulus values did not differ between the unfunctionalized and functionalized fillers in the 5 wt% MMT formulations or the 10 wt% SiO2 formulations. However, the storage modulus was greater for the 5 wt% unfunctionalized SiO2 compared to the functionalized SiO2, and the modulus was also greater for the 10 wt% unfunctionalized MMT compared to 10 wt% functionalized MMT. These results are likely due in part to agglomeration, which is confirmed by SEM (Figure 6-22 - Figure 6-25). Overall, no consistent trends in the room temperature moduli at any cure stage are seen that indicate that filler surface functionalization beneficially impacts either green strength or the modulus of the fully cured composites in these systems.

DSC was performed to confirm that the 'SC + 2hrs 220°C' samples were cured (Appendix I), and that no measurable exotherm was present. Having confirmed that the 220 °C thermal cure profile fully cured the samples, the thermally cured samples were then used for the thermomechanical analysis.

It was hypothesized that the addition of GPS-fillers would increase the Tg of the composites by crosslinking into the epoxy network and limiting polymer chain movement. This theory was tested by using variable temperature DMA. The glass transition temperatures for 'SC + 2hrs 220°C' samples are shown in Figure 6-17 and Figure 6-18. All of the systems were phase separated as evidenced by two glass transition temperatures, one distinct and one that appeared as a shoulder (Figure 6-19). The lower Tg is associated with the acrylate-rich phase, while the higher Tg is associated with the epoxy-rich phase.

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There are no consistent differences in modulus values between the functionalized and unfunctionalized fillers at the three different cure stages.

The storage modulus of the 'print cure only' samples offer insight into the print fidelity of the resin during the print and how the presence of MPTS-fillers influences the green strength of the parts. It was anticipated that the MPTS-fillers would increase the green strength by aiding in the formation of the acrylate. The GPS-fillers were not expected to participate in the acrylate network formation, therefore no 'print cure only' or 'UV print + flood cure' samples tested.

The relative green strengths are measured by the comparison of the torsional storage moduli values. Surprisingly, there were minimal differences in the green strength between SiO_2 and MMT for the 'print cure only' samples. This is surprising because the clay platelets are expected to orient in the direction of the printed bead which would improve the strength of the longitudinal printed part. Within the SiO_2 systems, there was variation between the functionalized and unfunctionalized samples but there were no consistent trends with functional group type or loading. After the additional UV flood cure, the modulus of all formulations increased due to pushing the extent of acrylate conversion and forming a greater degree of acrylate network, but there are still no consistent trends in based on type or surface functionalization of the filler.

After thermally curing the 'UV print + flood cure', the epoxy network was formed and the room temperature modulus was measured again. The thermal cure profile was the standard cure profile + 2hrs at 220°C (see Experimental). As expected, the room temperature storage modulus of the 'SC + 2hrs 220°C' samples increased after the thermal cure due to the epoxy network formation and the IPN formation. Increasing the filler loading increases the modulus. This is due to the fillers acting as reinforcement particles in the matrix. The modulus values did not differ between the unfunctionalized and functionalized fillers in the 5 wt% MMT formulations or the 10 wt% SiO₂ formulations. However, the storage modulus was greater for the 5 wt% unfunctionalized SiO₂ compared to the functionalized SiO₂, and the modulus was also greater for the 10 wt% unfunctionalized MMT compared to 10 wt% functionalized MMT. These results are likely due in part to agglomeration, which is confirmed by SEM (Figure 6-22 - Figure 6-25). Overall, no consistent trends in the room temperature moduli at any cure stage are seen that indicate that filler surface functionalization beneficially impacts either green strength or the modulus of the fully cured composites in these systems.

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Figure 6-17 :Glass transition temperatures of 'SC + 2hrs 220°C' functionalized and unfunctionalized SiO₂ formulations



Figure 6-18: Glass transition temperatures of 'SC + 2hrs 220°C' functionalized and unfunctionalized MMT formulations

The presence of the fillers does not significantly or consistently impact the values of the low-temperature (acrylate-rich phase) T_g or high-temperature (epoxy-rich phase) T_g . The 10 wt% functionalized SiO₂ have slightly lower glass transition temperatures compare to the unfilled system. Similar results have been found in literature, where the addition of fumed silica decreases the T_g of epoxy-acrylate formulations due to plasticizing effects and other unknown causes [22, 90, 93-97].



Figure 6-19: Examples VT DMA curves of 'SC + 2hrs 220°C' unfilled, unfunctionalized and functionalized filler samples. Heat/cool cycle values overlap, cool-down cycle measurements shown.

While the glass transition temperatures were not strongly influenced by the silylated fillers, the mechanical properties were expected to be. The GPS-fillers were hypothesized to increase the flexural modulus and strength by increasing the adhesion between epoxy matrix and filler surface. Three-point bend tests were conducted to test this hypothesis and investigate the impact of functionalized fillers on the flexural modulus and flexural strength of the composites.

Standard cure 'SC' samples and 'SC + 2hrs 220°C' samples were investigated to determine the effect of epoxy extent of cure on the mechanical properties, since the DSC of the 'SC' samples showed additional cure and the DSC of 'SC + 2hrs 220°C' samples did not. The results are shown in Figure **6-20**.



Figure 6-20: Three-point bend results of 'SC' and 'SC + 2hrs 220°C' unfunctionalized and GPS-functionalized fillers

There is no apparent trend in modulus or flexural strength for the 'SC' samples, regardless of the filler used or surface functionalization. These results are believed to result from the samples having differing extent of epoxy cures. Differing extents of cure result from curing the samples with a maximum temperature of 150°C, below the maximum T_g, which does not drive the epoxy cure to completion. The incomplete cure with the 'SC' profile was demonstrated by the presence of an exotherm during the first heat cycle of thermal DSC (Appendix I).

Three-point bend was then conducted on samples that were exposed to an additional higher temperature post-cure of 2hrs at 220°C. In contrast to the 'SC' samples, flexural modulus measurements are much more consistent for the 'SC + 2hrs 220°C' samples indicating that the partial cure was a factor in the inconsistent results in the 'SC' samples. For all MMT formulations, the flexural modulus values are within error. These values are slightly less than the unfilled modulus, and not much different than the SiO₂ formulations. These results were unexpected because the addition of MMT was hypothesized to increase the modulus by stiffening the material. The MMT platelets were expected to orient parallel to the print direction, which is perpendicular to the applied force in a three-point bend measurement. These results conflict with those found by Khosravi *et al.* where the addition of 5 wt% GPS MMT slightly increased the flexural modulus of an epoxy laminate [152]. The difference can be attributed to the better dispersion of GPS MMT resulting from the sonication step used during the composite fabrication and the samples being laminates, not 3D printed artifacts [152].

In the SiO_2 formulations, the unfunctionalized filled samples have slightly greater modulus and strength values than the unfilled formulation. However, the functionalized filler formulations have lower moduli and strength, to varying extents, than the unfunctionalized filler formulations. This could result from better dispersion of the unfunctionalized fillers than the functionalized fillers within the polymer matrix. Overall, filler functionalization does not have a beneficial effect on flexural modulus or flexural strength relative to the use of unfunctionalized fillers.

To understand if particle agglomeration was contributing to the degradation in mechanical performance, imaging was conducted on the three-point bend fracture surfaces of the 'SC' samples using a Zeiss GeminiSEM 500 Variable Pressure Field Emission Scanning Electron Microscope equipped with a Bruker XFlash 6|60 SDD Energy Dispersive Spectrometer. Bruker Esprit analysis software was used for EDS analysis. EDS analysis and SEM imaging was conducted by Sara Dickens at Sandia National Laboratories, Department 1819 Materials Characterization and Performance.

The SEM of three-point bend fracture surfaces of 'SC' unfilled samples are shown in Figure **6-21**. The surfaces show mirror, mist, and hackle zones which is evident of brittle failure.



No filler

Figure 6-21: SEM images of 'SC' unfilled three-point bend fracture surfaces

SEM images of three-point bend fracture surfaces of 'SC' 5wt% SiO₂ and 5wt% GPS SiO₂ samples are shown in Figure **6-22**. The surfaces show mirror, mist, and hackle zones in addition to river markings which is evidence of brittle failure. The very light areas on the surface of the 5wt% GPS SiO₂ are silica agglomerates, which are not present in the unmodified 5wt% SiO₂.



Figure 6-22: SEM images of 'SC' 5wt% and 5wt% GPS SiO₂ three-point bend fracture surfaces

Figure **6-23** contains SEM images of three-point bend fracture surfaces of 'SC' 10wt% GPS and 10wt% MPTS SiO₂. The surfaces display mirror, mist, and hackle zones which is evident of brittle failure. Both GPS and MPTS SiO₂ exhibit silica agglomerations. To confirm that the lighter areas are silica agglomerates, SEM/EDS was performed (Appendix I).



Figure 6-23: SEM images of 'SC' 10 wt% GPS and MPTS SiO2 three-point bend fracture surfaces

The SEM images of 'SC' 5wt% MMT and 5wt% GPS MMT are shown in Figure 6-24. The 5wt% MMT shows that the clay is homogeneously dispersed. The fracture surface is rough which suggests plastic failure [153]. The 5wt% GPS MMT shows that the clay is agglomerated, and the fracture surface demonstrates brittle failure. Similar SEM images for 5wt% GPS MMT were found by Khosravi *et al.* [152].



Figure 6-24: SEM images of 'SC' 5 wt% MMT and 5 wt% GPS MMT three-point bend fracture surfaces

The SEM images of 'SC' 10wt% GPS MMT and 10wt% MPTS MMT are shown in Figure 6-25. Both surfaces are very similar and exhibit clay agglomerates. The fracture surfaces demonstrate brittle failure occurred.



Figure 6-25: SEM images of 'SC' 10 wt% GPS and MPTS MMT three-point bend fracture surfaces

The addition of unfunctionalized and functionalized fillers did not significantly impact the brittle failure mechanism of the three-point bend composites. However, the SEM images do show that the unfunctionalized fillers have a more homogeneous dispersion within the dual-cure polymer matrix than the functionalized fillers. The agglomeration will result in localized stress points that will decrease the flexural modulus and strength values. These results agree with some of the three-point bend results, where the unfunctionalized SiO₂ is more homogeneously dispersed than the functionalized silica, which results in the unfunctionalized silica having greater flexural modulus values. There is not a significant difference between the flexural properties of the MMT and SiO₂ formulations, which suggests that other phenomenon besides agglomeration are influencing the results.

6.5 Conclusions

The addition of epoxy-functionalized and acrylate-functionalized SiO₂ and MMT were anticipated to impact the cure kinetics and thermomechanical properties of the resulting epoxyacrylate IPN. The surface functionalization on SiO₂ and MMT was confirmed using TGA and TGA-MS. The particle size of SiO₂ and MMT and functionalized SiO₂ and MMT was determined using DLS measurements of particles dispersed in DI water and did not vary significantly relative to the unfunctionalized particles.

Unfunctionalized SiO_2 imparts shear thinning behavior to these resin formulations, however the addition of functionalized SiO_2 resulted in Newtonian behavior. The difference in rheology is attributed to a combination of agglomeration and changes in the surface polarity of the SiO_2 on functionalization. All MMT formulations were Newtonian.

Investigating acrylate cure kinetics with pulsed exposure profiles, both types (silica and MMT) of methacrylate functionalized fillers had slightly slower initial reaction rates than all other formulations, and the methacrylate-functionalized MMT fillers also reached a lower overall conversion. This is likely due the polymer chain mobility decreasing after polymerizing with functional groups on the surface of a filler. The effect of pulse profile and duration was also investigated and, similarly to the previously studied epoxy-acrylate systems with similar acrylate/epoxy ratios, a continuous exposure profile resulted in greater conversions than the pulsed exposures. In this system, in contrast to the resin systems studied in **Chapter 4** and **5**, all the formulations reached full acrylate conversion, as measured by UV-DSC, in the continuous exposures. This is likely due to the BPA dimethacrylate in these formulations having greater mobility than the longer ethoxylated BPA dimethacrylate used in the previous system.

Isothermal cure measurements of epoxy gelation showed that the gel time is delayed by the addition of fillers and is further delayed by increasing the filler content. This is because the fillers negatively impact the mobility of both monomers and the growing polymer chains. However, the filler functionalization had no impact on epoxy gel time, even for fillers functionalized with epoxy functional groups.

Room temperature storage modulus values were measured at different stages of cure. No consistent effects of filler surface functionalization were observed for the 'print cure only' or 'UV print + flood cure' samples, demonstrating that the methacrylate functionalization of the particles does not significantly reinforce the acrylate network. The room temperature modulus values of the thermally cured 'SC + 2hrs 220°C' samples increased with the addition of unfunctionalized SiO₂ but the use of functionalized fillers decreased the moduli, relative to the unfunctionalized fillers. This is likely due to greater agglomeration of the functionalized fillers, as shown by SEM.

The glass transition temperatures were also largely independent of the filler and all formulations exhibited phase separation of the IPNs. The low-temperature (acrylate-rich phase) T_g , did not consistently vary with filler or filler surface functionalization. Similarly, the high-temperature (epoxy-rich phase) T_g , which was about 160°C, did not vary significantly with filler or filler surface functionalization.

Finally, flexural modulus and flexural strength measurements showed that the modulus and strength of fully cured samples increase with unfunctionalized SiO_2 addition but decease with the use of functionalized SiO_2 . This decrease is due to the greater extent of particle agglomeration in the functionalized filler samples. This matches the trends seen for the room temperature torsion modulus. The flexural modulus and strength values of MMT-filled 'SC + 2hrs 220°C' samples are relatively independent of formulation or surface functionalization and do not show a consistent impact from the use of functionalized fillers.

Unexpectedly, the functionalized fillers did not significantly impact the cure kinetics, network formation, or thermomechanical properties of the composites. These findings show that the fillers need to have improved dispersion or have a greater silane grafting density in order to significantly impact the rheology or thermomechanical properties of the composites. Initially, the ultimate goal of this work was to develop dual-functionalized particles, functionalized with epoxy and acrylate functional groups, and see what impact linking the two polymer networks would have on IPN properties. However, due to the minimal impacts on cure kinetics or mechanical properties found for the monofunctionalized fillers and the difficulty of accurately characterizing functionalization and conversion of dual-functionalized fillers, we instead investigated heterobifunctional monomers (Chapter 7).

6.6 References:

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CHAPTER 7 : INTERCONNECTED INTERPENETRATING POLYMER NETWORKS FORMED BY HETEROBIFUNCTIONAL HYBRID MONOMERS

Having understood how the resin composition and fillers impact the formation and material properties of independent interpenetrating polymer networks, the formation of interconnected interpenetrating polymer networks was studied. Acrylate-epoxy heterobifunctional monomers with different structures were examined to understand the influence of a short versus a long and bulky acrylate-epoxy crosslinker on the cure kinetics, green strength, and thermomechanical properties of interconnected IPNs.

It was hypothesized that the addition of a heterobifunctional monomer would add chemical crosslinks between the acrylate and epoxy networks and improve the thermomechanical properties compared to the independent IPNs by producing a tighter network and mitigating phase separation. The acrylate functional group on the hybrid molecule was expected form the acrylate network, while the epoxy functional group would form part of the epoxy network. Additionally, the hybrid would behave as a monoacrylate/monoepoxy, which would increase the conversion of the acrylate network. The unreacted epoxy ends of the hybrid would result in greater acrylate conversion due to aiding acrylate network plasticization by the epoxy monomer. By aiding in network formation and achieving a higher conversion, formulations with heterobifunctional fillers might require less diacrylate to form a structurally stable printed part.

Two heterobifunctional monomers were used, glycidyl methacrylate (GMA) and bisphenol A epoxy-acrylate (BPA) (Figure 7-2). Formulations with GMA were anticipated to have a faster acrylate reaction rate and reach a greater conversion. The difference is attributed to the small size of GMA compared to the longer and bulky BPA monomer. Increased amounts of GMA were expected to decrease the viscosity, due to the low viscosity of GMA relative to the other resins. The lowered viscosity was then expected to allow greater monomer mobility, which would allow for a greater extent of acrylate conversion. Additionally, for uncured resins, the GMA monomer was expected to have a faster onset of gelation compared the BPA monomer, due to small molecule having easier mobility.

Formulations containing the GMA hybrid monomer were expected to have the greatest glass transition temperature, flexural modulus, and storage modulus. This is attributed to an increased crosslink density resulting from the short rigid molecule. In contrast, formulations with BPA hybrid were expected to have a lower glass transition temperature than GMA formulations, which is attributed to a lower crosslink density due to its long and rigid BPA backbone. The IPN homogeneity of longitudinal and transverse printed samples were investigated. Print direction effects were not expected to be present due to the nature of dual-cure, however by replacing difunctional monomers with monoepoxy/monoacrylate hybrid materials, the epoxy and acrylate networks become less crosslinked and more linear. The linearity of the network means that there is less crosslinking that can occur across printed interfaces, which could result in print direction effects, similar to printing thermoplastic materials.

7.1 Introduction:

As described in previous chapters, interpenetrating polymer networks (IPNs) are defined as two networks that are interwoven at the molecular level, but not chemically bonded to one another [1]. By introducing a heterobifunctional monomer, specifically a monomer that has an epoxy functional group on one end and an acrylate functional group on the other end, an interconnected IPN can be formed. An interconnected IPN is defined as an IPN in which the two networks are chemically linking to each other through a heterobifunctional or 'hybrid' monomer.

The use of hybrid monomers to connect the two networks can alter the mechanical properties of the IPNs [2-5]. In epoxy/acrylate IPN systems the hybrid molecule forms parts of the acrylate network and the epoxy network and has been reported to result in higher network

conversion[3]. In some cases the hardness and adhesion strength also increase due to the increased crosslinking between the two networks-[6, 7].

For commercial applications, glycidyl methacrylate (GMA) is the most readily available epoxy-acrylate hybrid monomer. Other epoxy-acrylate hybrid monomers used in literature have been custom synthesized. One common epoxy-acrylate hybrid monomer is synthesized by reacting the diglycidyl ether of bisphenol A (DGEBA) with a less than a stoichiometric amount of acrylic acid to form an epoxy-acrylate hybrid monomer with a BPA backbone [2, 5, 6]. The synthesis method is shown in Figure **7-1**. Recent work on synthesizing novel epoxy-methacrylate monomers derived from vanillyl alcohol, stringyl alcohol, gastrodigenin, and tyrosol was conducted by Bassett *et al.*, where the objective was to create epoxy-acrylate thermoplastic homopolymers [4].



Figure 7-1: synthesis method of creating epoxy-acrylate BPA hybrid molecule [6]

Some previous work has explored the role of heterobifunctional hybrid monomers in the formation of epoxy-acrylate IPNs. For example, Kagawa *et al.* investigated the mechanical

properties of sequential IPNs consisting of DGEBA, diacrylate, a diluent monoacrylate, and epoxy-acrylate hybrid with a BPA backbone. The diacrylate was synthesized from DGEBA as well, except that all the epoxy functional groups are converted into acrylate functional groups, by use of an excess of acrylic acid. A range of compositions with different amounts of hybrid were explored and sequential IPNs containing 32.3 wt% hybrid, 64.2 wt% diacrylate, and 3.5 wt% diepoxy resulted in the highest Young's modulus, surface hardness, and transparency[2]. Only one broad T_g was observed for all the hybrid-containing IPNs, and the T_g values resided between the single, narrower diacrylate $T_g(71^{\circ}C)$ and the diepoxy $T_g(111^{\circ}C)$. As the hybrid content was decreased the T_g increased from 99°C to 108°C. The increase in T_g is due to the increase in diepoxy content , and the Tg of the diepoxy is greater than that of the diacrylate.

A DGEBA-based heterobifunctional epoxy-acrylate monomer was also investigated by Xiao *et al.* [5] . The resin formulation consisted of DGEBA, a DGEBA-derived diacrylate, and an epoxy-acrylate hybrid with a BPA backbone. In contrast to Kagawa *et al.*[2], simultaneous IPNs were investigated and were formed using triarylsulfonium salt as the initiator for both the cationic polymerization of the epoxy and the free radical polymerization of the acrylate. The mechanical properties of thin films composed of a blend of diepoxy resin and diacrylate resin versus a film composed solely of the epoxy-acrylate hybrid monomer were investigated. In the hybrid formulation, there may be diacrylate monomers and residual diepoxy monomers because the hybrid resin mixture was not separated into pure components after the acrylic acid functionalization. The hybrid film had a higher acrylate conversion and epoxy conversion and a higher modulus than the blended film. The blend of diepoxy and diacrylate resins resulted in phase separated system as evidenced by a broad T_g with two peaks, while the hybrid film had a single, narrower T_g that resided in between the two T_g 's of the blended film. The increase in acrylate conversion was hypothesized to be due to an inter-group interaction where the cationic polymerization of the epoxy decreased the oxygen inhibition effect for the radical polymerization of the acrylate. The formation of the acrylate network then impacted the arrangement of the epoxy groups, because the hybrid molecule had one end bonded to the already-formed acrylate network. This forced the epoxy groups attached to the opposite end of the hybrid molecule into closer proximity, which resulted in faster polymerization rates and higher epoxy conversions compared to the blend system.

A very similar hybrid linker was investigated in very recent work by Bassett et al.[3] who investigated the cure kinetics and thermomechanical properties of dual-cure epoxy/acrylate sequential IPNs formed via SLA printing. The formulation consisted of mixtures of a DGEBA (EPON 828) in varying mol ratios with phenyl methacrylate, dimethacrylate created from the conversion of the DGEBA using methacrylic acid, and an epoxy-acrylate BPA hybrid, also synthesized by partial conversion of the DGEBA. These components were sequentially cured using TPO and Epikure W. The addition of hybrid monomer resulted in a greater extent of epoxy conversion (16%) compared to the formulation without the hybrid monomer. The difference was attributed to the vitrification of the acrylate networks in the non-hybrid formulation impeding the epoxy network formation. In the hybrid formulation the acrylate conversion was greater than in the pure diacrylate, indicating that the hybrid mitigated the vitrification of the acrylate network. Overall, the presence of a hybrid monomer was found to have minimal impact on the thermomechanical properties of the continuous IPN but was found to have the highest toughness and tensile strength compared to formulations without the hybrid. The increased toughness and tensile strength were expected to result from the higher extent of cure and increased interconnection between the acrylate and epoxy networks.

The impact of using glycidyl methacrylate (GMA) as a bridging agent to form simultaneous interconnected IPNs in a hexanediol diacrylate (HDDA) and 3,4epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate (CE) system was investigated by Lantean *et al.* [8]. GMA was added at 5 and 10 mol% to a 75:25 mol:mol formulation of HDDA:CE with a free radical photoinitiator and a cationic photoinitator. Increasing the GMA mol% from 0 to 10 decreased the glass transition temperature but increased the Young's modulus. The T_g's of the resins containing GMA were lower than the pure HDDA and the pure CE. The lower T_g results from the decreased crosslink density of the HDDA caused by the GMA behaving as an HDDA chain terminator. The presence of the GMA molecule had minimal effect (<2%) on the acrylate network conversion but aided in the epoxy network conversion. This again was attributed to the GMA behaving as a HDDA chain terminator and decreasing the crosslinking density of the rapidly formed HDDA network. The decreased crosslink density allows for easier mobility of the CE monomer through the formed acrylate network which enables the monomers to react and form the epoxy network. There was a bell-shaped trend for Izod fracture toughness values based on the mol% GMA added to the system. The formulations with 5 mol% GMA resulted in the greatest toughness compared to 2, 7, and 10 mol % GME. For the 75:25 HDDA:CE formulation the toughness was almost four times the toughness without GMA. The authors did not present any theories as to why 5 mol% GMA was the best formulation for toughness, but chemically linking the epoxy and acrylate networks was believed to be a contributing factor. In contrast to the toughness results, elastic modulus increased with increasing GMA mol%. Although the authors did not propose an explanation for this, it is likely due to increasing the links between the epoxy and acrylate network by the short molecule, making the system more brittle.

The thermomechanical properties of interconnected IPNs generally reside between the properties of the pure diepoxy and pure diacrylate but are improved relative to independent IPNs formed without hybrid linkers. Based on the results from this previous work, we wanted to look at the effect of hybrids in our system. Specifically, we wanted to investigate the effect of heterobifunctional monomers with different backbones on the cure kinetics, network formation, and material properties of interconnected IPNs. We are interested in the impact of the hybrid

monomer on green strength, since we want to use these resins in DIW printing. The substitution of the monoepoxy/monoacrylate hybrid monomer for the difunctional monomers could result in a more linear network which would lower the green strength of the UV cured part. A low green strength would result in poor print fidelity. However, increasing the hybrid content enables more connection points between the acrylate and epoxy network, which could increase the thermomechanical properties. Additionally, linking the acrylate and epoxy networks could mitigate phase separation. Therefore, we are also interested in how the hybrid monomers impact the network homogeneity of the interconnected IPN.

7.2 Experimental procedure

The chemical structures of the of the materials used in these formulations can be seen in Figure **7-2**. The bisphenol-A glycerolate diacrylate was supplied by Arkema with acrylate equivalent weight of 242.3. The diglycidyl ether of bisphenol-A based epoxy resin (EPON 828) was supplied by Hexion having an epoxide equivalent weight of 188.5. The photo initiator used was TPO (diphenyl(2,4,6-trimethylbenzoyl) phosphine oxide)) and the latent curing agent used was 1-ethyl 3-methyl imidazolium dicyanamide, which were both purchased from Sigma-Aldrich and used as-received. The acrylic acid, potassium hydroxide, and hydroquinone were also purchased from Sigma-Aldrich and used as received. The BPA hybrid monomer was made following the procedure described below, and the molecular weight used for calculations was 449 g/mol. The glycidyl methacrylate monomer was purchased from Sigma-Aldrich and the molecular weight is 142.2 g/mol. The rheology modifier used was hydrophilic fumed silica (Cab-O-Sil® M-5) with a surface area of 200 m²/g and was purchased from Cabot.



Figure 7-2: Components of the hybrid monomer resins

7.2.1 Synthesis of BPA hybrid molecule

The BPA hybrid molecule was synthesized using a similar procedure to that used by Kagawa *et al.* [2]. Approximately ~25g of diepoxy was combined with toluene (200mL) in a 500 mL pear-shaped flask and heated to 60°C, with stirring, until the diepoxy was dissolved. The mol:mol ratio of epoxy functional group to acrylic acid was kept at 1:0.5, so that half of the epoxy

functional groups will ring open and form acrylate functional groups. Hydroquinone was added to the flask in a 33:1 mol:mol ratio of acrylic acid to hydroquinone. Potassium hydroxide was dissolved in acrylic acid in an 18:1 mol:mol ratio of acrylic acid to potassium hydroxide. The potassium hydroxide and acrylic acid mixture was then added dropwise to the epoxy/hydroquinone/toluene solution. The system was then heated at 80°C for 24 hours. The flask was then rotovapped at 48° C to remove the toluene. The resin was rinsed using DI H₂O until a neutral pH was obtained. An autocolumn runner (Combiflash RF200) was then utilized to purify the resin, using 40:60 ethyl acetate: hexanes. The volume of solution collected in each fraction was set at 30 mL. The 60-minute step program consisted of 2 minutes of 100% hexanes traveling through the column with the sample, 55 minutes of the 40:60: ethyl acetate:hexanes mixture, and 3 minutes of 100% ethyl acetate to flush out the column and the lines. The flow rate for all steps was 40 mL/min. Before the program started, the column was equilibrated, which means that 240mL of hexanes was flushed through the column before the sample was loaded. The sample loading type chosen was "Liquid" where 3g of resin were loaded directly onto a 40 g RediSep SiO₂ column using a 10 mL Leur lock syringe after equilibration. The fractions were analyzed using the internal 254nm UV detector. The hybrid fractions, as determined via TLC, were then all combined into one flask and rotovapped down to remove the ethyl acetate:hexanes solution. To ensure the hybrid resin was dry, the resin was placed in a vacuum oven at 45°C overnight before NMR and MS analysis were conducted.

NMR was conducted to determine whether the hybrid was pure, or if there were diepoxy or diacrylate present still in the resin. ¹H-NMR was conducted using deuterated dichloromethane and the spectra of the BPA hybrid and EPON 828 are shown in Figure **7-3**. In the BPA hybrid ¹H-NMR, the peaks between 5 and 6.6ppm correspond to the protons associated with the acrylate functional group. These results are similar to those found by Bassett *et al.* [3].



Figure 7-3: ¹H-NMR on BPA hybrid and EPON 828 in CDCl₃. Acrylate peaks in the hybrid are denoted by an '*'.

Because the NMR peaks of the EPON828 starting material and diacrylate by-product could overlap with the hybrid peaks, making it difficult to determine purity based solely on NMR liquid chromatography/mass spectrometry (LCMS) was performed to further analyze the purity of the hybrid molecule (Appendix 1).

7.2.2 Blend Nomenclature

Formulations with different glycidyl methacrylate weight percent and different bisphenol A epoxy-acrylate weight percent are shown in Table **7-1**. "Low mol%" corresponds to 4.5 mol% of the hybrid monomer, "intermediate mol%" corresponds to 8 mol% of the hybrid monomer, and "high mol%" corresponds to 12 mol%, in respect to total moles of material within the

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formulation. The total acrylate functional groups (FG) to epoxy FG are kept constant at a 1:2 mol:mol ratio for every formulation. The remaining wt % is composed of EPON 828, BPA glycerolate diacrylate, 5 wt% fumed silica, 5 mol% (relative to total epoxy FG) latent curing agent, and 1.2 mol % (relative to total acrylate FG) TPO as the photoinitator.

Component	Low hybrid GMA	Intermediate hybrid GMA	High hybrid GMA	Low hybrid BPA	High hybrid BPA
Total acrylate:epoxy FG ratio (mol:mol)	1:2	1:2	1:2	1:2	1:2
% epoxy FG from hybrid	7%	12%	18%	7%	18%
% acrylate FG from hybrid	19%	35%	45%	19%	45%
Photoinitiator	1.2 mol% vs total moles acrylate FG				
Latent cure agent	5 mol% vs total moles epoxy FG				
Fumed silica (wt%)	5	5	5	5	5

Table 7-1: Hybrid molecule formulations in terms of functional groups (FG)

7.2.2 Preparation of mixed resins

The diacrylate, diepoxy, and hybrid monomer were combined in a 125 mL polypropylene centrifugal mixer container and hand mixed. The combined resins were mixed for 60 seconds at 1800 RPM and 10.1 kPa in a Thinky ARV-310 planetary centrifugal mixer. The photoinitiator, latent curing agent, and fumed silica were added to the resin and hand mixed before being placed back into the mixer for 60 seconds at 1800 RPM and 10.1 kPa.

7.2.3 Cure conditions

As described in Chapter 3 there are three categories of samples based on the cure procedure. "UV print-cure only" samples refer to printed samples that are UV-cured during printing and are characterized without any further UV or thermal cure. The intensity used during printing is 7 mW/cm², which corresponds to a UV dose of 504 mJ/cm² per transverse printed mechanical bar and 414 mJ/cm² per longitudinal printed mechanical bar. 'UV print cure + flood cure' samples refer to print-cured samples that are UV flood cured after the *in situ* print cure. The UV print cure only samples are flood cured for 30 minutes using an ABM, INC 500W near/mid UV 2105C2 illumination controller with an intensity of 5.7 mW/cm². The standard thermal cure procedure starts by placing the samples in a room temperature oven that is then heated to 100°C at 1°C/min and held for 4 hours, then the oven temperature is increased to 150°C at 1°C/min and held for an additional 2 hours, finally the oven is ramped back down to room temperature at 1°C/min. These results are in an Appendix I. The additional thermal cure procedure 'SC + 220°C' starts by placing samples cured with the standard thermal cure (above) in a room temperature oven that is then heated to 220°C at 1°C/min held for 2 hours, then ramped down at 1°C/min back to room temperature.

7.2.4 Characterization

Viscosity, photocalorimeter differential scanning calorimetry (UV-DSC), and isothermal cure measurements were conducted on the uncured resins. Thermal DSC, 3-point bend, DMA, and variable temperature DMA were used to analyze printed and cured samples. The experimental parameters used for these measurements are described in Chapter 3.

7.3 Results & Discussion

7.3.1 Rheology

The rheology of the resins is dominated by the presence of the 5 wt% fumed silica rheology modifier. Therefore, the rheology was not expected to significantly change between the formulations. Additionally, the mol% of hybrid being added was relatively low, so the impact on rheology was also expected to be minimal, regardless of the hybrid structure. To test this theory,

the viscosity as a function of shear rate was measured for the different hybrid formulations (Figure **7-4**).

The shear thinning behavior can be quantified by fitting the apparent viscosity versus shear rate curves to a power law Equation **7-11**.

Equation 7-11: Viscosity power law equation of complex fluids $\eta = K \dot{\gamma}^{n-1}$

K is the consistency index, n is the flow index, η is the viscosity, and $\dot{\gamma}$ is the shear rate. The consistency index reflects the individual filler characteristics, whereas the flow index reflects the structural property of the entire resin [9]. The parameters in Equation **7-1** were obtained by fitting the viscosity curves over the linear portion of the curves (between 0.01 and 1 s-1) in Figure **7-8**.

The addition of the low viscosity GMA hybrid molecule initially decreases the shear thinning exponent, indicating superior shear thinning behavior. However, the addition of more GMA hybrid results in a similar flow index as the resins with no hybrid monomer and the 'low BPA hybrid'. This is likely due to increased entanglements between the epoxy and acrylate from increasing amounts of GMA hybrid. The high mol% BPA hybrid flow index is slightly greater than the other formulations, indicating that this formulation is less shear-thinning. This is likely due to the decreased amount of diacrylate and diepoxy, and increased entanglements of the BPA hybrid monomer. It is worth noting that the value of the flow index is sensitive to the range of viscosity values used [10], and that the 5 wt% fumed silica is most likely dictating the overall shear thinning behavior. The shear thinning behavior of the resins are ideal for DIW printing.

Table 7-2: Rheological properties of hybrid formulations

Formulation	n
No Monomer	0.15
Low mol% GMA hybrid	0.04
Low mol% GMA hybrid_1	0.06
Intermediate mol% GMA	0.11
Intermediate mol% GMA_1	0.12
High mol% GMA	0.11
Low mol% BPA hybrid	0.18
High mol% BPA hybrid	0.27



Figure 7-4: Viscosity of varying mol% GMA hybrid and BPA hybrid containing resins

7.3.2 Acrylate Cure Kinetics

It is important to understand what effect different *in situ* UV cure profiles used while printing have on the cure state of the printed part. The introduction of an acrylate/epoxy hybrid monomer can significantly impact the cure kinetics because the hybrid monomer can interact with both networks formed. This means that it is possible for the hybrid monomer to impact the cure kinetics of both networks. One method to investigate how the presence of a hybrid monomer and how the backbone of a hybrid monomer impacts the acrylate cure kinetics is via UV-DSC.



Figure 7-6:Pulsed UV-DSC at 80 mW/cm² for BPA hybrid formulations

Pulsed exposure experiments, consisting of twenty 2.4s UV pulses with a 5 minute dark time in between pulses were tested to mimic the episodic exposure and resulting cure kinetics a part would see during the print. With this pulsed exposure profile at 80 mW/cm², the reactions have reached maximum conversion after 5-6 pulses for GMA hybrid formulations (Figure **7-5**) and 7-8 pulses for BPA hybrid formulations (Figure **7-6**). The high and intermediate mol% GMA formulations reach a similar final conversion around 79%, while the remaining formulations reach a similar conversion of around 70%. The increased final conversion of the high mol% GMA formulation is likely due to the greater mobility of the hybrid monomer compared to the diacrylate molecule. The glycidyl methacrylate hybrid monomer is smaller than the diacrylate molecule, which allows for easier diffusion during polymerization and network formation.

The acrylate polymerization of the BPA hybrid formulations is slower than that of the GMA hybrid formulations and is similar to the no hybrid formulation due to the similarity in structure and size of the diacrylate molecule. The larger BPA hybrid molecule, compared to the GMA hybrid molecule, will have lower molecular mobility and is more apt to get trapped within the acrylate network as it forms. This is also why the overall conversion is lower than the conversion of the GMA hybrid systems.



Figure 7-7: Pulsed and continuous exposure UV-DSC at 80 mW/cm² for varying hybrid formulations

To investigate the effects of episodic UV exposure on the acrylate conversion, the results of the pulsed profile experiments were compared to the continuous UV exposure results, as shown in Figure 7-7. The addition of the GMA hybrid monomer results in higher conversions in continuous exposures than in pulsed exposures. This is because continuous exposure results in a greater concentration of free radicals generated, compared to pulsed exposures. The increased radical concentration causes a faster reaction rate and results in increased conversions before deceleration. Additionally, continuous exposures may overcome oxygen inhibition faster than pulsed exposures due to the constant generation of free radicals. As GMA content increases, the total conversion increases, this is due to the increased replacement of the diacrylate molecule by the 'monoacrylate' GMA molecule. The GMA molecule has greater mobility compared to the large diacrylate molecule allowing for more network formation. These results contradict those found by Lantean *et al.* where the increased amount of GMA resulted in lower conversion [8]. The lower conversion could result from the limited mobility of the GMA molecule resulting from the competing epoxy network formation formed via radical induced cationic polymerization.

In the BPA hybrid systems, the overall conversion is similar between the continuous and pulsed exposures. Additionally, the conversion is similar to the no hybrid formulation. This is expected to result from the size and structure of the BPA hybrid molecule being similar to the diacrylate molecule it replaces. Both the BPA hybrid and diacrylate molecules are larger than the GMA, and have less mobility resulting in lower conversion comparatively.

These results indicate that at an intensity of 7mW/cm², the replacement of diacrylate with a hybrid monomer does not negatively impact the acrylate conversion. This important because pulsed exposure UV-DSC is like the episodic exposure that the part sees during the print. For continuous exposure, the addition of a shorter hybrid molecule results in almost complete conversion of the acrylate network which is advantageous for applications where residual uncured acrylate could degrade the material properties.

7.3.3 Epoxy Cure Kinetics

Isothermal cure measurements give information regarding the time required for an epoxy network to form at a given temperature and indicate if and when vitrification occurs during the cure [11]. In this work, varying compositions of different hybrid monomers in an epoxy/acrylate dual-cure resins were prepared as described in Chapter 3. Isothermal cure measurements were conducted on uncured resins to investigate the impact of heterobifunctional monomers, having different chemical structures, on the epoxy cure kinetics. The impact of the unreacted acrylate resin on the epoxy network formation would be especially important if simultaneous initiating catalysts are used. For simultaneous initiation, there will be a competition of the epoxy and acrylate network formation, where the faster polymerization mechanism of the acrylate is expected to further impede the slower polymerization mechanism of the epoxy and impact or decrease the final conversion of the epoxy [12, 13]. This could result in lower than expected mechanical properties or phase separation.

It is important to acknowledge that the epoxy cure kinetics of the printed parts will be impacted by the formation of the acrylate network. The hybrid monomers that form part of the acrylate network are unable move during the formation of the epoxy network. Therefore, the gelation point of the epoxy will be delayed due to the limited diffusion of the diepoxy through the formed acrylate network. The delay will be more significant for GMA formulations, compared to BPA formulations, because there is a greater extent of network formation. This would limit epoxy monomer diffusion during the epoxy network formation This effect was shown previously in Chapter 4 for epoxy/acrylate resins without hybrid monomers. However, the cure kinetics of the epoxy network in the presence of the cured acrylate network were not studied for these hybrid formulations.

While the isothermal cure measurements performed do not reflect how the cure kinetics would be affected in sequentially polymerized IPNs, as investigated in the rest of the thesis, these results still can provide useful insight. It is hypothesized that the epoxy cure kinetics will change with the integration of a heterobifunctional monomer. This is because the hybrid monomer will interact with a both a forming epoxy network and an unpolymerized acrylate monomer. This could cause the hybrid monomer to behave as a monoepoxy diluent and speed up the gelation or the interaction with the unpolymerized acrylate monomer would slow down the epoxy cure kinetics by limiting epoxy-chain mobility.

To investigate the influence of the heterobifunctional monomers on epoxy cure kinetics, isothermal cure measurements were conducted at two temperatures. One temperature, 150°C, was chosen because it is above the initiation temperature of the latent curing agent (~130°C) [14]. After conducting the isothermal cure measurements at 150°C, vitrification occurred and so these experiments were then repeated at 200°C to avoid vitrification. The isothermal cure temperature of 200°C is above the T_g of the cured formulations (Figure **7-14**). The samples isothermally cured at 150°C show an initial tan delta peak and parallel increase of the storage and loss moduli

indicating gelation, followed by a subsequent increase in the tan delta second loss moduli indicative of vitrification, as seen in Figure **7-8**: 150°C isothermal cure measurements of the hybrid formulations with where the second increase in the loss moduli and second tan delta peak indicates vitrification

Figure 7-8: 150°C isothermal cure measurements of the hybrid formulations with where the second increase in the loss moduli and second tan delta peak indicates vitrification

Samples held at 200°C did not show vitrification and only showed gelation, as evidenced by single T_g and parallel increase in the storage and loss moduli (Figure **7-9**). The epoxy gelation time was faster at 200°C than at150°C, as expected due to the lowered resin viscosity.



Figure **7-9**: 200°C isothermal cure measurements of the hybrid formulations with a parallel increase in storage and loss moduli, storage moduli values in the 10 Pa⁶, and a single tan delta peak

The onset of gelation at 150°C is not significantly impacted by the presence of the hybrid monomers because the cure temperature is below T_g and monomer mobility is limited before vitrification occurs. The onset of gelation is a measurement of the time necessary to form a macro-epoxy network. The addition of the GMA initially slightly decreases the onset of gelation at 150 °C due to the increased mobility of the GMA hybrid molecule. However, increasing the amount of the 'monoepoxy' GMA hybrid monomer is believed to linearize the network by acting as chain extenders. This in combination with limited diffusion of the diepoxy monomers, which promote network branching, at this low temperature would delay the formation of the macro-epoxy network. While the BPA hybrid is still acting as a monoepoxy, the temperature limits the diffusion of the monomer and so it behaves like the diepoxy. This behavior is also seen in the acrylate cure kinetics where the measurements occurred at room temperature and diffusion of the BPA hybrid was similar to diffusion of the diacrylate.

The addition of hybrid molecules decreases the onset of gelation time at 200°C. At this increased temperature, it is believed that both hybrid monomers and diepoxy have increased mobility, where the relative increase is fastest for the short GMA molecule and slowest for the diepoxy. This contrasts with the limited mobility of the BPA hybrid at room temperature or 150°C, where the monomer behaves similarly to the mobility of the diacrylate at room temperature or diepoxy at a temperature below T_g. Increasing the amount of hybrid monomer increases the gelation time at 200°C (Table **7-3**). This is because increased amounts of hybrid monomer form a more linear network and requires more time for the macro-network to form. GMA hybrid has a faster gelation time than the BPA hybrid due to the GMA molecule being much smaller and lowering the viscosity of the formulation.

150°C Isotherm			200°C Isotherm		
Composition	Onset of gelation	# of	Composition	Onset of gelation	# of
mol% hybrid	S	samples	mol% hybrid	S	samples
none	325 (4)	2	none	61	1
low GMA	305 (24)	2	low GMA	19	1
intermed GMA	308	1	intermed GMA	24	1
high GMA	352 (15)	2	high GMA	35	1
low BPA	334 (21)	2	low BPA	23	1
high BPA	311 (42)	2	high BPA	45	1

Table **7-3**:Onset of gelation for varying mol% GMA hybrid and BPA hybrid containing resins at 150°C and 200°C isothermal temperatures. Standard deviation values are in parentheses.

7.3.4 Thermomechanical Properties

The mechanical stability of the printed parts is a function of the green strength arising from the acrylate network formed during the *in situ* UV cure prior to thermal cure. To determine how the amount and structure of the hybrid monomer impact the acrylate network formation and green strength, the room temperature storage modulus before thermal cure was measured. The room temperature storage modulus was measured after *in situ* UV cure during printing. This was followed by a flood cure for 'UV print + flood cure' samples. The 'UV print + flood cure' samples were then thermally cured in order to form the epoxy network. The thermal cure profile used was 4 hrs at 100°C, 2 hrs at 150°C with 1°C/min ramps, followed by an additional 2 hrs at 220°C, with a ramp rate of 1°C/min. The room temperature moduli values of 'SC + 2hrs 220°C' samples were then measured to determine the effect of hybrid content and structure on the fully cured mechanical properties. Additionally, for all cure conditions transverse and longitudinal print direction swere compared to investigate if the acrylate network formation, and any resulting print-direction effects, would change when adding a heterobifunctional hybrid that behaves as a 'mono-acrylate'.

It was hypothesized that print direction effects would be present for the hybrid formulations because of replacing the difunctional monomers with a heterobifunctional hybrid molecule. The difunctional epoxy or difunctional acrylate monomers form highly crosslinked three-dimensional networks. Therefore, the non-hybrid formulation is not expected to show print direction effects. In contrast, the hybrid monomer would behave as a monoacrylate/monoepoxy and would form linear structures, resulting in print direction effects.

7.3.4.1 'Print-cure only'

Room temperature storage modulus values of 'Print cure only'; longitudinal and transverse printed bars for GMA formulations are shown in Figure **7-10**.



Figure 7-10:Room temperature storage modulus of 'Print cure only' samples printed at 7 mW/cm²

Only GMA formulations were analyzed because the non-hybrid and BPA hybrid formulations had low green strength values and were not able to be handled for testing. Only the low mol% GMA formulations showed definitive print direction effects, where the transverse samples had a higher green strength than the longitudinal print samples. This is explained by the low mol% GMA formulation having the fastest reaction kinetics of the GMA and no hybrid formulations (Figure **7-5**) in combination with deadtime between light exposures during the transverse versus longitudinal prints.



Figure 7-11: Print pathways for transverse and longitudinal print directions

During the transverse print samples, the network is rapidly fused together across the bead interfaces, while in longitudinal prints there is significant deadtime between the printing of adjacent beads (Figure 7-11). For a rapidly curing network, this long deadtime would result in poor bead-to-bead adhesion within a printed layer due to the reduction of monomer and polymer chain mobility at the surface of the bead.

As the GMA mol% increases, the green strength decreases. One factor contributing to the decreased green strength modulus is due to the decreased amount of diacrylate and increased amount of hybrid monoacrylate which would change the extent of acrylate network formation as well as the crosslink density. The presence of more hybrid monoacrylate, as opposed to diacrylate, will result in a more linear network with a lower crosslink density [15, 16]. The decrease in crosslink density then reduces the modulus.

7.3.4.2 'UV print + flood cure'

The room temperature storage modulus values of 'UV print + flood cure' longitudinal and transverse printed bars is shown in Figure **7-12**



Figure 7-12: Room temperature storage modulus of 'UV Print + flood cure' samples

Although the 'no hybrid' transverse prints had lower average moduli than longitudinal prints, the standard deviations do overlap. For formulations with the GMA hybrid, the modulus of the UV-cured longitudinal samples. In contrast, for formulations with the BPA hybrid, the UV-cured modulus of the longitudinal samples is greater than the transverse printed samples, but the standard deviations overlap. This difference can be explained by the differences in acrylate cure kinetics between the GMA and BPA formulations. The acrylate cure kinetics of the GMA formulations are faster than the cure kinetics of the BPA and 'no hybrid' formulations. Therefore, in transverse printed samples where adjacent beads are in quick succession, the network is rapidly crosslinked across the bead interfaces. However, in longitudinal print samples the duration between the printing of one bead and the adjacent bead is much longer than in transverse samples (print pathways shown in Figure **7-11**). For a rapidly curing network, the longer time before the adjacent bead is deposited would result in poorer bead-to-bead adhesion due to the reduction of monomer and polymer chain mobility at the surface of the bead at higher acrylate conversion. A similar effect is seen in the 50 wt% acrylate resins at high print intensities (Figure **4-9**, Chapter 4). The high

acrylate conversion resulting from high intensity and a high concentration of acrylate reduces inter-bead adhesion and leads to print direction effects that are not observed at lower UV intensities or for lower acrylate wt % formulations. However, for the BPA hybrid, the bead-tobead adhesion within the longitudinal print is less sensitive due to the slower cure kinetics. This results in similar longitudinal and transverse print modulus values. Additionally, the replacement of diacrylate with hybrid monomer creates a more linear network that can also limit the crosslinking between bead interfaces.

For both GMA and BPA formulations as the hybrid content increases, the modulus decreases. One factor contributing to the decreased acrylate network modulus is the decreased amount of diacrylate and increased amount of hybrid 'monoacrylate'. Increasing the hybrid 'monoacrylate' by replacing the diacrylate will result in a more linear network with a lower crosslink density [15, 16]. This decrease in crosslink density then reduces the storage modulus.

7.3.4.3 'SC + 2hrs 220°C'

The room temperature storage modulus values of 'SC + 2hrs 220°C' longitudinal and transverse printed bars are shown in Figure **7-13**.



Figure 7-13: Room temperature storage modulus of 'SC + 2hrs 220°C samples

The moduli of all 'UV print + flood cure' samples (Figure **7-12**) increase after the thermal cure due to the formation of the epoxy network. There are no print direction effects for the non-hybrid formulation, which agrees with literature where fumed silica is used as a filler [10]. In the GMA hybrids there are no consistent trends with modulus values and print direction. The modulus values for the low mol% GMA are the same regardless of print direction and for the intermediate mol% GMA are within standard deviation of each other. However, the high mol% GMA transverse samples have a higher storage modulus than the longitudinal samples, which is consistent with the modulus for the 'UV print + flood cure' samples. In contrast, the BPA hybrid longitudinal samples have a higher modulus than the transverse samples, which is consistent with the modulus prior to thermal cure ('UV print + flood cure' samples). The print direction effects of the high mol% hybrid formulations are believed to result from the replacement of the difunctional monomers with enough monoacrylate/monoepoxy hybrid which creates a more linear and less crosslinked network, reducing the bonding between interfaces.

Having investigated the influence of hybrid monomers on the green strength and room temperature storage modulus of the interconnected IPN, the next step was to understand the influence on the interconnected IPN homogeneity.

The glass transition temperatures (T_g) of the 'SC + 2hrs 220°C' samples were measured by variable temperature DMA (Figure 7-14). All compositions form phase-separated IPNs, as evidenced by the appearance of two T_g transitions, a lower temperature T_g for the acrylate-rich phase and a higher T_g for the epoxy-rich phase (Figure 7-15). This is surprising because tethering the two networks together was expected to result in a single phase, similar to the results found by Kagawa *et al.*[2] and Bassett *et al.*[3]. However, both these systems used a significant amount of a monoacrylate which is expected to form a less crosslinked acrylate network and more easily allow the interpenetration of the epoxy molecules to form a single phase.



Figure 7-14: Glass transition temperatures for 'SC + 2hrs 220°C' samples

Based on results in **Chapter 5** and **Chapter 6**, it is expected that the glass transition temperature(s) of the IPN will be somewhere in between the glass transitions of the two pure resin systems [2, 17]. However, the T_g of the pure photopolymerized BPA glycerolate diacrylate was unable to be measured because of the high viscosity of the acrylate limiting the homogeneous dispersion of photoinitator as well as vitrifying before reaching full conversion. The slight differences in the low T_g (acrylate rich phase) and high T_g (epoxy-rich phase) with the addition of the hybrid monomers could be due to differences in either the acrylate network formation or the phase distribution within the IPN, where the acrylate-rich phase may be shifted towards the epoxy-rich phase depending on composition. This would cause an increase in the lower T_g .



Figure 7-15: VT DMA curves for hybrid formulations. Data below 50°C is disregarded and not reliable because the sample slips from the grips during the ramped cool down.

As previously mentioned, it was hypothesized that the hybrid would crosslink between the acrylate and epoxy networks and limit phase separation, by decreasing the phase domain size. This was then expected to result in a single T_g with a value in between the acrylate-rich and epoxy rich glass transition temperatures. However, the hybrid monomers that replaced the difunctional monomers decreased the individual phase crosslink density while simultaneously increasing the interphase crosslink density, resulting in a minimally changed T_g . However, the second T_g values are also greater than those found by Kagawa *et al.*[2] and Bassett *et al.*[3], which can be explained by the lack of a mono-acrylate diluent [18, 19].

The rubbery modulus of the formulations was also investigated to probe the network mobility at a temperature (245°C) significantly above T_g (Figure 7-16). The addition of the hybrid monomer minimally influences the rubbery modulus, except for the intermediate mol % GMA formulation. This formulation could have the optimal mol% of crosslinkers between the two networks, necessary to get ideal thermomechanical properties of the interconnected IPN, similar to the findings by Lantean *et al.* [8]. It is interesting that the type of hybrid has little influence on the rubbery modulus. This indicates that there is little to no impact from forming additional crosslinks when working with already highly crosslinked networks. Additionally, these results suggest that the overall crosslink density determines the properties of the composite rather than the crosslink density within the independent networks. This was also found in the T_g measurements.

Formulation	Rubbery Modulus	stdev
	MPa	
No Hybrid	20.5	0.1
Low GMA	21.9	0.3
Intermed. GMA	48.4	1.2
High GMA	26.3	0.7
Low BPA	19.4	0.6
High BPA	26.0	0.4

Figure 7-16: Rubbery modulus values taken at 245°C for the hybrid formulations

After investigating the T_g and room temperature modulus values of the 'SC + 2hrs 220°C' samples, three-point bend measurements were conducted. The three-point bend experiments were designed to investigate whether print direction effects existed after the epoxy network formed, thus creating an interconnected IPN. It was hypothesized that longitudinal samples would have greater flexural modulus and strength compared to the transverse samples because the direction of force is perpendicular to the direction of the printed layers.



Figure **7-17**: Diagram of the applied force on longitudinal and transverse samples during three-point bend measurements

The direction of the force applied on the samples during a three-point bend measurement for transverse and longitudinal samples are shown in Figure **7-17**. Three-point bend experiments provide a direct measurement of the flexural modulus and therefore give bulk material properties. This means that three-point bend gives information regarding the amount of force necessary to rupture the network which is determined by interlayer adhesion of the printed layers. This is a less-sensitive network measurement compared to torsional DMA, which is generally used to probe the extent of network formation without destroying the network. However, three-point bend measurements are more sensitive to surface or print defects which behave as local stress risers and failure initiation points.

The flexural modulus and flexural strength values for varying hybrid formulations are found in Figure **7-18**. For longitudinal samples, it is apparent that there is not a significant change in the storage modulus or flexural strength based on the presence of a hybrid monomer or the backbone of the monomer (BPA vs GMA). This is unexpected because the hybrid monomer was expected to alter the modulus and strength by forming an interconnected IPN. However, these results align with those found by Bassett *et al.* when conducting tensile measurements, where the presence of the BPA hybrid had minimal impact on Young's modulus or tensile stress [3]. In contrast, Kagawa *et al.* found that the addition of the BPA hybrid molecule increased the tensile stress and Young's modulus. However the formulations contained 20 wt% monoacrylate and the samples tested were molded not DIW printed where the surface defects of the DIW parts could act as stress concentrators and decrease the measured values [2].



Figure **7-18**:Three-point bend results for longitudinal and transverse printed 'SC + 2hrs 220°C' hybrid-monomer containing samples

Similar to longitudinal samples, the transverse samples show similar flexural moduli values and flexural strength values, except for the intermediate mol% GMA formulation. The

intermediate mol% GMA has a significantly greater modulus and strength than the other formulations. This could be because this formulation has the ideal mol% of crosslinkers between the epoxy and acrylate networks for maximum inter-bead adhesion. This agrees with the increased rubbery modulus value found in the variable temperature DMA results. The increased values of the transverse versus the longitudinal print for the intermediate mol% GMA formulation could be due to the rapid network formation and crosslinking between the adjacent bead interfaces of the transverse print. This agrees with the UV print + flood cure room temperature modulus results. However, it is also possible that these measurements could simply be outliers, because, although 5 samples were tested by 3-pt bend in each sample group all the samples came from the same print batch, so it is a possibility that there could have been unknown variables that differed slightly during the printing of the transverse intermediate wt% samples that resulted in this outlier performance. Further testing to increase the total sample size and to test samples from multiple different print and resin batches should be conducted to determine if these results are repeatable

Excepting the intermediate mol% GMA hybrid, the transverse samples have lower moduli than the longitudinal samples. This is expected because the direction of applied force in the three-point bend test is parallel to the transverse printed layer interfaces, where the interlayer adhesion is expected to be the weakest.

Aside from intermediate mol% GMA hybrid, the strength values did not show a strong print direction effect. The fracture surfaces were investigated using SEM, which indicated brittle failure occurred for all formulations.

The SEM of 'SC + 2hrs 220°C' longitudinal print three-point bend fracture surfaces of low mol% BPA and low mol% GMA formulations are shown in Figure **7-19**. Both surfaces have river patterns that are representative of brittle fracture.



Figure **7-19**: Low (top) and high (bottom) magnification SEM micrographs of fracture surfaces of SC + 2hrs 220°C low mol% of BPA hybrid and low mol% GMA hybrid samples.

The SEM of 'SC + 2hrs 220°C' longitudinal print three-point bend fracture surfaces of high mol% and low mol% GMA formulations are shown in Figure **7-20**. The fracture surface of the low mol% GMA are smooth, while the fracture surface of the high mol% GMA formulation has a mirror, mist, hackle region in addition to some river marks. All of these indicate brittle failure mechanisms. The SEM results contrast those found by Lantean *et al.* when introducing GMA hybrid into their simultaneous IPN system. Without the GMA molecule, the fracture surfaces appeared brittle. However, the addition of the GMA hybrid molecule resulted in a complex fracture surface, which is typical of toughened materials [8]. This is because hexanediol diacrylate, which is the resin system used by Lantean *et al.* [8], has a flexible chain and the addition of the GMA hybrid would tether the flexible network to the more rigid network of the

epoxy, thus creating a toughening mechanism. This is very different from the formulations used in this thesis, which were highly crosslinked BPA dimethacrylate and BPA diepoxy, both of which have similar rigid backbones.



Figure **7-20**: Low (top) and high (bottom) magnification SEM micrographs of fracture surfaces of SC + 2hrs 220°C high mol% of BPA hybrid and high mol% GMA hybrid samples

7.4 Conclusion

Two acrylate-epoxy heterobifunctional hybrid monomers with different backbones were added to an acrylate/epoxy sequential dual-cure resin system in order to investigate the impact on cure kinetics and network formation. The green strength of the UV cured samples was investigated as well as the thermomechanical properties of the UV and thermally cured samples.

The acrylate cure kinetics during pulsed exposures and continuous exposures was investigated using UV-DSC. Neither the total conversion nor rate of acrylate reaction were significantly influenced by the presence, amount, or type of hybrid for the pulsed exposures. In contrast, for continuous exposures, the addition of the GMA hybrid monomer resulted in greater total conversions than the other formulations. This was attributed to the high mobility of the GMA monomer and the increased concentration of free radicals generated during the continuous vs pulsed exposures. The total acrylate conversion was the same for the 'no hybrid' and BPAhybrid formulations for the pulsed and continuous exposures.

Overall, the modulus of 'UV print + flood cure' samples increased with the addition of the GMA hybrid, while the addition of BPA hybrid maintained or decreased the modulus. However, for both hybrid monomers, the relative modulus decreased as the individual hybrid content increased, due to the hybrid behaving as a monoacrylate and decreasing the crosslink density of the acrylate network. These results indicate that the presence of a heterobifunctional epoxy-acrylate monomer can influence the acrylate network formation, however the influence is dependent on the backbone of the hybrid monomer. Print direction effects were only observed in the GMA hybrid samples, where transverse prints had a higher modulus than the longitudinal prints. The print direction effects were attributed to the rapid cure kinetics of the GMA hybrid formulations compared to the BPA hybrid or BPA diacrylate monomers. This finding is similar to the print direction effects seen in the print-cure only 50 wt% acrylate sample described in Chapter
4, where the print direction effects result from poor inter-bead adhesion arising from high acrylate conversion and increased time between deposition of adjacent beads.

The room temperature moduli of 'SC + 2hrs 220°C' samples also showed print direction effects for high mol% GMA hybrid and low and high mol% BPA hybrid, but no print direction effects for the non-hybrid formulation. The ability of the diepoxy to form a three-dimensional network and bond between the printed layers eliminates the print direction effects for the no hybrid and low/intermediate mol% GMA formulations. The print direction effects of the high mol% hybrid formulations are believed to result from the replacement of the difunctional monomers with enough monoacrylate/monoepoxy hybrid which creates a more linear and less crosslinked network, reducing the bonding between interfaces.

Unexpectedly, the variable temperature DMA measurements indicated that phase separation occurred for all formulations, and glass transition temperatures associated with each phase did not significantly vary with the addition of either hybrid.

Interestingly, the intermediate mol% GMA formulation had a greater rubbery modulus than the other formulations, which were comparable to each other. This could indicate that this is the optimal formulation for crosslinking between the two networks, but further study would be needed to confirm this finding.

The flexural modulus and strength of the non-hybrid formulation were independent of print direction effects. For all the hybrid formulations, except the intermediate mol% GMA, the flexural modulus values of transverse three-point bend samples were lower compared to the longitudinal samples. The transverse samples had lower properties because the direction of the applied force was perpendicular to the printed bead interfaces. The flexural modulus and strength values of the longitudinal samples were all within standard error regardless of the formulation. Similarly, the flexural strength and modulus values of transverse printed samples were also within error of each other and independent of formulation. For the intermediate mol% GMA formulation

the transverse sample was an outlier, with much greater modulus and strength values than any other formulation and also greater than the longitudinally printed samples. This agrees with the rubbery modulus results where the intermediate mol % GMA formulation had the greatest moduli of all formulations. This might be because the intermediate mol% GMA formulation has the ideal amount of crosslinking between the two networks, and further investigation is warranted. The SEM fracture surfaces indicate that brittle failure occurred for all formulations, which agrees with the three-point bend results.

It was hypothesized that the addition of an epoxy-acrylate heterobifunctional monomer would bridge the acrylate and epoxy networks to each other and improve the mechanical properties versus independent IPNs. Formulations containing glycidyl methacrylate (GMA) were expected to have the greatest thermomechanical properties due to an increased crosslink density resulting from the short rigid molecule, whereas the bisphenol A glycerolate monoacrylate/monoepoxy was expected to have less improvement in the glass transition temperature or modulus due to its long but rigid BPA backbone.

The most important finding of this work is that connecting the epoxy and acrylate network and forming an interconnected IPN did not have a significant impact on the thermomechanical properties of the fully cured samples for this epoxy/acrylate system. One possible reason for the minimal influence is that the acrylate network and epoxy network are both highly crosslinked, high-modulus thermosets, and the addition of additional internetwork chemical crosslinks by the hybrid monomer does not significantly add to the crosslink density. These theories could be tested by using a different epoxy/acrylate dual-cure system where the epoxy and acrylate have significantly different backbones that will result in different thermomechanical properties for the acrylate vs epoxy networks. In such a system it may be easier to create measurable differences in the performance due to internetwork crosslinking by a hybrid monomer.

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CHAPTER 8 : CONCLUSIONS AND FUTURE WORK

8.1 Conclusions

This thesis investigated the influence of formulation, filler morphology and surface functionalization, and heterobifunctional monomers on the formation and properties of independent and interconnected interpenetrating polymer networks. The first part of this thesis discussed the influence of composition and cure conditions on the cure kinetics, thermomechanical properties and homogeneity of the independent interpenetrating polymer network. The second part of this thesis discussed how the addition of acrylate-functionalized and epoxy-functionalized fillers into a dual-cure system influenced the cure kinetics, network formation, and thermomechanical properties of the filler-integrated independent IPN. The third part of this thesis discussed the formation of interconnected IPNs via hybrid monomers, and how the different backbone of the hybrid monomers influenced the cure kinetics and thermomechanical properties.

In **Chapter 4**, the influence of acrylate content and UV print intensity and exposure profile on the green strength and print fidelity were investigated. Print direction effects were only observed for the highest print intensity (29 mW/cm²) and highest weight percent acrylate (50 wt%) formulation, due to the poor bead-to-bead adhesion of the longitudinal print compared to the transverse print. This difference in print direction is due to diminished inter-bead adhesion caused by high acrylate conversion and the increased time between printing adjacent beads for the longitudinal prints. It was also found that the print conditions which optimize printability, structural stability, and print fidelity do not, in most cases, match the UV exposure profiles and intensities that maximize acrylate conversion. This is important because incomplete acrylate conversion can lead to various adverse material qualities that can be detrimental to the structural integrity and long-term stability of the printed part, e.g. reduced green strength or lower chemical stability due to the presence of unreacted acrylate monomer. Issues like unreacted monomers or trapped free radicals that cause these instabilities are commonly solved in planar parts via an additional uniform UV flood exposure. However, this solution is not viable for complex and non-planar structures that are commonly created using additive manufacturing. This non-uniform curing issue should drive the development of tunable and novel resin chemistries that can promote maximum conversion of the acrylate network while optimizing print quality. By utilizing alternative radical initiation mechanisms, e.g. that enable dark or thermal cure, such novel resin chemistries could optimize additive manufacturing print quality for acrylate-based materials.

After investigating the various parameters influencing acrylate network formation and conversion, the samples were then subjected to the sequential thermal cure (**Chapter 5**). The most important finding of this study is that the T_g and flexural strength, strain-to-failure, and toughness values were not significantly altered by varying the acrylate content in the resin formulation. This highlights the versatility of a wide range of resin formulations that can be print-optimized in order to achieve the desired print properties, i.e. green strength, but reliably give similar mechanical properties after the final thermal cure. This is extremely valuable in AM where the same printed part can be printed using varying compositions and print conditions without the fear of sacrificing ultimate thermomechanical properties. For example, a complex part requiring a high green strength to maintain print fidelity would require a high acrylate composition. However, both the complex and simple part would have similar thermomechanical properties after the sequential thermal cure profile.

Having studied the influence of resin formulation and cure parameters on the formation and properties of independent IPNs, the next step was to develop dual-purpose rheology modifiers by functionalizing fillers and investigate the influence of functionalized fillers on IPN network formation (**Chapter 6**). Unexpectedly, the functionalized fillers did not significantly impact the cure kinetics, network formation, or thermomechanical properties of the composites. This was primarily attributed to the poor dispersion of the functionalized fillers in the resins. These findings show that the fillers need to have improved dispersion or have a greater silane grafting density in order to significantly impact the rheology or thermomechanical properties of the composites.

Initially, the ultimate goal of the filler work was to develop dual-functionalized particles, functionalized with both epoxy and acrylate functional groups, and see what impact linking the two polymer networks would have on IPN properties. However, due to the minimal impacts on cure kinetics or mechanical properties found for the monofunctionalized fillers and the difficulty of accurately characterizing functionalization and conversion of dual-functionalized fillers, we instead investigated heterobifunctional monomers (Chapter 7). The most important finding of this section is that connecting the epoxy and acrylate network and forming an interconnected IPN did not have a significant impact on the thermomechanical properties of the fully cured samples for this epoxy/acrylate system. One possible reason for the minimal influence is that the acrylate network and epoxy network are both highly crosslinked, high modulus, thermosets and the addition of additional internetwork chemical crosslinks by the hybrid monomer does not significantly add to the crosslink density. These theories could be tested by using a different epoxy/acrylate dual-cure system where the epoxy and acrylate have significantly different backbones that will result in different thermomechanical properties for the acrylate vs epoxy networks. In such a system it may be easier to create measurable differences in the performance due to internetwork crosslinking by a hybrid monomer.

This thesis work has demonstrated that, while resin composition and cure profile influences acrylate network formation within an IPN, the bulk material properties of the fullycured IPN are relatively independent of composition for these highly crosslinked resin systems. Furthermore, the addition of functional fillers or hybrid monomers does not strongly influence the resulting IPN formation. In these dual-cure systems, the properties of the cured sequential IPN are primarily dependent on the acrylate and epoxy resins used and the type of networks (i.e. highly crosslinked) that they form. If the base thermoset components formed networks with a lower crosslink density than the components used in this thesis, then the resulting network formation and mechanical properties might be more sensitive composition changes or the addition of hybrid monomers. Depending on the overall application, it might be more desirable to use an IPN system that is not sensitive to compositional changes where the changing compositions enable a broad printability range but have similar final mechanical properties. In contrast, for applications where tunable final properties are important, it would be more advantageous to use a different IPN system that is more sensitive to compositional changes or cure profile.

8.2 Future work

This section explores several avenues for future research that would benefit the additive manufacturing DIW community as well as probe further into understanding the cure kinetics and IPN formation of dual-cure thermoset resins.

8.2.1 Different epoxy/acrylate dual-cure systems

Chapter 5 investigated the influence of different thermal cure profiles on the homogeneity of an independent IPN network, while **Chapters 6** and **7** investigated the influence of functionalized fillers and heterobifunctional monomers on the formation of independent and interconnected IPNs, respectively. While the resin system used in each chapter varied slightly, they all used the same epoxy (EPON 828) and used acrylates having similar backbones as EOPN 828. The theory behind this was that the similar backbones would aid in miscibility. However, this made differentiating phases extremely difficult. AFM was unsuccessful due to similar moduli

values. SEM was unsuccessful due to non-selective etching chemicals. SAXS was also unsuccessful due to similar backbones.

Therefore, acrylates having a different backbone than EPON 828 should be investigated in order to more clearly differentiate phases and IPN homogeneity. Multifunctional acrylates would also be an interesting study as they would form drastically different networks and possibly interact more with the functionalized fillers due to more interactive sites.

Another interesting study would be to use epoxy-acrylate dual cure systems that are known to phase separate and investigate whether heterobifunctional monomers could mitigate the phase separation. This would also require the acrylate and epoxy monomers to have significantly different backbones. However, the hybrid monomer could share a similar backbone to either the acrylate or the epoxy in order to enhance miscibility.

8.2.2 In situ print pressure monitoring

The rheology (**Chapter 6**) and cure kinetics (**Chapter 4**) of different resin formulations can differ significantly depending on the resin composition and filler types, and different printer parameters such as UV light intensity, print pressure, pump ratio, and print speed may be required to print different formulations. Changes in resin types and print parameters can require laborious re-optimization to obtain high quality final parts. One approach to reduce the time needed for process optimization is the development of in-situ process monitoring. In-situ process monitoring can be used to more rapidly optimize print parameters during a single print session or to identify changes in properties and flag a process issue such as clogging due to fillers or UV cure propagation up the print tip. Pressure monitoring offers a method to correlate printing parameters with mechanical properties via measuring changes in extrusion pressure during the print. Five different resin systems are worth investigating to start with. Resin 1 should be a dual-cure epoxy-acrylate resin where the change in pressure is monitored as the *in situ* UV intensity is varied. It is anticipated that as the intensity increases, the pressure would increase due to back-cure or clogging at the tip of the extrusion nozzle. This resin can also serve a dual-purpose where it is extruded at different temperatures. The syringe can be heated from room temperature to 80°C. As the temperature increases, the pressure should decrease due to a drop in viscosity until the resin begins to cure within the syringe. Resin 2 should be an epoxy system with a short pot life. As the resin cures within the syringe, the pressure should increase until extrusion becomes impossible. Resin 3 should be an epoxy system with a long pot life, to compare to the short pot life resin. Both resins will be extruded for the same amount of time while investigating the differences in extrusion pressure and mechanical properties. Correlating the changes in print pressure to mechanical properties enables the ability to streamline resin selection and processing parameters in order to achieve desired properties in an effective manner.

8.2.3 Modeling cure kinetics

To complement the findings in **Chapter 4** & **Chapter 5**, molecular dynamics of the acrylate cure kinetics as a function of *in situ* print intensity and exposure profile can be used to further understand the network formation and resulting green strength of the acrylate network in the dual-cure IPN [1-4]. The UV-DSC cure kinetics and conversion data of the acrylate network (found in **Chapter 4**) could be combined with molecular dynamics modeling in order to correlate and predict the influence of UV intensity and exposure profile on the acrylate polymerization process, crosslink density, and resulting total conversion of the network [1-3]. Similar molecular dynamics modeling has been utilized to determine the effect of cross-linkers [5] and conversion rate [4] on the crosslink density and thermomechanical properties of DGEBA epoxies.

Additionally, modeling could allow for kinetic and conversion estimates of other systems, such as multifunctional acrylates or methacrylates vs. diacrylates [3].

Atomistic modeling can also be utilized to explore phase behavior and compatibility of polymer blends, and how changes in chemical structure may alter phase behavior [6, 7]. Applying such modeling techniques would be beneficial in understanding which IPN systems may phase separate during simultaneous or sequential polymerization [8]. Modeling can also aid in understanding the influence of composition and cure profile on phase separation in the UV + thermally cured IPN [9]. Utilizing molecular dynamics simulation, the radial distribution function and change in free volume as a function acrylate network formation and epoxy network formation could be estimated [10]. This would allow for estimating material properties, e.g. green strength for structural stability, fully cured modulus, T_g , etc., of the epoxy-acrylate dual-cure IPN as a function of resin formulation, *in situ* print intensity, and thermal cure profile. Utilizing modeling would allow for a better understanding of how cure kinetics and conversion influence the IPN network formation. Modeling could also be used to narrow down and better inform which formulation and what network conversion would result in a homogeneous microstructure and ideal mechanical properties.

8.2.4 Print fidelity

Chapter 4 briefly investigated the print fidelity of high aspect-ratio walls as a function of resin formulation and *in situ* UV print intensity. The high aspect-ratio walls gave information regarding the conditions necessary to mitigate sagging or leaning of a complex structure under its own weight. Additionally, shrinkage of the acrylate network can be measured by the differences in actual dimensions versus the target wall dimensions. However, printing a vertical wall structure does not give information regarding the ability to print overhangs or spans over

unsupported space. The vertical wall also does not provide information on the structural integrity of the part at varying resolutions (i.e. bead widths).

While no ASTM standard currently exists for determining the print fidelity of AM printed parts, there are an abundance of readily available CAD designs that can be used to determine print fidelity. One CAD structure is shown in Figure 8-, where the limits of each resin formulation can be tested as a function of print intensity by printing overhangs of varying angles, spans of different lengths, features of assorted sizes, and shapes of varying complexity [11, 12]. Using a more common metric to determine the print fidelity allows for a more direct comparison between the properties of each resin as a function of formulation and print conditions. The fidelity of overhangs and spans should be investigated after the acrylate network has formed in the UV cure step to determine structural stability as a function of acrylate conversion and green strength. These should also be remeasured after the thermal cure to determine the degree, if any, to which the softening of the acrylate network during the thermal cure effects the overall structural integrity of the print. The resolution of the fine features and complex shapes should be measured post UV cure and post thermal cure to determine if any shrinkage occurred during the acrylate network formation.



8.2.5 Network Theory & IPN Formation

A more in-depth investigation regarding gelation theory and swollen modulus theory and how they affect the formation of the acrylate network in a dual-cure sequential IPN [13]. Specifically, the gel point and swollen modulus at different extents of acrylate conversion could be investigated in order to understand network formation and phase separation of the fully cured IPN. It was theorized that during the sequential thermal cure, which occurs for the UV in situ print + flood cure samples, there are residual trapped epoxy monomers within the crosslinked acrylate network as well as surrounding the acrylate network. Therefore, during the thermal cure, phase separation results from the epoxy curing around the acrylate network with minimal penetration. At higher cure temperatures the phase separation is mitigated because the increased temperature allows the trapped epoxy monomers within the acrylate network to diffuse and bond to the epoxy outside the pre-formed acrylate network. However, it is also possible that the formed acrylate network can only support so much epoxy swelling, which then causes the excess epoxy resin to be expelled from the network and cause phase separation. In order to support or reject the latter argument, experiments measuring the influence of the Flory-Huggins solubility parameter and molecular weight between crosslinks at equilibrium swelling should be investigated for each formulation.

The theoretical modulus of a swollen gel can be calculated by the following equation:

$$\mathbf{E} = \boldsymbol{\varphi}^{1/3} (\boldsymbol{\rho}^* \mathbf{R}^* \mathbf{T}) / \mathbf{M}_c$$

Where φ is the volume fraction of the formed network, ρ is density, R is the gas constant, T is the temperature where the modulus is being measured at, and M_c is the molecular weight between crosslinks. The density of the gel could be measured using helium pycnometery or Archimedes density measurements. M_c could by calculated using the equation: $3RT\rho/E_r$, where T is the temperature where the minimum storage modulus rubbery modulus (E_r) occurred [14]. However, it is worth noting that the determination of M_c is generally inaccurate for free-radical polymerized networks due to the large fluctuations in network density and network inhomogeneity [15, 16]. The calculation of M_c generally assumes that there is a Gaussian distribution of the polymer conformation at equilibrium. For the resin system used in this thesis, there is a potential for a non-Gaussian chain distribution due to the *in situ* pulsed UV exposure or IPN network formation. This difference will cause a deviation in the results compared to theory. Another approach is to consider the acrylate network as a swelled network, and to determine M_c by applying the Flory-Rehner equation: $[ln(1-\phi_2)+\phi_2+\chi\phi_2^2]=\rho_2V_1M_c(1-2M_c/M_2)(\phi_2^{0.33}-\phi_2^2)$. This would entail conducting a series of equilibrium swelling experiments similar to those done by Sen et al.[17]. However, it is assumed that the system is not at equilibrium with the epoxy, therefore the results may be skewed. Additionally, an accurate value of the Flory-Huggins parameter would need to be obtained for each composition investigated.

While the value of the Flory-Huggins interaction parameter (χ) is well known for many polymer-solvent systems, chi is not well known for epoxy-acrylate systems because χ can change as a function of composition. The miscibility between the epoxy and acrylate at a given temperature, pressure can vary based on polymer concentration and network structure(branched vs. linear) [18, 19]. One way to begin the investigation of χ would be to choose a linear acrylateepoxy system, and establish a binary phase diagram, with the understanding that the crosslinked networks may have differing χ values. A correct χ value needs to be established for the dual-cure epoxy-acrylate system in order to correctly calculate M_c using swelling experiments.

The Flory-Stockmayer equation can be applied to determine when a crosslinked network will gel depending on the functionality of the reactants. In typical step-growth mechanisms, gelation coincides with a significant decrease in the conversion rate, however in free-radical polymerization mechanisms, the turnover in the rate of conversion occurs after gelation. Therefore, in acrylate polymerization, deceleration occurs after gelation, and propagation can continue after gelation [20]. This results in increased polymer network formation/conversion post-gelation. It is also important to note that these equations are also limited in use in dual-cure formulations due to the presence of the unreacted epoxy monomers. The epoxy monomers dilute and plasticize the acrylate network during its formation, therefore changing the cure kinetics of the sequential or simultaneous IPN system [21-23].

By successfully determining the values of M_c and chi, the appropriate swelling conditions that result in a homogeneous IPN network can be determined. This will allow for correlations between print parameters and resin formulation with acrylate network structure and resulting IPN formation. Therefore, relations between the acrylate network formation and resulting green strength of the printed part can be better understood. Additionally, by understanding the acrylate network formation and understanding how M_c varies for differing UV cure conditions, SEM or TEM could be done on the printed sample to investigate the morphology as a function of M_c .

8.2.6 Additional Hybrid monomers

To complement the findings in **Chapter 7**, it is worth exploring the effects of other heterobifunctional monomers on the material properties of interconnected IPNs. Monomers with varying chain lengths and backbones should be investigated. For example, polyethylene glycol epoxy-acrylate (

Figure 8-1) would be an interesting heterobifunctional monomer given its long backbone. Though the addition of GMA or BPA did not significantly influence the mechanical properties of the composite, it is hypothesized that this would result in increased toughness and elongation than the GMA or BPA hybrids due to the decreased crosslink density and less rigid backbone.



Figure 8-1: Poly(ethylene glycol) epoxy-acrylate hybrid monomer

8.2.7 Investigate UV/thermal dual-cure rheology

Chapter 4 gave an in-depth study on correlating acrylate cure kinetics with green strength. Throughout the remainder of this thesis, acrylate cure kinetics studied via UV-DSC and the epoxy cure kinetics studied via isothermal measurements. However, there is not an in-depth investigation on the cure kinetics/network formation of the IPN throughout the entire formation. Nor is there a correlation of acrylate conversion and onset of gelation. The network formation and cure kinetics of the acrylate during UV exposure and the epoxy during thermal exposure can be studied via UV rheometry.

The acrylate network can be measured during a programmed exposure profile and intensity using the same light source used for UV-DSC. This enables a direct correlation between acrylate cure kinetics and conversion measured via UV-DSC and the cure kinetics, network formation, modulus measured on the rheometer. Additionally, the advanced Peltier system allows for the UV-cured parallel plates to then be heated so that the rheology during the formation of a dual-cure IPN can be investigated. This characterization technique can aid in the understanding of how cure conditions impact the formation and homogeneity of the resulting IPN.

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APPENDIX:

Table SI-1: Intensity measurements of various UV-light sources								
Intensity			Power %					
Device	(mW/cm ²)	1	5	10	20	40	80	
Dual UV probes	Intensity @ 365nm	1.2	6.9	14.3	29	57.3	106.3	
Bulk UV cure light	Intensity @ 365nm	5.7						
UV-DSC radiometer	Intensity @ 365nm	5.3	33.4	85.9	161.1	275.9	364.8	
UV-DSC DSC*	Intensity	9	37.0	83.0	170.0	362.0	637.0	

Radiometer Measurements

*UV-DSC DSC intensity measurements are measured by the DSC itself, where the DSC converts heat generated during exposure into an intensity value. Intensities less than 10 mW/cm² delivered to the DSC cell are not able to be accurately measured and are required to be measured via an external radiometer mimicking the UV-DSC set-up [1].



Chapter 3: Investigation of photoinitiators to be used in resins throughout this thesis.

Figure SI-1: Photoinitiators investigated to use in this thesis

Chapter 3: Comparisons of 'Print cure only' and 'UV print + flood cure' modulus values for different photoinitiators and different photoinitiator weight percent loadings. Irgacure 651 was used for the AMT formulations (Chapters 4 & 5) while TPO was used for the JWK resins (Chapters 6 & 7).



Figure **SI-2**: Room temperature green strength of AMT formulations using different photoinitiators and different photoinitiator wt%. Standard deviation is between 2-3 samples.



Figure **SI-3**: Tan delta of AMT formulations using different photoinitiators and different photoinitiator wt%. Standard deviation is between 2-3 samples.

Chapter 4 & 5: Gel fraction measurements of 15 and 50 wt% acrylate formulations at various stages of cure. The procedure followed that of Park *et al.*[2] and the toluene solution was replaced every day for a total of 3 extractions. The 'print + flood' cure gel fraction were expected to match the acrylate wt % and 5 wt% silica filler within the formulation. Both formulations show greater than expected gel fractions, indicating the possibility that some epoxy resin must have been trapped within the acrylate network.



Figure SI-4: Gel Fraction measurements of 15 wt% and 50 wt%

Chapter 5: variable temperature DMA results for 'SC' and 'SC + 2hrs 250°C' molded 0 wt% and 100 wt% acrylate samples. The T_g for each system is taken as the peak in tan delta during the heat cycle. The T_g values decrease for the 'SC + 2hrs 250°C' due to IPN coalescence.



Figure SI-5: Variable temperature DMA measurements of 'SC' molded 0 wt% and 100 wt% acrylate with 5 wt% SiO₂ filler



Figure SI-6:Variable temperature DMA measurements of 'SC + 2hrs 250°C' molded 0 wt% and 100 wt% acrylate with 5 wt% SiO₂ filler

Chapter 5: variable temperature DMA results for the varying acrylate content at different thermal profiles. The cure temperature of 250°C results in obvious IPN homogeneity as dictated by the narrowing of the peaks compared to the 200°C peaks.





Figure SI-7: Variable temperature DMA results for different thermal cure profiles for 15 wt%, 30 wt%, and 50 wt% acrylate IPNs

Chapter 6: background on Sol-gel SiO₂

Sol-gel silica is a special type of silica that starts as a one-phase solution that transitions into a two-phase system of solid silica, with either desired functional groups or surface hydroxyls, and solvent. The -OH groups on the formed silica react with organo-silanes to create a hydrophobic surface that disperse more easily within hydrophobic polymers [3]. The formed particles are typically 8-50 nm and some are able to be homogeneously dispersed within a polymer matrix up to 60 wt% [4]. For epoxy composites, specifically, the unsaturated free bonds and surface hydroxyls on the silica surface are believed to react with the epoxy resin and improve interfacial bonding [5]. At loadings of 40 wt%, a significant increase in viscosity is seen and Adebahr et al. found a 90% increase in fracture toughness and modulus of silica/epoxy composites [4, 5]. Similarly, at much lower wt%, Zhang et al. found an increase in storage modulus with increased wt%. The nanosilica was believed to suppress macromolecular mobility of the polymer, which reduced the elongation at break but increased stiffness and toughness of the composite [6]. The investigation of sol-gel silica on the cure kinetics and microstructure of epoxy composites was investigated by Rosso *et al.*, where a higher volume percent of silica led to a higher conversion of the epoxy [7]. This resulted from the formation of an amino-rich interphase region surrounding the particles that ehanced the homopolymerizatin of the epoxy and gave a higher degree of crosslinking compared to the neat epoxy. Going one step further, Zheng et al. found that in a phenolic amine/DGEBA system with nanosilica, slower heating rates reached full converison faster than fast heating rates, and that a higher extent of cure occurred at higher temperatures [5]. In addition to mechancial properties, the thermal properties of sol-gel silica/epoxy nanocomposites have been investigated. For example, Hernández-Padrón et al. found that the degradation temperature increases with increasing sol-gel silica content [8]. While sol-gel silica offers the creation of small particle sizes with very narrow size distributions, there are some drawbacks. One drawback for use with aqueous polymer dispersions is that ethanol, or another

alcohol, is typically used to control the hydrolysis and condensation reactions, which compromises the stability of aqueous polymer dispersions [9].

Chapter 6: AFM topography, adhesion, and modulus mapping of standard cure were conducted to probe the phase separation and phase domain sizes on two formulations (Figure **SI-8** and Figure **SI-9**). AFM was conducted by Ana Baca (Materials Characterization Dept. 1819) on a Bruker Dimension Icon AFM in quantitative nanomechanical mapping. 10wt% MMT resin (single T_g homogeneous) and unfilled resin (phase separated via presence of two T_g 's). These images suggest the moduli of the epoxy and acrylate networks are too similar and that phase separation is not detectable using AFM.



Figure SI-8: AFM images of 'SC' 10wt% MMT in a 2:1 EPON:BPA dimethacrylate resin



Figure SI-9:AFM images of 'SC' unfilled 2:1 EPON828:BPA dimethacrylate resin



Chapter 6: Zoomed out UV-DSC measurements for silylated fillers

Figure SI-10: UV-DSC measurements at 80 mW/cm² of functionalized and unfunctionalized fillers

Chapters 5 & 6: SAXS measurements were used to probe for phase separation and domain size of the resins (Figure **SI-11**). SAXS was conducted at ORNL by Samantha Rinehart (Kansas City National Security Campus, Materials Engineering D896). JWK 1-56-2_150C cured is from Chapter 6 and is an unfilled standard cure sample consisting of EPON828 and BPA dimethacrylate. AMT 1-38-1 is from Chapter 5 and is a 50 wt% acrylate standard cure sample and 50 wt% acrylate and standard cure + 2 hrs 250°C sample. The decreased scattering in the JWK unfilled sample is due to the lack of filler material in the resin. At the length scale of SAXS, which is 1-60nm, SAXS is measuring the interaction between the filler and the resin matrix, not the domains of the possible different phases within the matrix. If the domains were larger than 60nm, they would not be detected using SAXS and other methods would have to be utilized such as USAXS or VSAXS.



Figure SI-11: SAXS measurements of 'SC' and 'SC + 2hrs 250°C' 50 wt% acrylate and 'SC' unfilled formulations

Chapter 6: TGA-MS of silylated fillers



Figure SI-12: TGA-MS on the GPS- SiO_2 at an 800°C isotherm

To investigate this hypothesis, an isothermal TGA-MS was performed at 800°C for 1000 minutes to investigate whether the ion current plateaued after a certain amount of time at a given temperature. It can be seen in Figure **SI-12** that after 300 minutes, the ion current for the epoxy species plateau and begins to decrease. This occurs because there is a finite amount of grafted silane that is decomposing over time. This indicates that the m/z values of 43 and 57 and are not background noise but they represent the GPS silane decomposition species because there is a finite amount of grafted material.



Figure SI-13:TGA-MS data on the GPS-MMT

The TGA-MS data for GPS-MMT is shown in Figure **SI-13**. In general, most of the weight loss is from water (blue line), while the other major peaks are from the epoxy functional groups on the silane (green and orange lines). In the 200-600°C temperature range that is associated with measuring the silane grafting density, the TGA-MS shows that the weight loss is coming from water and the grafted and intercalated epoxy silane. These results confirm that MMT was successful functionalized with the GPS silane.



Figure SI-14: TGA-MS data on MPTS- SiO_2

The TGA-MS data for MPTS-SiO₂ is shown in Figure **SI-14**. Within the 60-730°C temperature range, most of the weight loss comes from water and fragments associated with the methacryl silane. The m/z values of 41, 69, 71, and 175 are specific to the methacryl silane, and the m/z of 18 is water. These results confirm that SiO₂ was successful functionalized with the MPTS silane.



Figure SI-15:TGA-MS data on MPTS-MMT

The TGA-MS data for MPTS-MMT is shown in Figure **SI-15**. In the 200-600°C temperature range that is associated with measuring the silane grafting density, the TGA-MS shows that the weight loss is coming from water and the grafted and intercalated methacryl silane. The m/z values of 41 and 71 are specific to the methacryl silane, and the m/z of 18 is water. These results confirm that MMT was successful functionalized with the MPTS silane.


Figure SI-16: TGA-MS data on HMS-SiO₂

The TGA-MS data for HMS-SiO₂ is shown in Figure **SI-16**. Within the 60-730°C temperature range, most of the weight loss comes from water, carbon monoxide, and fragments associated with the hexyltrimethoxysilane. These results confirm that SiO_2 was successful functionalized with the HMS silane.



Figure SI-17:TGA-MS data on HMS-MMT

The TGA-MS data for HMS-MMT is shown in Figure SI-17. In the 200-600°C

temperature range, most of the weight loss comes from water, carbon monoxide, and fragments associated with the hexyltrimethoxysilane.

Chapter 6: BPA glycerolate dimethacrylate versus ethoxylated BPA dimethacrylate in the 30 wt% Acrylate formulation from Chapter 5.

Print + flood cure					
Sample	Storage Modulus MPa				
Ethoxylated BPA dimethacrylate	47.9 ± 3.6				
BPA dimethacrylate	81.6 ± 6.4				
'SC'					
Sample	Storage Modulus MPa				
Ethoxylated BPA dimethacrylate	511.4 ± 11.9				
BPA dimethacrylate	844.0 ± 62.9				
'SC'					
Sample	Tan Delta (Tg) °C				
Ethoxylated BPA dimethacrylate	183.1 ± 1.8				
BPA dimethacrylate	200.9 ± 3.4				

Figure **SI-18:** Room temperature storage modulus values of 'Print + flood cure' and 'SC' and glass transition temperature for the 'SC' of 30wt% acrylate (ethoxylated BPA dimethacrylate versus BPA glycerolate dimethacrylate) the formulations used in Chapter 5 (1:1 mol:mol diepoxy:triepoxy)



Chapter 6: Variable temperature DMA measurements of 'SC' JWK samples.

Figure SI-19: Glass transition temperatures of 'SC' MPTS-SiO2 and MPTS-MMT



Figure SI-20: Glass transition temperatures of 'SC' GPS-SiO2 and GPS-MMT





Figure SI-21:Thermal DSC extent of cure measurements of 'SC' functionalized and unfunctionalized SiO₂ formulations



Figure SI-22:Thermal DSC extent of cure measurements of 'SC' functionalized and unfunctionalized MMT formulations

Chapter 6: DSC extent of cure measurements for 'SC + 2hrs 220°C'samples :

The DSC extent of cure measurements on the standard cure 'SC' samples cured at a maximum temperature of 150°C had exotherms after the first heat cycle, which suggests that the 'SC' samples were not fully cured (see Appendix I). Therefore, an additional higher temperature post-cure of 2hrs at 220°C was conducted. DSC was then utilized to measure the extent of cure on the 'SC + 2hrs 220°C' samples. The results are shown in Figure **SI-23** and Figure **SI-24**. All samples treated with the 220°C post cure have no measurable exotherm, indicating that the samples are fully cured or have a high enough conversion such that any additional reaction is not measurable via DSC.



Figure **SI-23**: Thermal DSC extent of cure measurements of 'SC + 2hrs 220°C' functionalized and unfunctionalized SiO₂ formulations



Figure SI-24: Thermal DSC extent of cure measurements of functionalized and unfunctionalized MMT formulations

Continuous		Pulsed			
Formulations	% Conversion	St.Dev	Formulations	% Conversion	St.Dev
No filler	82.0	10.5	No filler	68.2	4.6
5wt% SiO ₂	108.3	3.3	5wt% SiO ₂	71.0	1.3
5wt% HMS SiO ₂	108.2	0.6	5wt% HMS SiO ₂	64.6	-
5wt% GPS SiO ₂	110.2	6.1	5wt% GPS SiO ₂	70.2	-
5wt% MPTS SiO ₂	104.0	9.3	5wt% MPTS SiO ₂	66.4	2.3
10wt% SiO ₂	105.4	1.4	10wt% SiO ₂	71.8	2.2
10wt% GPS SiO ₂	108.4	1.8	10wt% GPS SiO ₂	71.7	-
10wt% MPTS SiO ₂	106.2	4.3	10wt% MPTS SiO ₂	63.9	0.5
Formulations	% Conversion	St.Dev	Formulations	% Conversion	St.Dev
No filler	82.0	10.5	No filler	68.2	4.6
5wt% MMT	103.2	2.8	5wt% MMT	72.0	1.9
5wt% HMS MMT	101.3	0.6	5wt% HMS MMT	64.9	-
5wt% GPS MMT	108.1	6.1	5wt% GPS MMT	72.2	0.9
5wt% MPTS MMT	98.2	9.0	5wt% MPTS MMT	59.5	1.3
10wt% MMT	98.1	9.3	10wt% MMT	69.6	1.8
10wt% GPS MMT	77.7	0.5	10wt% GPS MMT	71.7	-
10wt% MPTS MMT	90.3	6.5	10wt% MPTS MMT	64.1	2.3

Chapter 6: UV-DSC pulsed and continuous exposure total conversion values.

Figure SI-25: Total conversion values for filled systems for pulsed and continuous UV-DSC exposures

Chapter 6: SEM/EDS of 'SC' samples to investigate dispersion and agglomeration of functionalized and unfunctionalized fillers. Energy-dispersive X-ray spectroscopy (EDS) was conducted on the 10 wt% GPS-SiO₂ in order to investigate the dispersion of the MMT within the fractured surface (Figure **SI-26**). The fumed silica is composed of silicon (blue) and oxygen (green) and the polymer matrix is made up primarily of carbon (red) and oxygen (green). The lighter areas shown in the secondary SEM image are silica agglomerates. Similarly, agglomeration was not observed in unfunctionalized MMT composites, however agglomeration was found to occur in functionalized MMT composites.



Figure SI-26: SEM/EDS on 'SC' 10 wt% GPS-SiO2

SEM/EDS was conducted on the 5wt% MMT and 5 wt% GPS-MMT samples in order to confirm that the light-colored features in SEM were agglomerates of the GPS-MMT within the IPN polymer matrix. Figure **SI-27** and Figure **SI-28** are the EDS/SEM images of unfunctionalized and GPS-functionalized MMT, respectively, where the clay is predominately silicon (blue), aluminum (purple), and oxygen (green) and the polymer matrix is mainly carbon (red) and oxygen (green). The unfunctionalized MMT EDS images (Figure **SI-27**) show

homogeneous dispersion of the clay within the matrix and also indicates similar clay size distribution. However, the GPS-MMT EDS images (Figure **SI-28**) show clay agglomerates.



Figure SI-27: SEM/EDS on 'SC' 5wt% MMT



Figure SI-28: SEM/EDS on 'SC' 5wt% GPS-MMT



Chapter 6: ImageJ analysis of particle size distribution of SEM/EDS images of 5 wt% MMT and 5 wt% GPS MMT

Figure SI-29: ImageJ analysis of particle size distribution of SEM/EDS images of 5 wt% MMT and 5 wt% GPS MMT

Chapter 7: MS of hybrid monomer to determine purity

To further analyze the purity of the hybrid molecule, liquid chromatography (LC) was performed by Jessica Kustas (Sandia National Laboratories, Dept. 1852 Materials Science). Liquid chromatography was performed with a photodiode array (PDA) detector and mass spectrometry (MS) detection was performed using an Aquity UPLC and a Xevo TQ-S micro tandem quadrupole MS (Waters Corp, Waltham, MA). Electrospray ionization was utilized in positive mode. PDA data was collected between 210 and 400 nm (Figure **SI-30** - Figure **SI-32**). UPLC conditions: ACQUITY UPLC HSS T3 1.8µm, mobile phases A2 (water 0.1% formic acid) and B2 (methanol), flow rate 0.3 mL/min, injection size 1.0 microliter. Hold 1 min at 50% B2, ramp 50% B2 to 95% B2 at 5 minutes, hold 2 min at 95% B2, to 50% B2 at 8 minutes. PDA conditions: scan 210-400 at 20 Hz resolution 1.2 nm.



Figure SI-31: PDA signal versus retention time for BPA glycerolate diacrylate analyses



Figure SI-32: PDA signal versus retention time for BPA hybrid analyses



Figure SI-33: MS TIC Signal versus retention time for EPON 828, BPA glycerolate diacrylate, and BPA hybrid analyses

The peaks at 3.38, 4.02, 4.12, and 5.37 in the BPA hybrid closely match the MS total ion current (TIC) signal versus retention time for EPON 828. The peak at 4.69 matches that of the BPA diacrylate. The combined NMR and LC results show that the hybrid contains both epoxy and acrylate functional groups and that the hybrid is mostly pure with little <10% diepoxy or diacrylate impurities.

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VITA Jessica W. Kopatz

EDUCATION

The Pennsylvania State University, University Park, PA

Ph.D. Materials Science & Engineering, Fall 2016 - Spring 2021

B.S. Materials Science & Engineering, Fall 2012 - Spring 2016

Minor in Psychology

PUBLICATIONS

- 1. **Kopatz, J.**, Unangst, J., Cook, A., Appelhans, L. "Compositional Effects On Cure Kinetics, Mechanical Properties and Printability Of A Dual-Cure Epoxy/Acrylate Resin System for DIW Additive Manufacturing". Additive Manufacturing. 2021
- Kopatz, J., Unangst, J., Cook, A., Appelhans, L. "Compositional and Cure Profile Impacts on IPN formation And Mechanical Properties Of A Dual-Cure Epoxy/Acrylate Resin". Polymer. 2020 *In progress*
- 3. **Kopatz, J.**, Cook, A., Appelhans, L. "Interconnected IPN Of A Dual-Cure Epoxy/Acrylate Resin System Using Heterobifunctional Monomers". Macromolecules. 2020. *In progress*
- 4. Saad Ahmed, Jonathan Hong, Wei Zhang, **Jessica Kopatz**, Zoubeida Ounaies, and Mary Frecker "Various design approaches to achieve electric field-driven segmented folding actuation of electroactive polymer (EAP) sheets". Conference on Behavior and Mechanics of Multifunctional Materials and Composites XII. Denver, CO Date: MAR 05-08, 2018.

CONFERENCE PRESENATATIONS DURING GRADUTE STUDIES

- 7 Contributed oral presentations as a firsts author (6 national and 1 international)
- 5 Contributed poster presentations as a first author