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Developing and Characterizing a Rapid Prototyping Stereo-Lithography Machine to Produce Interpenetrating Polymer Network Systems

Lena R. Butterfield
University of Nebraska-Lincoln, lena.butterfield@gmail.com

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DEVELOPING AND CHARACTERIZING A RAPID PROTOTYPING STEREO-
LITHOGRAPHY MACHINE TO PRODUCE INTERPENETRATING POLYMER
NETWORK SYSTEMS

by

Lena R. Butterfield

A THESIS

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Rapid prototyping and interpenetrating network systems (IPNs) ideas and technologies were studied in order to develop a rapid prototyping machine capable of producing IPNs. This work was done as collaboration between the University of Nebraska-Lincoln and the University of Rouen, France, and is part of a project of controlling material property distribution by means of gradient IPN production within a rapid prototyping machine.

A standard stereo-lithography rapid prototyping (RP) machine was built and then modified for the purpose of producing an IPN system composed of an acrylic component, bisphenol A propoxylate diacrylate (BPA-PDA) and an epoxy component, 3,4 epoxycyclohexylmethyl 3,4 epoxycyclohexane carboxylate (ECH). The acrylic and epoxy based system was produced within the machine by photo curing followed by thermal post curing. Various weight compositions of the IPN system were produced and characterized.

Control IPN systems were produced with the same materials and compositions as the samples made in the RP machine. These were bulk samples photo cured under a polychromatic light source, and then analyzed by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), atomic force microscopy (AFM), dynamic mechanical testing (DMA), and
tensile testing. The results show a change in the thermal stability with composition, a single glass transition temperature that changes with composition, homogeneous phase distributions, and changes in mechanical properties. These are consistent with the expectations that the system is a true IPN at the molecular level.

From TGA, DSC, AFM, and DMA analysis of the RP machine made system showed similar characteristics to the bulk polymerized IPN system. This includes changes in thermal stability with composition, a single glass transition temperature changing with composition, and observed homogeneous phase distributions. These characteristics follow the same trends as those of the control system, leading to the identification of the system as true IPNs. However, lower glass transition temperatures and thermal stabilities were observed for the samples made within the RP machine.

Lowered thermal stabilities and glass transition temperatures of thermally cured acrylic and epoxy homopolymers, observed in TGA and DSC, reveals that the rapid prototyping machine light source is not as powerful as the light used in the bulk curing, resulting in a similar, but different curing. Yet, it was concluded that the rapid prototyping machine is capable of producing IPN systems but requires increased light source power to increase the curing conversion of the acrylic and epoxy based system.
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Contents

List of Figures ........................................................................................................................................... viii
List of Tables ................................................................................................................................................ x
List of Appendix Figures ............................................................................................................................ xi

1 Introduction ............................................................................................................................................. 1
  1.1 Problem Statement ............................................................................................................................. 1
  1.2 General Approach and Results .......................................................................................................... 2
  1.3 Sequence of Presentation .................................................................................................................... 2

2 Background ............................................................................................................................................. 3
  2.1 Rapid Prototyping Background ........................................................................................................ 3
    2.1.1 Types of Rapid Prototyping ...................................................................................................... 3
    2.1.2 Advances in Rapid Prototyping ................................................................................................. 5
  2.2 Photo Curing Background .................................................................................................................. 7
    2.2.1 Types of Photo Curable Resins .................................................................................................. 7
    2.2.2 Photo curing Applications ......................................................................................................... 9
    2.2.3 Photo Curing Challenges ........................................................................................................... 11
  2.3 Interpenetrating Polymers Network Systems Background .................................................................. 12
    2.3.1 Types of Interpenetrating Polymers ......................................................................................... 13
    2.3.2 IPN Applications ....................................................................................................................... 14

3 IPN System Selection ............................................................................................................................. 16
  3.1 Radical Component ............................................................................................................................ 16
  3.2 Cationic Component .......................................................................................................................... 17

4 Basic Stereo-lithography Machine Development ................................................................................ 19
  4.1 Theory ................................................................................................................................................ 19
  4.2 Design ............................................................................................................................................... 20
  4.3 Testing and Evaluation ....................................................................................................................... 26

5 IPN Stereo-lithography Machine Development .................................................................................. 29
  5.1 Modifications for Acrylic Homopolymer Printing ........................................................................... 29
  5.2 Modifications for Epoxy Homopolymer Printing ............................................................................ 33
  5.3 IPN Stereo-lithography Machine ....................................................................................................... 34
    5.3.1 RP IPN Sample Production Procedure ..................................................................................... 35
6 Future Machine Design .......................................................................................... 38
  6.1 Initial Design Weaknesses ........................................................................... 38
  6.2 Design Changes ......................................................................................... 39
7 IPN Identification Methods ................................................................................. 41
  7.1 Thermogravimetric Analysis ...................................................................... 41
  7.2 Differential Scanning Calorimetry ............................................................... 42
  7.3 Atomic Force Microscopy ........................................................................... 45
  7.4 Dynamic Mechanical Analysis ................................................................... 47
  7.5 Tensile Testing ............................................................................................ 49
8 Procedures for Each Characterization ................................................................. 52
  8.1 Thermogravimetric Analysis ....................................................................... 52
  8.2 Differential Scanning Calorimetry ............................................................... 53
  8.3 Atomic Force Microscopy ........................................................................... 54
  8.4 Dynamic Mechanical Analysis ................................................................... 54
  8.5 Tensile Testing ............................................................................................ 56
9 Results and Discussion ....................................................................................... 57
  9.1 Control Samples ......................................................................................... 57
    9.1.1 Thermogravimetric Analysis ................................................................. 57
    9.1.2 Differential Scanning Calorimetry ........................................................ 62
    9.1.3 Atomic Force Microscopy ...................................................................... 64
    9.1.4 Dynamic Mechanical Analysis ............................................................. 67
    9.1.5 Tensile Testing ..................................................................................... 70
  9.2 RP Samples ................................................................................................ 72
    9.2.1 Thermogravimetric Analysis ................................................................. 73
    9.2.2 Differential Scanning Calorimetry ........................................................ 76
    9.2.3 Atomic Force Microscopy ...................................................................... 78
    9.2.4 Dynamic Mechanical Analysis ............................................................. 81
  9.3 Thermal Cured Samples .............................................................................. 82
    9.3.1 Thermogravimetric Analysis ................................................................. 83
    9.3.2 Differential Scanning Calorimetry ........................................................ 84
10 Summary .......................................................................................................... 86
  10.1 Experimental Analysis .............................................................................. 86
  10.2 Future Work ............................................................................................... 88
References

Appendices

A.1 Linear Displacement per Revolution of Acme Rod ........................................ 94
A.2 Theoretical Curing Time Analysis Example ....................................................... 95
A.3 Control System DSC Curves ........................................................................ 96
A.4 RP System DSC Curves .................................................................................. 113
A.5 Thermally Cured Homopolymer DSC Curves .................................................. 116
A.6 Control System Isothermal DMA Testing ....................................................... 117
A.7 Control System Temperature Sweep DMA Testing ......................................... 120
A.8 RP System Temperature Sweep DMA Testing ............................................... 123
A.9 Control System Combination Sweep DMA Testing ......................................... 125
A.10 Control Sample Stress-Strain Curves .............................................................. 133
### List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Radical curing mechanism [12]</td>
</tr>
<tr>
<td>2</td>
<td>Cationic curing mechanism [12]</td>
</tr>
<tr>
<td>3</td>
<td>IPN schematic [23]</td>
</tr>
<tr>
<td>4</td>
<td>Radical crosslinker; Bisphenol A propoxylate diacrylate.</td>
</tr>
<tr>
<td>5</td>
<td>Radical photo initiator; 2-hydroxy-2-methylpropiophenone</td>
</tr>
<tr>
<td>6</td>
<td>Cationic crosslinker; 3,4 epoxycyclohexylmethyl 3,4 epoxycyclohexane carboxylate</td>
</tr>
<tr>
<td>7</td>
<td>Cationic photo initiator; Triarylsulfonium hexafluoroantimonate</td>
</tr>
<tr>
<td>9</td>
<td>RP system mechanical components</td>
</tr>
<tr>
<td>10</td>
<td>EasyDriver motor driver [33]</td>
</tr>
<tr>
<td>11</td>
<td>Sanguino [34]</td>
</tr>
<tr>
<td>12</td>
<td>Wiring diagram of electronic components</td>
</tr>
<tr>
<td>13</td>
<td>405nm laser, 20mW</td>
</tr>
<tr>
<td>14</td>
<td>SL machine</td>
</tr>
<tr>
<td>15</td>
<td>SL machine vat with partially printed object</td>
</tr>
<tr>
<td>16</td>
<td>10 x 5 x 1 mm block produced in SL machine</td>
</tr>
<tr>
<td>17</td>
<td>SL machine shape complexity testing</td>
</tr>
<tr>
<td>18</td>
<td>LED light source [35]</td>
</tr>
<tr>
<td>19</td>
<td>355 LED light spot size [35]</td>
</tr>
<tr>
<td>20</td>
<td>LED bracket for single polymer curing</td>
</tr>
<tr>
<td>21</td>
<td>Acrylic polymer testing: Exposure time of 30, 60, 90, and 120 seconds from left to right</td>
</tr>
<tr>
<td>22</td>
<td>Epoxy homopolymer testing: Exposure time of 10 minutes resulting in sample size of 5 x 5 x 0.1 mm</td>
</tr>
<tr>
<td>23</td>
<td>Double LED bracket for IPN SL machine</td>
</tr>
<tr>
<td>24</td>
<td>IPN testing in machine</td>
</tr>
<tr>
<td>25</td>
<td>Belt and pulley on cylindrical rod system</td>
</tr>
<tr>
<td>26</td>
<td>Future machine research components</td>
</tr>
<tr>
<td>27</td>
<td>TGA example</td>
</tr>
<tr>
<td>28</td>
<td>DSC example</td>
</tr>
<tr>
<td>29</td>
<td>Determining glass transition temperature</td>
</tr>
<tr>
<td>30</td>
<td>AFM example. Left: topographic image (1μm x 1μm). Right: phase contrast image (1μm x 1μm)</td>
</tr>
<tr>
<td>31</td>
<td>DMA temperature sweep example with a constant frequency of 10 Hz</td>
</tr>
<tr>
<td>32</td>
<td>DMA storage modulus master curve example</td>
</tr>
<tr>
<td>33</td>
<td>Stress-Strain curve example</td>
</tr>
<tr>
<td>34</td>
<td>TGA full degradation curve for non-post cured samples: acrylic/epoxy</td>
</tr>
<tr>
<td>35</td>
<td>TGA close-up degradation curve for non-post cured samples: acrylic/epoxy</td>
</tr>
<tr>
<td>36</td>
<td>TGA degradation curve 90°C post cured samples: acrylic/epoxy</td>
</tr>
<tr>
<td>37</td>
<td>TGA full degradation curve of 150°C post-cured samples: acrylic/epoxy</td>
</tr>
</tbody>
</table>
Figure 38: TGA degradation curve of 150°C post cured samples: acrylic/epoxy.............................. 60
Figure 39: 1st derivative 150°C of post-cured samples: acrylic/epoxy........................................... 61
Figure 40: Glass transition temperature of non-post cured, 90°C post cured, 150°C post cured samples.................................................................................................................... 63
Figure 41: ΔCp of non-post cured, 90°C post cured, 150°C post-cured samples............................ 64
Figure 42: AFM results of acrylic/epoxy composition, 1μm square; Topographical image on left, phase contrast image on right............................................. 65
Figure 43: DMA temperature sweep of control acrylic/epoxy samples at 10 Hz............................. 67
Figure 44: Storage modulus limits with composition at 20°C......................................................... 68
Figure 45: Onset frequency limits for lower and upper modulus limits at 20°C............................... 69
Figure 46: Ultimate stress and strain in 150°C post cured samples.................................................. 71
Figure 47: TGA of machine samples: acrylic/epoxy................................................................. 73
Figure 48: TGA comparison of machine and control IPN samples: acrylic/epoxy............................. 74
Figure 49: TGA comparison of acrylic/epoxy RP and control samples........................................... 75
Figure 50: Tg comparison between RP samples and control samples.............................................. 77
Figure 51: ΔCp comparison between RP samples and control samples......................................... 78
Figure 52: AFM results of acrylic/epoxy compositions, 1μm square; Topographical image on left, phase contrast image on right............................................. 79
Figure 53: DMA temperature sweep of RP acrylic/epoxy samples at 10 Hz................................... 81
Figure 54: DMA temperature sweep of non-post cured acrylic/epoxy RP and control samples................................................................. 82
Figure 55: Mass degradation comparison of thermal and UV curing of epoxy homopolymer................. 83
Figure 56: Mass degradation comparison of thermal and UV curing of acrylic homopolymers................................. 84
List of Tables

Table 1: Linear movement of light source per motor step. .......................................................... 23
Table 2: Acrylic spot diameter with respect to curing times ......................................................... 31
Table 3: Theoretical vs. actual curing time of 1mm thick acrylic samples................................. 32
Table 4: RP IPN samples procedure. ......................................................................................... 36
Table 5: Tg and ΔCp values of samples....................................................................................... 62
Table 6: Mechanical properties of control system. .................................................................... 70
Table 7: Tg and Cp of RP samples in comparison to control samples. ......................................... 76
Table 8: Tg comparison of thermal and UV curing. ..................................................................... 85
List of Appendix Figures

| Figure A-1: | DSC curve of non-post cured 100/0 acrylic/epoxy control sample | 96 |
| Figure A-2: | DSC curve of non-post cured 90/10 acrylic/epoxy control sample | 96 |
| Figure A-3: | DSC curve of non-post cured 80/20 acrylic/epoxy control sample | 97 |
| Figure A-4: | DSC curve of non-post cured 70/30 acrylic/epoxy control sample | 97 |
| Figure A-5: | DSC curve of non-post cured 60/40 acrylic/epoxy control sample | 98 |
| Figure A-6: | DSC curve of non-post cured 50/50 acrylic/epoxy control sample | 98 |
| Figure A-7: | DSC curve of non-post cured 40/60 acrylic/epoxy control sample | 99 |
| Figure A-8: | DSC curve of non-post cured 30/70 acrylic/epoxy control sample | 99 |
| Figure A-9: | DSC curve of non-post cured 20/80 acrylic/epoxy control sample | 100 |
| Figure A-10: | DSC curve of non-post cured 10/90 acrylic/epoxy control sample | 100 |
| Figure A-11: | DSC curve of non-post cured 0/100 acrylic/epoxy control sample | 101 |
| Figure A-12: | DSC curve of 90°C post cured 100/0 acrylic/epoxy control sample | 101 |
| Figure A-13: | DSC curve of 90°C post cured 90/10 acrylic/epoxy control sample | 102 |
| Figure A-14: | DSC curve of 90°C post cured 80/20 acrylic/epoxy control sample | 102 |
| Figure A-15: | DSC curve of 90°C post cured 70/30 acrylic/epoxy control sample | 103 |
| Figure A-16: | DSC curve of 90°C post cured 60/40 acrylic/epoxy control sample | 103 |
| Figure A-17: | DSC curve of 90°C post cured 50/50 acrylic/epoxy control sample | 104 |
| Figure A-18: | DSC curve of 90°C post cured 40/60 acrylic/epoxy control sample | 104 |
| Figure A-19: | DSC curve of 90°C post cured 30/70 acrylic/epoxy control sample | 105 |
| Figure A-20: | DSC curve of 90°C post cured 20/80 acrylic/epoxy control sample | 105 |
| Figure A-21: | DSC curve of 90°C post cured 10/90 acrylic/epoxy control sample | 106 |
| Figure A-22: | DSC curve of 90°C post cured 0/100 acrylic/epoxy control sample | 106 |
| Figure A-23: | DSC curve of 150°C post cured 100/0 acrylic/epoxy control sample | 107 |
| Figure A-24: | DSC curve of 150°C post cured 90/10 acrylic/epoxy control sample | 107 |
| Figure A-25: | DSC curve of 150°C post cured 80/20 acrylic/epoxy control sample | 108 |
| Figure A-26: | DSC curve of 150°C post cured 70/30 acrylic/epoxy control sample | 108 |
| Figure A-27: | DSC curve of 150°C post cured 60/40 acrylic/epoxy control sample | 109 |
| Figure A-28: | DSC curve of 150°C post cured 50/50 acrylic/epoxy control sample | 109 |
| Figure A-29: | DSC curve of 150°C post cured 40/60 acrylic/epoxy control sample | 110 |
| Figure A-30: | DSC curve of 150°C post cured 30/70 acrylic/epoxy control sample | 110 |
| Figure A-31: | DSC curve of 150°C post cured 20/80 acrylic/epoxy control sample | 111 |
| Figure A-32: | DSC curve of 150°C post cured 10/90 acrylic/epoxy control sample | 111 |
| Figure A-33: | DSC curve of 150°C post cured 0/100 acrylic/epoxy control sample | 112 |
| Figure A-34: | DSC curve of 150°C post cured 100/0 acrylic/epoxy RP sample | 113 |
| Figure A-35: | DSC curve of 150°C post cured 80/20 acrylic/epoxy RP sample | 113 |
| Figure A-36: | DSC curve of 150°C post cured 50/50 acrylic/epoxy RP sample | 114 |
| Figure A-37: | DSC curve of 150°C post cured 20/80 acrylic/epoxy RP sample | 114 |
| Figure A-38: | DSC curve of 150°C post cured 0/100 acrylic/epoxy RP sample | 115 |
| Figure A-39: | DSC curve of thermal cured acrylic homopolymer | 116 |
| Figure A-40: | DSC curve of thermal cured epoxy homopolymer | 116 |
| Figure A-41: | DMA isothermal testing of 100/0 acrylic/epoxy control sample | 117 |
Figure A- 42: DMA isothermal testing of 80/20 acrylic/epoxy control sample. .................................................. 117
Figure A- 43: DMA isothermal testing of 50/50 acrylic/epoxy control sample. .................................................. 118
Figure A- 44: DMA isothermal testing of 20/80 acrylic/epoxy control sample. .................................................. 118
Figure A- 45: DMA isothermal test of 0/100 acrylic/epoxy control sample. .................................................. 119
Figure A- 46: DMA temperature sweep of 100/0 acrylic/epoxy control sample with an amplitude of 1.5 μm. .................................................................................................................. 120
Figure A- 47: DMA temperature sweep of 80/20 acrylic/epoxy control sample with an amplitude of 1.7 μm. .................................................................................................................. 121
Figure A- 48: DMA temperature sweep of 50/50 acrylic/epoxy control sample with an amplitude of 0.10 μm. .................................................................................................................. 121
Figure A- 49: DMA temperature sweep of 20/80 acrylic/epoxy control sample with an amplitude of 0.02 μm. .................................................................................................................. 122
Figure A- 50: DMA temperature sweep of 0/100 acrylic/epoxy control sample with an amplitude of 0.007 μm. .................................................................................................................. 122
Figure A- 51: DMA temperature sweep of 80/20 acrylic/epoxy RP sample with an amplitude of 1.3 μm. .................................................................................................................. 123
Figure A- 52: DMA temperature sweep of 50/50 acrylic/epoxy RP sample with an amplitude of 0.1 μm. .................................................................................................................. 124
Figure A- 53: DMA storage modulus master curve of 100/0 acrylic/epoxy control sample .................................................................................................................. 125
Figure A- 54: DMA storage modulus master curve of 80/20 acrylic/epoxy control sample .................................................................................................................. 126
Figure A- 55: DMA storage modulus master curve of 50/50 acrylic/epoxy control sample .................................................................................................................. 126
Figure A- 56: DMA storage modulus master curve of 20/80 acrylic/epoxy control sample .................................................................................................................. 127
Figure A- 57: DMA storage modulus master curve of 0/100 acrylic/epoxy control sample .................................................................................................................. 127
Figure A- 58: DMA loss modulus master curve of 100/0 acrylic/epoxy control sample. .................................. 128
Figure A- 59: DMA loss modulus master curve of 80/20 acrylic/epoxy control sample. .................................. 128
Figure A- 60: DMA loss modulus master curve of 50/50 acrylic/epoxy control sample. .................................. 129
Figure A- 61: DMA loss modulus master curve of 20/80 acrylic/epoxy control sample. .................................. 129
Figure A- 62: DMA loss modulus master curve of 0/100 acrylic/epoxy control sample. .................................. 130
Figure A- 63: DMA tan delta master curve of 100/0 acrylic/epoxy control sample. ............................................. 130
Figure A- 64: DMA tan delta master curve of 80/20acrylic/epoxy control sample. ............................................. 131
Figure A- 65: DMA tan delta master curve of 50/50 acrylic/epoxy control sample. ............................................. 131
Figure A- 66: DMA tan delta master curve of 20/80 acrylic/epoxy control sample. ............................................. 132
Figure A- 67: DMA tan delta master curve of 0/100 acrylic/epoxy control sample. ............................................. 132
Figure A- 68: Stress-strain curve of non-post cured samples: acrylic/epoxy ......................................................... 133
Figure A- 69: Stress-strain curve of 90°C post cured samples: acrylic/epoxy ......................................................... 133
Figure A- 70: Stress-strain curve of 150°C post cured samples: acrylic/epoxy ......................................................... 134
1 Introduction

The current thesis is a study of interpenetrating polymer networks (IPNs) and rapid prototyping (RP) in an attempt to combine the two. Although rapid prototyping techniques are highly developed, there has been little attempt to vary the properties of the prototype being printed. The use of interpenetrating polymers as the rapid prototyping material is one way that may give the prototyping advantage of property variation.

The development of a gradient interpenetrating polymer focuses on at least two main polymers. To gradually change the stiffness within a rapid prototyped object, for example the first polymer may be a very rigid and strong polymer while the second polymer may be a softer and more flexible polymer. The gradient is created by having control of the degree of polymerization of each component within the system resulting in a sample capable of having a rigid end gradually changing to a more flexible end. This is one example of the property variation possible with this rapid prototyping idea.

There are many advantages to gradually changing material properties throughout a rapid prototyped part. If one needed a part with a rigid base and a soft flexible part attached to it, there is generally a weakness at the point of attachment leading to a likely point of failure. However, using gradient interpenetrating polymers, this weak point can be eliminated by eliminating the need to have an attachment point. The gradient of the Interpenetrating polymer would provide a gradual change between the two desired properties as opposed to an abrupt material change.

1.1 Problem Statement

This thesis is multidisciplinary and has two main goals. The first goal is to design and build a rapid prototyping machine capable of producing IPN samples. The second goal is to identify and characterize the printed IPN system.
1.2 General Approach and Results

The rapid prototype machine design started with the development of a standard rapid prototyping machine capable of producing prototypes from a single polymer. The machine design was then modified in order to be capable of producing IPNs.

IPN samples produced outside of the RP machine, referred to as the control system, were identified and characterized first by thermal, mechanical and phase distribution analysis. IPN samples produced inside the RP machine, referred to as the RP machine samples were then characterized and compared to the control samples. This led to the conclusion that the RP machine is capable of IPN production.

1.3 Sequence of Presentation

The presentation will begin with the background information about rapid prototyping, photo curing, and IPNs. Next, the IPN system chosen for the rapid prototyping application is described. This is followed by the rapid prototype machine designed to produce the IPN system. A section describing the IPN characterization methods used follows along with the method procedures. This leads to the results and discussion of the IPN identification and characterization of the control samples and then the machine samples for comparison.
2 Background

2.1 Rapid Prototyping Background

Rapid prototyping is a technology that converts a computer aided design (CAD) drawing into a three dimensional tangible object. The prototypes can be produced by RP machines relatively quickly and cost effectively compared to other methods of prototyping such as machining [1]. This is beneficial for a designer to be able to quickly and cost effectively see a design in a three dimensional form. There are different methods of rapid prototyping but they all follow the same basic processes for creating a prototype.

The first step to rapid prototyping is to create a computer aided design using programs such as SolidWorks or Pro/ENGINEER. The design then is converted to an STL file which is most commonly used for RP and differs from other CAD type files because it focuses only on the surface geometry of the design. The STL model is then “sliced” according to desired overall accuracy and RP method used. The G-code of the model is then generated which is a common programming language used to communicate desired locations and speeds to computer controlled machines and tools. The slicing and G-code generation can be accomplished with the help of rapid prototyping based programs. The G-code is then translated into machine movement by a microcontroller board and a prototype can be printed one layer at a time with each layer representing one “slice” of the sliced design.

2.1.1 Types of Rapid Prototyping

There are many different kinds of RP methods but there are five types that are the most common. These include stereo-lithography, laminated object manufacturing, selective laser sintering, fused disposition molding, and solid ground curing.

Stereo lithography (SL) was patented in 1986 and was commercially available in 1988 [2]. The method of SL creates prototypes by photo curing resin. A vat is filled with liquid resin
and the printing platform is positioned one layer thickness below the resin surface. Each two
dimensional layer is formed by the movement of a laser beam on the resin surface, curing and
therefore solidifying the resin into the desired shape. After the formation of each layer, the
platform drops its position equivalent to one layer of thickness. The process continues by curing
the resin on top of the previously cured layer, building from the bottom to the top of the
prototyped object. The prototype ends up completely submerged in the resin when the building is
complete. The platform is then raised out of the resin where the prototype can be removed,
cleaned, and post cured if desired.

Laminated Object Manufacturing (LOM) is a rapid prototyping method first invented in
1986 [2]. LOM is a method of cutting sheets of a material, such as metal or polymer films, and
stacking them into a three dimensional object. A laser beam cuts each layer shape and then cross
hatches the remaining material surrounding the shape to aid in detachment. The platform then
rises, detaching the cut shape and lowers so the roll of material can be advanced. The next layer
is then laminated to the previous by use of a hot roller and the process continues until the
prototype is completed [3]. The advantage to this type of rapid prototyping is that it is relatively
cheap and the materials used are readily available [4].

Selective laser sintering (SLS) was first developed in 1988 [2] and commercially
available in 1995. It is a rapid prototyping technique that uses a laser beam to sinter layers of
powdered material to produce a three dimensional prototype. One layer of powder, in most cases
consisting of polymer or metal, is distributed on the entire surface of the building platform. A
laser beam is used to diffuse the powder together forming a two-dimensional cross sectional
shape. After the layer is cooled, the building platform drops down for the distribution of the next
layer of powder. When the three-dimensional prototype is completed, it will be completely
submerged in the remaining powder. The part is removed, and the left over powder can be reused
for another prototype [5].
Fused Disposition Molding (FDM) was first developed in 1988. This technique of rapid prototyping involves extruding melted thermoplastic-type materials layer by layer to create the three dimensional object [2]. Solid thermoplastic-type material is forced through a nozzle that both melts and extrudes the material at a small diameter. The soft extruded material is used to build the three dimensional object layer by layer. Like the other methods of rapid prototyping, the first layer is built on the build platform which is lowered at the completion of the previous layer.

Solid ground curing (SGC) is similar to SL in that it creates a three dimensional objects by a photo curing resin. Unlike SL however, SGC photo cures an entire layer at one time. This is done by the use of a UV lamp and mask. The mask is responsible for controlling the two dimensional image of light passing through for each layer. Once one layer is cured, the uncured resin is removed and wax is used to create a new flat surface by filling the gaps around the developing three dimensional object(s). A new layer of resin is then sprayed over the top of the solidified resin and wax surface. The mask changes to the necessary shape and the next layer is created. The process ends with the prototype surrounded in the wax which has to be removed [4].

2.1.2 Advances in Rapid Prototyping

The standard rapid prototyping methods developed in the 1980s are still the most widely known and commercially available forms of rapid prototyping. However, the technology keeps advancing in accuracy and materials used in order for rapid prototyping to be continually compatible with its customers changing needs and ideas.

The ability to print three dimensional objects in color is a big advancement in the rapid prototyping technology. Three dimensional printers are available that are capable of printing in full color. The company zCorporation, for example, has a printer with the capability of printing gradients of color from 390,000 color choices [6]. This technology allows for prototypes to resemble, almost perfectly the future product. This technology works by depositing liquid
adhesive on a layer of powder in the desired cross sectional shape. The adhesive is deposited by means of a print head and is also responsible for the color change of the object.

The production of micro sized objects has been a challenge in the past, but with increasing complexity of printing ability and accuracy, rapid prototyping is becoming an efficient way of producing these small parts. Micro parts are used in small electronics and will have higher demand as these products continue to decrease in size. Li et al. [7] developed a system for micro rapid prototyping which uses a micro-sized laser to sinter a layer of micro thickness in the desired object cross section. With the use of powder as the building material, creating a heterogeneous micro part is possibly by powder mixing.

Along with micro parts, material and property variation can have an advantage to many different rapid prototyping applications. The ability to have abrupt changes in materials and properties is somewhat fundamental but the ability to have changes gradually throughout an object by rapid prototyping is a technology being widely researched and developed currently. Wei and Xiaofeng [8] for example, produced a functionally gradient material rapid prototyping technique that involves sintering of powdered metals which are mixed at varying compositions throughout the prototyping process. This allows for property and material variation throughout the object.

Rapid prototyping of material property enhancements are also being widely studied. Kumar and Kruth [9] study the development of composite materials by the use of rapid prototyping in hopes to improve the prototype properties. The creation of composite prototypes was studied in many different ways of rapid prototyping including SLS, LOM, FDM, and SL. The addition of reinforcements in the form of powder or fibers to the build material can enhance specifically the mechanical properties of the printed objects.
2.2 Photo Curing Background

Photo curing is the science of solidifying a liquid resin by use of ultra violet light. The use of photo curing has been around for many years but is becoming much more common and applicable today as its technology advances.

The photo curable resin can either be composed of polymer chains or monomers. With use of monomer based resin, exposure to ultra violet light will promote the polymerization of the monomers. In most cases, a photo initiator is required to initiate the polymerization with in the monomer resin. The photo initiator is very important because it is directly related to the amount of time it takes for the resin to fully cure. It must have a high absorption rate of the light source while also having only a short excitation stage as to not create quenching by oxygen [10]. Aside from the monomer and photo initiator, there is one other important component that can be present in ultra violet resins which is the oligomer. The oligomer usually accounts for the largest percent by weight of the resin and is similar to a polymer in that it is made up of monomers. It differs from a polymer however, because it does not consist of a large number of monomers, therefore having a small chain. The oligomer present in the resin is responsible for many of the cured polymer’s characteristics and properties such as gloss, reactivity, scratch resistance, yellowing resistance, ect. Additives may also be added in order to achieve other desired properties of the cured polymer such as coloring [11].

2.2.1 Types of Photo Curable Resins

There are two different types of photo curing resins. These include free radical curing and cationic UV curing. The basic chemistry varies slightly based on the type of curing taking place. The photo initiator will either create free radicals or protons whether it is of the free radical or cationic curing method, respectively. The biggest advantage of free radical curing is that the curing can happen in a fraction of a second whereas the cationic curing may take seconds
to as long as minutes to cure. The cationic curing method however produces materials with low shrinking where the free radical curing method does not [12].

When a free radical is created, a monomer will join with it creating another free radical and thus causing another monomer to attach to it until a long molecule is created. This chain reaction of curing occurs very quickly and will not stop until a polymer chains movement is inhibited by another chain or oxygen reacts with the chain end. An example of a radical curing mechanism can be seen in Figure 1.

![Radical curing mechanism](image)

**Figure 1:** Radical curing mechanism [12].

There are three main polymer types that undergo radical polymerization including unsaturated polyester/styrene, thiol-polyene, and acrylate monomers [13].

Unsaturated polyester/styrene is a thermosetting resin and is commonly applicable in the electrical, automotive, and aircraft industries. This is a low cost resin and has good mechanical properties along with good chemical resistance and electrical insulation [14] however it has a relatively slow curing rate. Thiol-polyene resins are high in cost and are mainly used for protective coatings and adhesive applications. Acrylate monomers have the advantage of polymerizing extremely fast compared to the other photo curable resins. The resulting polymers have excellent mechanical, optical and chemical properties helping to make acrylate monomers one of the most desirable photo curable resins on the market [13].
Cationic photo curing occurs by the production of ions. This curing process is not terminated by the exposure to oxygen and can be done without the need of an oxygen free environment [15]. An example of a cationic curing mechanism can be seen in Figure 2.

![Cationic curing mechanism](image)

**Figure 2:** Cationic curing mechanism [12].

There are two main polymer types that undergo cationic polymerization including epoxides and vinyl ethers [13].

Epoxides are a thermosetting resin that has very low shrinkage, low moisture absorption and adheres well to substrates and fibers. These properties make epoxides a very useful matrix in composite materials resulting in high performance composite materials [16]. The disadvantage to epoxides is the low curing rate [13]. Similar to epoxides, vinyl ethers have very good adhesion making them a great matrix for composite materials. They also have low shrinkage, high impact strength and a high curing rate [17].

### 2.2.2 Photo curing Applications

As photo curing technology and chemistry advances, the applications that can benefit from this science increase. Some of these photo curing applications include, but are not limited to, ink jet printing, curable coatings, dentistry, and rapid prototyping.

The technology of ink jet printing has advanced alongside with photo curing technologies. As printing has become more necessary for business needs, faster methods of printing have been developed. The development of UV curable inks increased the ink jet dry
time therefore increasing the productivity rate. This printing soon made it possible for color plots and graphics printing on fabrics [18].

Ultra violet curable polymer coatings are used for both decretive and functional needs. Today, many house hold items are made of plastic and the use of UV curable coatings makes it possible to easily decorate these items. Some of these items might include cellular telephones and lap top computer cases. The use of ultra violet curable resins for decorative coating applications has a lot of benefits to the manufacturing process such as an increase in productivity, rapid drying time compared to other methods of plastic coloring, and lower energy costs as compared to conventional thermal curing methods [19].

Ultra violet curable coatings are not only used for cosmetic needs but are also used for functional needs. Some of these applications include curing on wood, PVC piping, and steel. UV coatings on woods provide a scratch resistant surface which is applicable for both furniture and hard wood floors. A soft flexible oligomer is responsible for the scratch resistant property of the coating. Coatings on PVC pipe can decrease the level of irritancy of the pipe by increasing the chemical resistance and reactivity of the pipe while coatings on steels are used to improve the chemical resistance properties of the material [11].

Dentists have been using composite veneering techniques for only about ten years. The use of this ultra violet curing technique has replaced previous methods of using porcelain. The advantages of using UV curable materials are that they have very good physical properties, such as low porosity, and are easy for the dentist to handle. One major problem with using photo curing materials as dental prosthetics is the low curing depth possible [20].

Photo curable materials used for rapid prototyping have been used for a couple decades. As mentioned before, the forms of rapid prototyping that currently use photo curing are stereo lithography and solid ground curing. By using a computer aided design (CAD) program a three dimensional prototype can be made from the image displayed on the computer by photo curing liquid resin layer by layer. This is described in more detail in section 2.1.1.
2.2.3 Photo Curing Challenges

Although photo curing is an advancing technology, there are still some challenges. Curing depth is one example of a photo curing challenge. Several studies have been done in order to find the maximum curing depth of photosensitive materials. These studies have been mostly focused in dentistry but the general idea can be applied to other applications of photo curable materials. Tanoue et al. [20] compared different curing light sources and found a large difference in the depths on the same material. With the use of a veneering material it was found that the metal halide lamp was the most effective when compared to halogen, mercury, xenon, and fluorescent lamps – all of which had comparable wave lengths. Exposure time was also a big factor in curing depth. The study exposed the veneering material for times ranging from 20 to 90 seconds. As expected, the increase in time had an increase in curing depth, although the depth seemed to level off after some time. This study shows that for any given application, the light source intensity and wavelength along with the duration of curing time will have an impact on the curing depth.

Another challenge with photo curing is development of shadow areas. When curing a coating on a three dimensional piece, shadows can be easily cast on areas of the part. These shadows prevent curing in those areas. In order to get rid of the shadowing problem, several solutions have been proposed. The use of reflective walls in a photo curing chamber can decrease the amount of shadow areas by reflecting the light in all directions. Dual curing processes have also been used to eliminate shadows. The use of light and heat for curing simultaneously to cure a resin containing both UV and thermal curable components can get around this problem by creating an interpenetrating polymer network system. The best solution to shadowing is the use of a plasma chamber. The plasma chamber allows the UV atoms to fill the entire chamber volume. This form of photo curing has been proven to be the best solution in completely eliminating shadow areas [21].
2.3 Interpenetrating Polymers Network Systems Background

The use of Interpenetrating polymers (IPNs) is a polymerization science that has become increasingly popular and studied recently. An IPN is defined as a combination of at least two polymers in network form. The polymers are merely intertwined and not covalently bonded together and cannot be separated unless the chemical bonds within the individual polymers themselves are broken. A mixture of polymers is not the same thing as an IPN because the separate polymers within an IPN do not actually chemically bond together. A combination of polymers that do not follow the above specifications is not to be considered an IPN [22]. Figure 3 below shows an interpenetrating polymer system composed of two different homopolymers represented as blue and yellow.

![IPN schematic](image)

**Figure 3:** IPN schematic [23].

IPNs have come a long way and have been widely used in today’s applications because of some of their excellent material properties. An IPN can be a very tough but flexible material and can be very resistant to impact. They have also been seen to dampen sound and/or vibrations. Because of these qualities, IPNs can be very useful and can have many applications in today’s society [24].
2.3.1 Types of Interpenetrating Polymers

There are many different types of IPN networks. Some of the most commonly used are simultaneous, sequential, gradient, thermoplastic, latex, and semi interpenetrating networks [25].

A simultaneous synthesis method (SIN) starts with a mixture of two different monomers along with both cross linkers and activators. The monomers are then polymerized simultaneously, each taking a different route of reaction without interfering with the reaction of the other IPN component [25]. A sequential synthesis method first polymerizes the first monomer and then sequentially adds the next monomer plus cross linker to be polymerized in and around the previously polymerized network [24].

Latex IPNs are formed from latexes usually in a core and shell structure. Two latexes are mixed and then a film is formed. The film cross-links both polymers forming and IPN system [25].

Gradient interpenetrating polymer networks are constructed when the cross linked polymer density of each polymer changes from location to location. This is done by changing the ratios or polymerization between the polymers present. This form of polymerization can be very useful in gradually changing the properties of a material with location [26].

Thermoplastic interpenetrating networks use chemical crosslinking as opposed to physical crosslinking in order to create each polymer network. The advantage of a chemical crosslinking bond type is that the IPN will not melt or flow with elevated temperatures and is more stable [26].

Semi interpenetrating polymer networks have only one cross linked polymer network. The other polymer network is not cross linked and is considered to be linear. This is different than full IPN networks where all of the polymer networks are cross-linked [24].
2.3.2 IPN Applications

In dentistry, IPNs are used in dentures and other denture based polymers along with composites reinforced with fiber. The properties of the IPNs used in dentistry are very desirable for both pre polymerization and post polymerization. The IPN has very good interfacial adhesion after polymerization which is very important for modern dentistry. The IPNs used in dentistry are of the semi-IPN type and are composed of PMMA and methacrylate monomers (MMA) liquid with use of dimethacrylate monomers as cross-linkers. Reinforced IPNs with fiber are used for denture purposes. Using the reinforcement can make dentures that are much tougher than the already tough interpenetrating polymer network [27].

IPNs are also used for other biomedical applications other than dental such as Polytetrafluoroethylene, (PTFE) and poly(dimethyl siloxane) (PDMS), which are used to synthesize IPN membranes. The result is a flexible membrane used especially for second degree burn victims, known commercially as Silon. This material transports body fluids from the burn site by use of the PDMS while the PTFE provides strength to the material. The material is also waterproof because of the PTFE and is transparent so the burn area can be easily inspected. Other uses of IPNs as biomedical materials include bone implant composites, cartilage scaffolds, slow drug release systems, and many more [28].

Gradient IPNs are applicable for optical solutions. A common use of gradient interpenetrating polymer networks is the production of optical rods. These rods have a parabolic decrease in optical index towards the rod surface. This is done by having two polymers interpenetrating with one having a high refraction index while the other has a low index. The two are interpenetrated in a way that the gradient is parabolic [29]. This same idea of light refraction can be used for other optical applications such as contact lenses. Many contact lenses achieve optical index variation with the help of gradient IPNs along the curved shape of the lens to aid in vision correction. [26].
An important advantage to interpenetrating polymers over a single polymer network is that IPNs have a very high sound and vibration damping effect over a large range of temperatures. Single polymer networks, however, may have just as high of a damping effect but the temperature range is likely to be much less. This is because IPNs can exhibit a very large glass transition region where the region covers the temperature region of the two independent polymers. This is very useful for applications with weather change or in factory conditions. This damping property can be used for a variety of applications including car parts, windows, and factory damping equipment [26].
3 IPN System Selection

For the purpose of rapid prototyping, an IPN system was chosen where both components could be cured under an ultra violet light source. This is because UV curing can be done at very high rates and only where light exposure occurs, which can lead to complex curing patterns in a limited amount of time in comparison to thermal curing [13]. Also, to aid in the simplicity in rapid prototyping system design, an IPN system which can polymerize simultaneously is preferred.

In order to create a simultaneous IPN, each network needs to undergo polymerization in different ways so that copolymerization and grafting reactions can be hindered between the two polymer systems [30]. As described in section 2.2.1, there are two different ways a polymer can undergo polymerization. Because of this, the IPN system needs to be composed of a component undergoing radical polymerization and a component undergoing cationic polymerization. Also, for the future goal of creating a rigid to soft gradient IPN within the rapid prototyping machine, a rigid and a soft component need to be selected as the two polymer networks.

3.1 Radical Component

The radical component of the IPN system is composed of the crosslinker Bisphenol A propoxylate diacrylate (BPA-PDA) and the photo initiator 2-hydroxy-2-methylpropiophenone. These molecules can be seen in Figure 4 and Figure 5.

![Figure 4: Radical crosslinker; Bisphenol A propoxylate diacrylate.](image)
BPA-PDA is an acrylic type resin. Acrylates are known to be one of the most reactive UV curable monomers undergoing radical reaction making it a good choice for a rapid prototyping purpose. Because of its low modulus, it is chosen to be the soft component of the IPN system. In the sections to follow, the radical component will be referred to as the acrylic component of the IPN system.

3.2 Cationic Component

The cationic component of the IPN system is composed of the crosslinker 3,4 epoxyxyclohexylmethyl 3,4 epoxyxyclohexane carboxylate (ECH) and the photo initiator Triarylsulfonium hexafluoroantimonate. The molecules can be seen in Figure 6 and Figure 7.

Figure 5: Radical photo initiator; 2-hydroxy-2-methylpropiophenone.

Figure 6: Cationic crosslinker; 3,4 epoxyxyclohexylmethyl 3,4 epoxyxyclohexane carboxylate.
Figure 7: Cationic photo initiator; Triarylsulfonium hexafluoroantimonate.

This is an epoxy type resin. Epoxy resins are known to have high tensile and compressive strengths along with excellent thermal stability [31]. Because of its high strength, the epoxide was chosen as the rigid component of the IPN system. A vinyl ether resin would have been the other choice as a cationic component of the IPN system, but this was avoided because copolymerization can occur in acrylate and vinyl ether IPN systems [13]. In the sections to follow, the cationic component will be referred to as the epoxy component of the IPN system.
4  Basic Stereo-lithography Machine Development

The first goal is the development of a rapid prototyping machine capable of producing the acrylic and epoxy based IPN system. In order to accomplish this, the most appropriate type of rapid prototyping method needed to be selected. Because of the IPN system selected, SL or SGC are the most logical machine technologies to choose because of their use of an ultra violet light source for the purpose of curing and solidifying the liquid resin. SL was found to be a more well-known type of rapid prototyping with more products commercially available than solid ground curing. For these reasons and because of the simplicity of the idea, SL was the form of rapid prototyping technology chosen for the purpose of rapid prototyping IPNs.

SL machines are commercially available but the available systems involve curing one type of resin with the use of a laser with no property variation. Initially it was desired to purchase a standard SL rapid prototyping machine and then adapting it to print IPNs followed by gradient IPNs. Companies such as MakerBot, make and sell inexpensive rapid prototyping machines for home and recreational use, however, no SL machines of this type were available. Professional SL machines could be found however, for the price of around $250,000.

Because of the unavailability of affordable standard SL rapid prototyping machines, one needed to be constructed from scratch. Other than affordability, this machine would also have the advantage of being easily adaptable to the changing needs and developing knowledge of creating rapid prototyped IPN samples followed by the future goal of gradient IPN production.

4.1  Theory

A standard SL machine has a mechanical aspect that needs to be linked to programming software for machine control. The physical design of the machine needs to include a vat used to contain the liquid resin. Within this vat, the building platform needs to home the ability to move all the way up and down within the vat without interference along the Z direction (vertical). A
laser or other small point light source is needed for resin curing precision. The light beam of the light source needs to be moveable in the X and Y directions (horizontal) in order to cure each printed layer’s two dimensional shape. Figure 8 below shows the aspects needed for the SL machine development.

![Diagram of SL machine](image)

**Figure 8:** Standard stereo-lithography theory [4].

In order for the SL machine to run, it needs to be in communication with the computer controlling it. A driver board is used for this purpose that controls the motion of the motors and operation of the light source. Computer software is needed to translate a three dimensional computer aided design drawing into the X, Y, and Z machine movements in the form of G-code. This G-code is what is communicated from the computer to the driver board for machine control.

### 4.2 Design

The main ideas of the basic SL machine design came from a website called Instructables. The designer, Rob Hopeless had posted a public tutorial titled “Build a Laser 3D Printer – Stereolithography at Home” on the site [32]. At the time, this was the only available low cost SL machine design available to the public.
The SL rapid prototyping machine is made up of three axis’: X, Y, and Z. The X, and Y axis are responsible for maneuvering the laser to create a two dimensional shape while the Z axis is responsible for moving the build platform up and down giving it the third dimension. Every axis consists of an acme rod coupled to a stepper motor. Stepper motors are commonly used in robotics because they have a precise turning interval for a certain amount of power given. With the use of acme leadnuts threaded on the rod and attached to bearing blocks on a linear rail, all directions can be controlled. The acme leadnuts are attached to the bearing blocks by manufactured components. Figure 9 shows the mechanical components of the machine where the X axis is moving from left the right, the Y axis is moving in and out of the page, and the Z axis is moving up and down.

![Figure 9: RP system mechanical components.](image)

From the figure, it can be seen that the Y axis uses a pair of bearing blocks and rails which is responsible for moving the entire X axis in the Y direction. The component being moved along
the X axis linear rail is the laser bracket responsible for housing the laser. The Z axis is responsible for moving the build platform within the beaker vat.

Limit switches were placed at each end of the linear rails which are not seen pictured in Figure 9. These limit switches signal the machine to stop all movement if the linear block comes into contact with one. This is a safety feature meant to prevent the motor from running outside its limits.

All components within the machine were housed in a structure made of plywood. By aligning and securing the linear rods and stepper motors within the wooden structure, all other components fit into place. Four adjustable feet were placed under the base of the plywood structure in order to adjust and level the building platform.

Each axis is controlled by its own stepper motor driver which is responsible for delivering the appropriate amount of power to move the motor the desired amount of steps. The motor drivers used are called EasyDrivers and can be seen in Figure 10.

![EasyDriver motor driver](image)

**Figure 10: EasyDriver motor driver [33].**

The EasyDriver is capable of micro stepping at 1/8th of a step. The stepper motor being used has 200 whole steps per revolution so 1/8th stepping results in 1600 steps per revolution [33].
The stepping can also be set to full step, half step, and quarter step which is controlled by grounding the MS1 and MS2 inputs in different combinations. When determining the stepping needed for an application it is important to understand that the higher the number of steps per revolution, the higher the accuracy will be but the lower the possible movement speed can be. The accuracy of the stepping with use of the acme rod making 16 turns per linear inch can be seen in Table 1.

<table>
<thead>
<tr>
<th>Stepping</th>
<th>Linear Accuracy, mm/step</th>
</tr>
</thead>
<tbody>
<tr>
<td>Full</td>
<td>0.00794</td>
</tr>
<tr>
<td>1/2</td>
<td>0.00397</td>
</tr>
<tr>
<td>1/8</td>
<td>0.00099</td>
</tr>
</tbody>
</table>

Because the Z axis is not required to move quickly, the stepping was set to 1/8th step. The X and Y axis however require a larger speed which can be accomplished with 1/2 step.

The component responsible for translating and transferring the G-code to each stepper motor driver is the microcontroller board called the sanguino. The motor stepping calculations, found in section A.1, are useful for understanding the machine accuracy but are also essential in the programing of the sanguino which is pictured in Figure 11.
All components are connected to the Sanguino including, the three stepper motor driver boards, the limit switches, and the laser. A breadboard was used for the wiring of all components for the ability to have easy wiring manipulations. The wiring diagram of all electronic components can be seen below in Figure 12.

![Wiring diagram of electronic components](image)

**Figure 12:** Wiring diagram of electronic components.

The function and control of these components are programmed into the sanguino by use of the software Arduino. The software ReplicatorG translates the CAD into the G-code language and allows for the selection of laser movement speed, layer thickness, and laser point size. The sanguino along with the Arduino and ReplicatorG software makes it possible to convert a design to a tangible prototype.
The build material chosen for this simple SL machine design was Ultra-Light-Weld 3099 by Dymax which is an adhesive curable by UV and visible light sources. The curing of the Dymax resin was done with a blue laser with a wavelength of 405nm and power of 20mW seen in Figure 13.

![Figure 13: 405nm laser, 20mW.](image)

With the use of an adjustable iris, the laser beam spot diameter can be controlled. It requires a power of 3.3 volts which is accomplished with a voltage regulator as seen in the wiring diagram in Figure 12. When working with high intensity light sources, UV safety glasses should be worn to prevent eye injury. The completed SL machine along with these safety glasses can be seen in Figure 14.

![Figure 14: SL machine.](image)
4.3 Testing and Evaluation

After the construction of the standard SL rapid prototyping machine, its functionality was tested by making computer aided designs and printing them to ensure that the machine could demonstrate the basic functions of a typical SL machine. Figure 15 below shows a partially printed object in the vat of the rapid prototyping machine.

![Figure 15: SL machine vat with partially printed object.](image)

Simple rectangular blocks were first printed in order to test the laser movement speed along with the layer thickness. An example of a test block can be seen in Figure 16 below.

![Figure 16: 10 x 5 x 1 mm block produced in SL machine.](image)
The test block in Figure 16 has the dimensions of 10 x 5 x 1 mm with each layer printed at 0.1mm. The speed of the laser was 100 mm/min and the build time was 12 minutes. Several blocks were created for the purpose of testing the laser time exposure and layer thickness needed to successfully cure the Dymax resin into solidified layers. It was determined that a speed of 150 mm/min with a layer thickness of 0.5mm was adequate to making solidified objects, however, it should be kept in mind that with increasing layer thickness, the accuracy of the object decreases.

Once the laser movement speed and layer thickness was understood in relationship to resin curability, the machine was tested by making more complex objects. Testing its ability to print in comparison to the complexity of an object is important for validating that it is accurate even with increased complexity. Figure 17 below shows examples of the results from the shape complexity testing.

![Figure 17: SL machine shape complexity testing.](image)

The objects in Figure 17 are an endless knot, a car, a whistle, a snake, an airplane, and a bolt. All of these objects show that the machine is capable of complex printing. The whistle is a
very good example of complex printing because it not only looks like a whistle but it is actually functional too.

The development of the standard SL rapid prototyping machine was successful for the purpose of proving its capabilities of photo curing resin to create three dimensional objects from computer aided designs. This machine demonstrates control and accuracy with varying object complexity which can be seen from its printed samples. However, because it is necessary for this machine to make IPN samples, adaptations are necessary.
5 IPN Stereo-lithography Machine Development

Because there are two polymers involved in the creation of IPNs, the machine was first adapted to work with the acrylic homopolymer and then the epoxy homopolymer. Once both the acrylic and the epoxy polymers were successfully cured, the machine was modified in order to cure both polymers simultaneously to form an IPN system. The modifications of the machine were done in collaboration with Marc Gode from the University of Rouen, France.

5.1 Modifications for Acrylic Homopolymer Printing

The photo initiator of the acrylic polymer has a broad wavelength range for curing in the ultra violet spectrum. Because of this, the biggest modification needed is a change in light source. The previously used 20mW laser with a wavelength of 405nm is not adequate for curing of the acrylic resin because it is out of the ultra violet wave length range. There are many different ultra violet light source options including lasers, a polychromatic light source with a filter, or an LED. Because lasers are relatively expensive, and polychromatic light sources add complexity to the design, an LED light source with a wave length of 355nm was selected. This LED was selected from the company SETi and can be seen in Figure 18.

![LED light source](image)

Figure 18: LED light source [35].
The LED measures at 0.88 inches in length and 0.33 inches in maximum diameter. It has a ball lens causing the light to focus to a point size between 1.5 – 2.0 mm in diameter at a power of 500 μW. Figure 19 shows the light beam dimensions.

![Figure 19: 355 LED light spot size [35].](image)

In order to cure the acrylic resin with the smallest diameter possible, a new mount was designed to ensure that the LED lens was between 15 and 20 mm away from the curing surface. This distance is much less than the previous distance needed for the 405 nm laser used because the LED uses a lens to converge the light to a point unlike the 405nm laser used before. The LED bracket design can be seen in Figure 20 below and was used in place of the previous 405nm laser mount.

![Figure 20: LED bracket for single polymer curing.](image)
A series of tests were conducted to prove that the 355nm, 500μW LED is capable of curing the acrylic homopolymer within the machine. The tests were conducted by curing the resin at varying times while keeping the LED stationary. Instead of using a vat full of resin, a petri dish with a resin depth of 1mm was placed on the machine’s build platform. Because radical type resins are sensitive to oxygen exposure, the tests were conducted in an oxygen free environment with the use of Argon gas. The exposure time was increased from 30 to 120 seconds in increments of 30 seconds. The resulting polymerized spots can be seen in Figure 21.

![Figure 21: Acrylic polymer testing: Exposure time of 30, 60, 90, and 120 seconds from left to right.](image)

As the exposure time increased, the spot diameters also increased. Table 2 shows the spot diameters with respect to LED exposure times of the radicular polymer resin.

<table>
<thead>
<tr>
<th>Diameter (μm)</th>
<th>Exposure Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>863</td>
<td>30</td>
</tr>
<tr>
<td>925</td>
<td>60</td>
</tr>
<tr>
<td>1075</td>
<td>90</td>
</tr>
<tr>
<td>1175</td>
<td>120</td>
</tr>
</tbody>
</table>
The sample exposure time can be compared to the theoretical time to create the same sample diameter. From the chemistry of the acrylic resin, it is known that there are $4.42 \times 10^{19}$ photo initiator molecules per millimeter of resin. It can be assumed that one photon is responsible for the activation of one photo initiator molecule within the resin. The theoretical curing times for each sample’s diameter can be found with this info along with the Plank relation of a photon given by the equation

$$E = \frac{hc}{\lambda}$$

(1)

where $E$ is the energy in Joules of each photon, $h$ is Planck’s constant, $c$ is the speed of light, and $\lambda$ is the wavelength of the light source.

The theoretical time calculations were carried out for all four samples with varying experimental LED exposure times. A calculation example can be found in section A.2 and the results can be seen below in Table 3.

<table>
<thead>
<tr>
<th>Diameter $\mu$m</th>
<th>Actual Time (seconds)</th>
<th>Theoretical Time (seconds)</th>
<th>Percent Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>863</td>
<td>30</td>
<td>28</td>
<td>7</td>
</tr>
<tr>
<td>925</td>
<td>60</td>
<td>33</td>
<td>82</td>
</tr>
<tr>
<td>1075</td>
<td>90</td>
<td>44</td>
<td>105</td>
</tr>
<tr>
<td>1175</td>
<td>120</td>
<td>53</td>
<td>126</td>
</tr>
</tbody>
</table>

From the results in Table 3, it can be seen that as the diameter increases, the error of the theoretical curing time increases. This is likely because the photons of the LED light source are more heavily focused at the center of the sample preventing the photons from interacting with the surrounding photo initiator molecules. However, because the smallest diameter curing time
differs only by two seconds from the theoretical time, the LED light source is curing the resin as expected at small diameters.

The machine was capable of curing the acrylic homopolymer, however, with the 500μW LED light source, the curing is slow. The curing time can be reduced with the use of a higher powered light source in the future. Despite the slow curing, the main goal of being able to cure the acrylic IPN homopolymer within the rapid prototyping machine was achieved.

5.2 Modifications for Epoxy Homopolymer Printing

Being able to cure the epoxy IPN homopolymer within the rapid prototyping machine is the next step in the overall goal of producing an IPN in the machine. The epoxy resin is known to have slower curing times than the acrylic resin. At the time of these machine manipulations, it was thought that the epoxy resin was more sensitive to wavelengths around 250nm. In order to help decrease the curing time of the epoxy resin, an LED with an increased power of 5mW with a wavelength of 255nm was chosen. This light source was also chosen from the company SETi and has the same dimensions as the 355nm LED as seen Figure 18. Different from the 355nm LED, this light source is composed of 9 LED lights that are converging into one light spot by use of a ball lens. The resulting spot size is slightly larger than the 355nm LED.

The LED was tested by curing the epoxy resin in the same way that the acrylic resin was cured. The LED was held stationary and cured a thin layer of the resin contained in a petri dish on top of the machine’s build platform. The test is to see if the curing of this resin is possible with the use of the LED. One area of epoxy resin was cured with the LED and can be seen in Figure 22.
Figure 22: Epoxy homopolymer testing; Exposure time of 10 minutes resulting in sample size of 5 x 5 x 0.1 mm.

The resulting polymerized sample from the curing test measured at 5 x 5 x 0.1mm and took 10 minutes to cure. Even with the increased power of the LED light source for the epoxy resin, the curing time needed is still much greater than that of the acrylic resin. Also, a thickness of only 0.1mm indicates that only the surface of the resin was cured. This could indicate that the curing of the surface blocks the light photons from curing lower depths of resin.

The results of the epoxy curing test suggest that modifications to the chemistry need to be made or the light source power needs to be increased. If the curing time can be decrease for the epoxy component of the IPN, the functionality of the final IPN rapid prototyping machine would be greatly increased.

5.3 IPN Stereo-lithography Machine

Now that the stereo-lithography machine is capable of producing the acrylic and epoxy homopolymers of the IPN individually, the next step is to be able to create the actual IPN within the machine. To produce IPNs within the machine, both the 255nm and 355nm LED light sources need to be within the machine. A new light source bracket was designed to accomplish this. The goal of this new bracket was that both light sources will be focused on the exact same location of the resin surface. This will simplify the G-code programming of the machine by not having to compensate for a light source placement off set. The proposed design can be seen in Figure 23.
Figure 23: Double LED bracket for IPN SL machine.

The design is made of a bracket support and two LED holders attached by screws to the support piece. The screw attachment of the LED holders allows for positioning of the LED lights in order to focus them on the same location of the liquid resin surface.

The LEDs are controlled in the X and Y directions in the same manner as the original machine design. Because there are two light sources, the programming in ReplicatorG was altered in a way that each light has its own control to turn on and off. This control allows the light sources to be controlled individually and not as a single unit. The future goal of producing an IPN gradient may be achieved by incorporating a photo sensitive photo initiator into the chemistry of the homopolymers. The double light source bracket along with the light source control could be beneficial to this goal by having the ability to control the amount of photo curing of each IPN component based on its photo sensitive wavelength exposure.

5.3.1 RP IPN Sample Production Procedure

The IPN stereo-lithography machine design was tested again with the acrylic and epoxy IPN homopolymers as well as three different IPN acrylic/epoxy composition of 80/20, 50/50, and 20/80. Similar to the homopolymer testing done before, all samples were prepared in an oxygen
free environment with the use of argon gas. A petri dish was again placed on the build platform of the machine to contain the resin so that a small amount could be used. For this test, however, larger block shaped samples were produced by printing multiple layers for each sample. With a simple G-Code program in the ReplicatorG software, two dimensional layers were printed with the dimensions of 10 x 4mm. After each polymerized layer, a thin layer of resin of about 0.2mm was brushed onto the cured surface and the printing program was run again. Each sample was made of six layers resulting in samples around 1mm in thickness. Because of the double light source bracket, a combination of the two wavelengths could be used based on the acrylic/epoxy composition. This also enabled increased power for improved curing results of the epoxy component. The LED linear speeds could also be adjusted based on the composition ratios for the purpose of increasing the exposure time. Each of the compositions had slightly different procedures as described in Table 4.

<table>
<thead>
<tr>
<th>Composition acrylic/epoxy</th>
<th>LED wavelength 255 nm</th>
<th>355nm</th>
<th>LED Speed mm/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0</td>
<td>X</td>
<td></td>
<td>40</td>
</tr>
<tr>
<td>80/20</td>
<td>X</td>
<td></td>
<td>40</td>
</tr>
<tr>
<td>50/50</td>
<td>X</td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>20/80</td>
<td>X</td>
<td>X</td>
<td>20</td>
</tr>
<tr>
<td>0/100</td>
<td>X</td>
<td>X</td>
<td>20</td>
</tr>
</tbody>
</table>

All of the IPN samples produced by the IPN rapid prototyping machine were successfully photo cured with all resulting in a solid rectangular shape. After the photo curing process within the IPN rapid prototyping machine, the samples were post cured at 150°C to complete any incomplete curing processes present. An image of the resulting printed IPN sample with the composition of 80% acrylic component and 20% epoxy component can be seen pictured below in Figure 24.
The sample properties were analyzed and compared to a series of control IPN samples produced in molds with the use of a monochromatic light source. The testing and analysis of the control samples along with the machine samples are discussed in detail in section 9.2.
6 Future Machine Design

The initial IPN stereo-lithography machine design was successful in producing samples containing both acrylic and epoxy homopolymers which will be identified and characterized as IPNs in section 9.2. However, the future goals of creating a gradient IPN at high precision will require a new machine with an improved design. The experience and knowledge gained from the initial machine design and function will aid in the new SL machine design.

6.1 Initial Design Weaknesses

The initial machine design had several weaknesses that will be eliminated in the future machine design. These weaknesses include the threaded rod linear system, wooden structural body, LED diode light source and the lack of research components.

The threaded rod linear system worked for the purposes of the initial machine to convey rotation into linear motion. This is not the most accurate method of linear motion and can also not be used at high speeds because of the friction between the rod and the acme leadnut.

The wooden structure of the machine does not allow for precise squaring and aligning of the structure itself and the components attached to it. It also presents difficulty in disassembling and reassembly of the machine components for alterations.

The LED diodes have a very low power which results in long curing times of the resin. In order to decrease the curing time of the resin and prototype creation, a light source with an increase in power is necessary. The LED also is limited by single wavelengths. The ability to have a variation of wavelengths would introduce the ability to include wavelength variation studies within the machine.

The initial SL machine is lacking the ability to research and understand the curing process and environment of the IPN systems. The addition of environmental sensor and control
systems would make the future IPN stereo-lithography machine capable of helping better understand how the environment affects the curing kinetics.

6.2 Design Changes

To compensate for the observed initial IPN stereo-lithography machine design weaknesses, several changes were proposed for the future design. A belt and pulley system along with a cylindrical linear rod system would provide smoother linear motion along with higher precision. An example of an axis incorporating this linear system can be seen below in Figure 25.

Figure 25: Belt and pulley on cylindrical rod system.

Figure 25 is representative of the X axis where the laser bracket would be connected at the base of the linear bracket seen in red. Every axis would follow this same design idea.

The machine structural body made of polycarbonate sides and aluminum supports would be used in place of wood. This would allow for a perfectly squared structure enabling improved component alignments within the machine. This will contribute to the overall accuracy of the prototype created. The polycarbonate sides would also allow improved visibility of the printing progress of the machine.

A polychromatic or laser system needs to be incorporated into the future machine design. The polychromatic light source would introduce the ability to research the wavelength variation and its effects on curing of the resin. However, in the case that the polychromatic light source cannot provide enough power for a rapid curing time of the resin, a laser system with adequate
power needs to be used. In this case, the wavelength variation research can be done outside of the machine with a polychromatic light source before the purchase of a laser with the most effective wavelength. Along with wavelength variation, other research components need to be designed into the future machine as summarized in Figure 26.

Figure 26: Future machine research components.

A sensor box would be responsible for monitoring many beam characteristics such as the ones listed in Figure 26 by moving the light source directly over the sensor box before rapid prototyping begins. The temperature sensor would be responsible for reading the temperature of the resin at the point of the light source contact while the level sensor would accurately measure the layer thickness of the resin. A heater can be incorporated for the study of curing effects resulting from elevated resin temperature. Improved atmosphere control would also be incorporated into the machine with the use of environment sensors (oxygen and temperature).
7 IPN Identification Methods

The main goal of the stereo-lithography machine was to produce an IPN so it is important that the IPN samples produced within the machine can be validated as IPNs. In order to identify the machine produced samples as IPNs, they were compared to a control set of samples produced with a polychromatic light source. Both the control and machine samples were characterized for comparison. The methods of analysis were Thermogravimetric analysis, differential scanning calorimetry, atomic force microscopy, dynamic mechanical analysis, and tensile testing.

7.1 Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) is a method of thermal analysis used to study the mass degradation of a material with increasing temperature. With this analysis, the sample’s thermal stability can be understood by plotting the mass percent loss with relationship to the increasing temperature. It is also useful to plot the derivative curve to evaluate the change in degradation with temperature. An example of this curve can be seen below in Figure 27.

![TGA example](image)

*Figure 27: TGA example.*
From the figure above, several conclusions can be made of the sample being analyzed. It can be seen that the sample begins to degrade at around 350˚C and with the help of the 1st derivative curve, it can be seen that the highest rate of degradation occurs at around 400˚C. The material is completely degraded by around 425˚C.

The use of TGA can help in the identification of an IPN. Athawale et al. [36] found that in an IPN composed of uralkyd and acrylic components, the thermal stabilities of the different IPN compositions fell between those of the pure components. More specifically, Wang et al. found that in an IPN composed of polyurethane and epoxy the thermal stability increased with increasing amounts of the epoxy component [37].

### 7.2 Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) is a method of thermal analysis used to study transitions within a material such as the glass transition temperature, melting and crystallization. The DSC contains a heating cell that holds one pan that contains the sample of interest and another pan that is empty, serving as a reference. The glass transition temperature (Tg) of a material is the temperature at which a phase change occurs from the glass like state to the rubbery state. By measuring the heat flow required to change the temperature of the sample in relationship to the reference pan, the Tg can be seen graphically. The amount of energy it takes to complete the glass transition is referred as the ΔCp which is the difference in specific heat capacity between the rubbery state and glassy state of the material. An example of a DSC experiment can be seen in Figure 28.
In this example, it can be seen that this particular sample was analyzed twice by the DSC. The purpose of the first DSC run is to both analyze and finish the post curing process of the material as shown with the red curve. The red curve shows that the material was not fully cured before the 1st run of the DSC analysis. The first peak of the curve represents endothermic melting of the sample while the second peak represents exothermic crystallization.

With the sample fully cured after the first DSC analysis run, the Tg can be more clearly seen and determined with the second run represented as the blue curve. The Tg is subtle in this particular case but the transition can be seen occurring at around 50°C. For a better explanation of Tg determination, an example with a clearer Tg is depicted in Figure 29.

Figure 28: DSC example.
Figure 29: Determining glass transition temperature.

In this figure, the red line represents the 2nd run of the DSC analysis while the green dotted lines are the tangent lines to the curve. The tangents of the curve leading up to the start of the transition and the tangent of the curve occurring after the transition are first drawn. The tangent occurring through the transition area is then drawn. The points where the tangents intersect, labeled A and B in Figure 29 are considered to be the start and end points of the full transition. The median temperature between points A and B is the glass transition temperature. In this example, point A is at about -30°C while point B is about -20°C. This gives a Tg value of -25°C. The heat flow difference between points A and B is the ΔCp value of the glass transition.

When using DSC and the resulting glass transition temperatures in the identification of an IPN, the results are not necessarily conclusive. Two different situations have been reported to occur with the Tg temperatures of IPN materials varying in composition. Vlad et al. [38] reported finding two separate glass temperatures for the IPN composed of polyurethane and polysiloxane. In every compositional case, the samples showed one Tg at the Tg value of polyurethane homopolymer and one Tg at the Tg value of polysiloxane homopolymer. In another study,
Athawale et al. [36] observe that the IPNs at various compositions contain a single Tg value. This value lies between those of the pure components. A single Tg can suggest good interpenetration in the system. A single glass transition is ideal because high interpenetration of the material is desired however seeing two glass transitions does not mean that an IPN is not present.

### 7.3 Atomic Force Microscopy

Atomic force microscopy (AFM) is used to observe the surface of a sample in a three dimensional form. It is a very precise form of measurement and can obtain details in the order of a nanometer [39]. The AFM gathers the surface information by moving a force probe along the material while recording its change in displacement therefor gathering the topographic information of the sample surface. The topographic map is then displayed with color differences representing different height ranges at the surface.

AFM has the ability to also picture property differences at a material surface by property sensitive imaging. When measuring the stiffness of a material, the force probe will experience varying degrees of contact resistance at the surface [39]. Like the topographic image, an image is generated with different colors represent different properties at the sample surface which shows the material phase contrast. These property variations are discovered by using the tapping mode of the AFM. With this method, the AFM tip is set to oscillate at a frequency. When the tip comes into contact with the sample surface, the vibrational movements change based on the different characteristics of the surface. This will have an effect on the phase angles of the oscillation with a high phase angle difference suggesting a large material property variation [40]. An example of an AFM image of an IPN can be seen in Figure 30 where the left image is the topographical view of the surface and the right image is the phase contrast image of the sample surface.
Figure 30: AFM example. Left: topographic image (1μm x 1μm). Right: phase contrast image (1μm x 1μm).

The topographical and phase contrast images of the above figure represent the same region of surface area of the sample. The height difference of the topographical image is around 70nm with the lighter areas representing increased heights compared to the dark regions. The phase angle difference in the phase contrast image is around 2.5° with the lighter color representing stiffer region and the darker representing a softer region of the sample surface. Because this is a relatively small angle, this material can be considered homogeneous at the microstructural level.

This method of polymer analysis can be very useful in understanding the heterogeneity of a material and is often used in the analysis of polymer blends and copolymers [41]. In the application of identifying and characterizing IPNs, the homogeneity of the IPN samples can be observed helping in the determination of the best IPN compositional makeup. Wang et al. [37] found that heterogeneity increased with increase of the softer polyurethane component within the polyurethane and epoxy IPN system. Qin et al. [42] discovered the opposite with more phase boundaries observed with increase in the tougher vinyl ester component in the polyurethane and vinyl ester IPN system suggesting increased heterogeneity.
7.4 Dynamic Mechanical Analysis

Dynamic Mechanical Analysis (DMA) is used to analyze a material’s response to an applied oscillating force. The DMA measures the storage modulus, loss modulus and phase lag of the sample. The storage modulus is representative of the elastic response of the sample and the loss modulus is representative of the viscous response of the sample. The combination of the storage and the loss modulus is called the complex modulus while the loss divided by the storage modulus is the tan delta value. By measuring these material properties with change in temperature and/or oscillation frequency, information about the glass transition temperature and the relaxation process of the material can be analyzed. The oscillating force on the sample can be applied in several different ways including tension, three-point bending, single cantilever, and double cantilever. The selection of the testing mode depends highly on sample type and geometry. An example of a sample undergoing a temperature sweep from a -100 to 30°C at a constant frequency of 10 Hz can be seen in Figure 31.

![Figure 31: DMA temperature sweep example with a constant frequency of 10 Hz.](image)

In this example, the storage modulus and tan delta can be seen changing with an increase of temperature. The modulus can be seen rapidly decreasing along with the occurrence of the peak of the tan delta. This peak is representative of the glass transition temperature of the sample.
and can be seen occurring at around -30°C in this example. Damping properties of the sample can also be analyzed by observing the temperature range that the tan delta peak spans. Damping is the material's ability to dissipate any energy that would otherwise be added to the system by the applied force [37].

Using the temperature sweep testing method of DMA on an IPN system, differences in the glass transition temperature and the damping properties with changing composition can be analyzed. For example, Wang et al. [37] found a decrease in glass transition with the softer polyurethane component of the polyurethane and epoxy based IPN system by observing the tan delta curves. It was also found that the damping of the system increased with the soft polyurethane component. With the observation of only one peak for each IPN composition of the system, good compatibility between the two components of the IPN system was concluded.

Additional information about the molecular movement and relaxation of the material can be analyzed by doing a combination sweeps of both temperature and frequency. This analysis is done by conducting a frequency sweep at temperature intervals. The frequency sweep curves at each temperature interval can then be shifted around a determined reference curve to create a master curve. An example of a storage modulus master curve can be seen in Figure 32.

![Figure 32: DMA storage modulus master curve example.](image-url)
This process is called time temperature superposition (TTS) and gives the ability to analyze the material over a frequency range that is much larger than the DMA machine is capable of measuring. By selecting a common reference temperature for the TTS of the master curves, varying compositions of an IPN system can be compared. By observing how the lower and upper limits of the storage modulus change with changing composition, IPN modulus selection is possible by changing the composition of the system accordingly. Similarly to the storage modulus, master curves of the loss modulus and tan delta can be created by TTS as well.

7.5 Tensile Testing

Tensile testing is an important material analysis to be performed. The results of a tensile test can help in material selection for varying engineering applications. Mechanical properties of a material can be found by doing tensile testing and these properties can help in the prediction of material behavior in various forms of loading [43]. Important information can be determined from a tensile test such as the maximum stress a material can withstand before failure, or the maximum stress a material can withstand before plastic deformation.

When performing a tensile test, the sample is placed between two grips. A strain gage is placed in the middle of the sample’s length and the sample is subjected to tension. The initial gage length and the sample’s initial cross sectional area are the two most important measurements to initially have. The force applied to the sample is converted to stress values as represented by the equation

\[ \sigma = \frac{F}{A_0} \]  

where \( F \) is force and \( A_0 \) is the original cross-sectional area. The change in gage length resulting from the tension is converted to strain values by the equation
where $L_0$ is the original gage length and $\Delta L$ is the difference between $L_0$ and the current gage length, L. Normally, a stress vs. strain curve is generated for the tensile test. An example of this curve can be seen in Figure 33.

\[
\varepsilon = \frac{\Delta L}{L_0}
\]  

(3)

In the curve, there are two different deformations occurring in the sample: Elastic and plastic. Elastic deformation occurs initially in the linear region of the curve. In this deformation region, the sample would go back to its original form if the force were to be released. After a certain amount of stress is applied to the sample, it will most likely enter plastic deformation where the original form will not be reached if the tensile force were to stop. From the Elastic deformation region of the curve, the young’s modulus can be found of the material. This can be determined by finding the slope of the linear line or by the following relationship:

Figure 33: Stress-Strain curve example.
Along with young’s modulus, the ultimate stress, ultimate strain, the yield strength, and the point of failure can be seen. The ultimate stress is the maximum stress that occurs within the curve. This value could occur at the failure point or at some other point before failure. Similarly, the ultimate strain is the maximum strain reached by the sample. The yield strength is the point at which plastic deformation starts to occur or in other words, the point when the curve is no longer linear. The right end of the curve is the failure point of the sample.

Tensile testing can help in the characterization and identification of IPNs. IPNs are known to have very good mechanical properties [37] such as increased toughness, tensile strength and ultimate strain [44]. Atwawale et al. [36] found that the tensile strengths of IPNs composed of UA and PGMA components increased with increasing amounts of the tougher component, PGMA. It was also found that the elongation at break increased with the increasing amount of the softer component of UA. Wang et al. [37] found similar results with the ultimate strength increasing as the ultimate strain decreased in a polyurethane and epoxy based IPN system. This suggests the ability to control mechanical properties such as elongation capacity and toughness of IPNs based on the compositional makeup.

$$E = \frac{\sigma}{\varepsilon} \quad (4)$$
8 Procedures for Each Characterization

The control samples were produced with 11 different acrylic/epoxy weight ratios of 100/0, 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, 10/90, and 0/100. Three different sets of samples were prepared to be analyzed. The first set of samples were polymerized using a polychromatic light source for 10 minutes in a nitrogen environment without post curing. The second and third sets of samples were cured using the same protocol as the first with the addition of thermal post curing at, respectively, 94°C and 150°C for four hours under normal atmospheric conditions. These samples were produced by Emilie Bobo from the University of Rouen, France. The production of the machine samples is described in section 5.3.1.

8.1 Thermogravimetric Analysis

A Netzsch TGA 209 apparatus was used for the TGA analysis. Samples of each composition were prepared from the control system by cutting cross-sectional slices from the bulk samples and removing the outer edges to make samples in the shape of a cube. Each cube had a mass somewhere between 10-15mg. Because the RP samples are small and thin, they were prepared by cutting multiple small pieces to fit in the pan until a total mass close to 10mg was achieved.

At least two tests were done on each composition in order to check for reproducibility of the TGA results. For each composition, one TGA pan was used and one baseline curve was generated. The pan was initially cleaned with acetone and also cleaned between each of the three tests. Each experiment was done from a temperature of 30°C to 700°C at a rate of 10°C/min in an oxygen free, nitrogen environment. After each compositional test, a new pan was used and a new baseline was created.
8.2 Differential Scanning Calorimetry

A Perkin Elmer DSC 8500 apparatus was used for the DSC analysis. Samples were prepared from the control system by cutting cross-sectional slices from each bulk sample compositions and removing the outer edges to make samples capable of fitting into a pan. Each sample had a mass somewhere between 10-15mg. Samples were prepared from each of the compositions of the RP system by cutting a single circular piece capable of fitting in the pan. Each if the RP samples weighed close to 10mg each. For each sample, a pair of a pans matching in weight with an allowable difference of ±0.03 mg were used. One pan contained the sample, while the second served as an empty reference pan.

The expected glass transition temperature of the pure acrylic sample is expected to be around -35˚C [45] while the glass transition temperature of the pure epoxy sample is expected to be around 197˚C [46]. In order to capture the glass transition anywhere between these two extreme values, a temperature range of -70˚C to 250˚C was used. A base line was first created with the furnace empty and then the DSC was calibrated with use of the reference materials of Indium and C\textsubscript{13}H\textsubscript{10}O. Indium has an onset melting point of about 156.6˚C while C\textsubscript{13}H\textsubscript{10}O has an onset melting point of 47.9˚C. It is important that the two reference materials chosen have a large difference in melting points in order to accurately calibrate for the entire temperature range. The change in heat capacity of indium is 28.62 J/g and is used for the accurate energy calibration. By running each of these reference materials in the DSC and taking note of the measured onset melting points and change in heat capacity, the values could be compared to the theoretical values during machine calibration for improved accuracy.

After machine calibration, each sample was run two times in the desired temperature range of -70˚C to 250˚C and a temperature increase of 50˚C/min. The first run was used to evaluate any post curing phenomena that took place while the second curve was used to obtain the Tg and ΔCp values of the given composition. These values were then evaluated and compared to one another to aid the characterization of the IPN material.
8.3 Atomic Force Microscopy

This experimental procedure was performed by Wenlong Li from the University of Nebraska-Lincoln. Dimension 3100 SPM System along with Digital Instrument Nanoscope IIIa were used for the AFM analysis. The control and machine samples with the acrylic/epoxy compositions of 100/0, 80/20, 50/50, 20/80, and 0/100 were used for the analysis. The samples were prepared by first freezing using liquid nitrogen. Each sample was then cracked to obtain a transverse cross-section surface. This surface should be flat so that there is no interference with the movement of the probe. Freezing the samples aided in obtaining this surface. The samples were then cut to 5mm in diameter and 2.5mm in height. The samples were situated on silicon wafers and kept in petri dishes to avoid sample contamination.

The calibration of the AFM apparatus was performed by a specialist. The operation mode was set to tapping mode with a resolution of 0.5nm and an accuracy of 1nm. The probe type used was a silicon tip. The cantilever start and end frequencies were set to 100 kHz and 400 kHz respectively. These are the frequency limits that will be scanned to locate resonance [47]. Each sample was evaluated at a scan scale of 5μm, 1μm and 500nm at a scan rate of 0.8 Hz to 1 Hz. Both height and phase data was collected for each sample, resulting in a topographical and phase contrast image of the surface area.

8.4 Dynamic Mechanical Analysis

A Q800 Dynamic Mechanical Analyzer was used for the DMA. The control non-post cured system was initially tested isothermally in order to determine the best testing parameters for the acrylic/epoxy sample compositions of 100/0, 80/20, 50/50, 20/80, and 0/100. Non-post cured samples were tested because of the tendency of the post cured samples to break during testing due to their increased brittleness with thermal curing. The mode of testing was set to tension at a
temperature of 35°C with a log frequency sweep from 0.1 Hz to 100 Hz. Samples were polished to have a width around 3 mm and a thickness around 1 mm.

Each sample was inserted into the machine by first locking the free clamp and aligning the sample within it. The free clamp was then raised and locked to a position to obtain a sample length of approximately 10 mm. The sample was then tightened within the fixed clamp. The sample was then released and retightened within the free clamp to ensure there were no unexpected stresses present in the system. A torque of 5 in lbs was used to secure the stiffest pure epoxy sample within the clamps while the pure acrylic and 80/20 acrylic/epoxy samples were secured only by finger tightening. The 50/50 and 20/80 acrylic/epoxy samples were tightened with a torque of 2 in lbs and 4 in lbs respectively.

A preload was needed in order to keep the samples in tension throughout the entirety of the experiment. Preloads ranging from 0.01 N and 0.1 N were tested for each sample, along with an amplitude which would result in a load that was 1/3rd of the value of the used preload. By comparing storage modulus vs. frequency plots of the various preload and amplitude levels, the best preload, which maximized the measured modulus, was selected for temperature and frequency sweep testing of each sample.

A temperature sweep test was done on each of the control samples at the determined preload and amplitude values. Using the same preload and amplitude conditions as the control system, temperature sweep tests were also performed on the RP samples. Each sample was tested with a temperature range of -100°C to 50° higher than the glass transition temperature observed from the DSC analysis. Following the temperature sweep testing, the control system was also tested using a combination sweep method. The combination sweep included a frequency sweep from 0.1 Hz to 100 Hz at 10° temperature intervals with the same temperature range as used for the temperature sweep testing for each sample composition. By TTS of the combination sweep results, master curves were made and analyzed for each of the sample compositions.
8.5 Tensile Testing

The experimental procedure was performed by Wenlong Li from the University of Nebraska-Lincoln. MTS 810-Instron Machine along with the Bose Electroforce 3200 apparatus were used for the tensile test analysis. The MTS 810-Instron Machine had a maximum force at 25 kN while the Bose Electroforce 3200 apparatus had a maximum force cap at 225 N. Aramis 2M 3D Stereo-optical Surface Strain Measurement device was also used to measure the strain occurring in the sample during the test. The control system samples with the acrylic/epoxy compositions of 100/0, 80/20, 50/50, 20/80, and 0/100 were used for the analysis. The samples were cured in a silicon mold with the dimensions of 80mm x 10mm x 5mm. No additional sample preparation was needed before testing. This test was not performed on the RP samples because of their small size and non-uniform shapes.

The samples were placed in the grips with a testing length between 25mm and 30mm. The strain measurement device was placed at the center of the sample length. The tests were performed at a strain rate of 0.001 per second until sample failure. Each sample was tested three times to check for reproducible results. Resulting stress vs. strain data was retrieved from the testing for analysis.
9 Results and Discussion

9.1 Control Samples

The control samples were produced for the purpose of characterizing the system and identifying it as an IPN system. The characterization of this system was done with TGA, DSC, AFM, DMA, and tensile testing. These samples were prepared by the procedure described in section 8. The information gathered about the control system will help in the characterization of the machine samples in section 9.2.

9.1.1 Thermogravimetric Analysis

Each sample was analyzed three times to ensure reproducibility. All compositions produced reproducible results. From the results, the first samples tested of each composition were compared to one another. The mass degradation curve from this comparison of the non-post cured samples can be seen in Figure 34 and Figure 35 below.

Figure 34: TGA full degradation curve for non-post cured samples: acrylic/epoxy.
Figure 35: TGA close-up degradation curve for non-post cured samples: acrylic/epoxy.

Figure 35 shows the two homopolymers, acrylic and epoxy, as the most stable. It can be seen that as the percentage of acrylic component decreases, the thermal stability decreases. This is the trend until the 50/50 sample. As the percentage of acrylic component decreases from 50/50, the thermal stability increases again. This suggests that as more epoxy component is introduced to the system, the curing of the acrylic component is interfered. It is interesting that the 50/50 sample is the least stable, suggesting that the acrylic component introduced to the epoxy system also interferes with the curing of the system. Figure 34 shows, however, that despite variations in initial degradation temperatures, the temperature at which the highest rate of degradation occurs is similar for all non-post cured samples and is at around 400°C.

The 90°C post cured samples analyzed by the TGA show degradation differences from the non-post cured samples. The 90°C post cured sample degradation comparison can be seen as a close up view in Figure 36.
Similar to the non-post cured samples, the 90°C post cured samples all have a similar temperature at which the highest rate of degradation occurs at around 400°C. The post curing does however affect the stability of some of the sample compositions. While post curing does not have a negative effect on the highly epoxide samples, it does have negative effect on the acrylic samples. The acrylic homopolymer and highly acrylic samples such as the 80/20 composition show a large decrease in thermal stability from the non-post cured samples.

As the samples are introduced to additional post curing, the highly acrylic composed samples continue to decrease in thermal stability while the highly epoxy composed samples may even increase in stability. A set of samples were post-cured at 150°C. This is the post curing temperature at which the epoxy component of the samples should be completely cured. The TGA mass degradation curves of these samples can be seen in Figure 37 and in Figure 38.
Figure 37: TGA full degradation curve of 150°C post-cured samples: acrylic/epoxy.

Figure 38: TGA degradation curve of 150°C post cured samples: acrylic/epoxy.
Figure 38 shows that the samples with the highest amounts of epoxy components are the most stable including the 0/100, 10/90, and 20/80 samples. It also shows a decrease in stability in the highly acrylic components in comparison to the non-post cured and 90°C post-cured samples. In Figure 37 a larger variation of temperatures can be seen at which the highest rate of mass is degrading. This can be more easily observed by taking the first derivative of the degradation curves as has been done in Figure 39.

![Graph showing the first derivative of degradation curves.](image)

**Figure 39: 1st derivative 150°C of post-cured samples: acrylic/epoxy.**

From the derivative curves, it is observed that all of the peak mass degradation rates fall between the acrylic and epoxy homopolymer samples. The acrylic homopolymer sample has the lowest peak temperature at 350°C while the epoxy has the highest at 400°C. This agrees with the findings of Athawale et al. [36] that the thermal stability of IPN components falls between those of the homopolymers. By looking more closely, it can even be observed that the thermal stability
is increasing with the epoxy component of the IPN. This agrees with the more specific findings of Wang et al. [37] that the thermal stability of an IPN increases with compositional change. The TGA is the first indication of an IPN system present.

9.1.2 Differential Scanning Calorimetry

Each sample was run on the DSC once to finish the post curing processes, and once to obtain the Tg and ΔCp values of each IPN sample. Curves from the DSC analysis can be found in section A.3 with the results of Tg and ΔCp summarized in Table 5.

<table>
<thead>
<tr>
<th>Composition acrylic/epoxy</th>
<th>Non-Post Cured</th>
<th>90°C Post Cured</th>
<th>150°C Post Cured</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tg, C, ΔCp, J/gC</td>
<td>Tg, C, ΔCp, J/gC</td>
<td>Tg, C, ΔCp, J/gC</td>
</tr>
<tr>
<td>100/0</td>
<td>-31 0.65</td>
<td>-31 0.51</td>
<td>-27 0.51</td>
</tr>
<tr>
<td>90/10</td>
<td>-25 0.57</td>
<td>-24 0.51</td>
<td>-24 0.55</td>
</tr>
<tr>
<td>80/20</td>
<td>-22 0.52</td>
<td>-21 0.44</td>
<td>-17 0.49</td>
</tr>
<tr>
<td>70/30</td>
<td>-12 0.41</td>
<td>-15 0.25</td>
<td>-11 0.37</td>
</tr>
<tr>
<td>60/40</td>
<td>-7 0.30</td>
<td>-10 0.31</td>
<td>2 0.34</td>
</tr>
<tr>
<td>50/50</td>
<td>21 0.32</td>
<td>15 0.14</td>
<td>12 0.28</td>
</tr>
<tr>
<td>40/60</td>
<td>31 0.24</td>
<td>27 0.22</td>
<td>14 0.19</td>
</tr>
<tr>
<td>30/70</td>
<td>33 0.18</td>
<td>41 0.14</td>
<td>33 0.13</td>
</tr>
<tr>
<td>20/80</td>
<td>45 0.12</td>
<td>51 0.07</td>
<td>100 0.19</td>
</tr>
<tr>
<td>10/90</td>
<td>130 0.19</td>
<td>99 0.21</td>
<td>137 0.15</td>
</tr>
<tr>
<td>0/100</td>
<td>135 0.48</td>
<td>175 0.11</td>
<td>150 0.33</td>
</tr>
</tbody>
</table>

One glass transition temperature was observed for each sample tested. The Tg values were between the values of -31°C and 175°C which correspond to the theoretical Tg values of the acrylic and epoxy components respectively. For the acrylic component used, BPA-EDA Richards et al. [45] observed a glass transition of -34°C. By use of dynamic mechanical analysis, Kim et al. [46] observed the glass transition of the epoxy component used, ECH to be 197°C. Both published glass transition temperature values for the homopolymers are similar to those measured. The difference is expected in the epoxy component because of the typical behavior of
the DMA testing method to produce higher Tg values than the DSC testing method [48]. The Tg values of the IPN systems varying in composition increase with a decreasing fraction of the epoxy component. This can be more clearly seen in graphical form as shown in Figure 40.

Figure 40: Glass transition temperature of non-post cured, 90°C post cured, 150°C post cured samples.

As seen in the figure, the increase in Tg with decreasing acrylic fraction is consistent with or without being post cured. This indicates good interpenetration within the system as suggest by Athawale et al. [36]. The change in ΔCp with changing composition can also be easily observed in graphical form as seen in Figure 41.
Figure 41: $\Delta C_p$ of non-post cured, 90°C post cured, 150°C post-cured samples.

Similar to the Tg values, the $\Delta C_p$ trend is similar regardless of the post curing treatment. $\Delta C_p$ tends to decrease with decreasing acrylic fraction with a minimum peak at around the composition of 20/80 and 30/70 acrylic/epoxy samples.

9.1.3 Atomic Force Microscopy

AFM was performed on five 150°C post cured samples including the acrylic and epoxy homopolymer samples along with the 20/80, 50/50, 80/20 acrylic/epoxy compositions. The topographical and phase contrast images of the various acrylic/epoxy composition samples can be seen in Figure 42.
Figure 42: AFM results of acrylic/epoxy composition, 1μm square; Topographical image on left, phase contrast image on right.
In the figure, the topographical images are on the left while the phase contrast images are on the right for every sample. In the topographical images, the brighter regions represent the higher regions of the surface in comparison to the darker regions. In the phase contrast images, the epoxy component is represented as the brighter regions while the acrylic component is represented as the darker regions.

In the 20/80 sample, phase boundaries can be seen by the acrylic component causing the epoxy component to appear in clusters. In the 80/20 acrylic/epoxy sample, both the components can be seen clustering slightly. However, when you compare the 80/20 acrylic/epoxy topographical image to the phase contrast image, it can be seen that the brighter epoxy regions may in fact be the result of the height differences at the surface.

Unlike the 20/80 and 80/20 acrylic/epoxy samples, the 50/50 acrylic/epoxy sample appears to be much smoother with no obvious component clustering. This suggests that the 50/50 sample is more homogenous than the 20/80 or the 80/20 samples. This does not agree with the findings of Wang et al. [37] who describe finding heterogeneity changing with changing IPN composition. Improved homogeneity with the 50/50 composition could suggest an increase in mechanical properties as well which will be observed in section 9.1.5.

When comparing the pure epoxy sample with the 20/80 acrylic/epoxy sample and the pure acrylic sample with the 80/20 acrylic/epoxy sample, similarities in the phase contrast images can be seen. In the pure epoxy sample, phase boundaries are observed clustering lighter colored regions similar to that of the 20/80 acrylic/epoxy sample. In the pure acrylic sample, clustering of both lighter and darker regions are observed, similar to that of the 80/20 acrylic/epoxy sample. Because of these similarities, the 20/80 and 80/20 acrylic/epoxy samples are also concluded to be homogeneous.
9.1.4 Dynamic Mechanical Analysis

From the isothermal testing of the control system, it was determined that all sample compositions would be tested with a preload of 0.02 N. The isothermal results can be seen in the appendix, section A.6. Temperature sweeps of the non-post cured control system including acrylic/epoxy compositions of 100/0, 80/20, 50/50, 20/80, and 0/100 were performed. The full results can be found in the appendix, section A.7. The tan delta curves of the results can be seen in Figure 43 below.

![Figure 43: DMA temperature sweep of control acrylic/epoxy samples at 10 Hz.](image)

From the figure, it can be seen that the glass transition temperature increases with the increase of the tougher epoxy component. This confirms the results of the DSC as described in section 9.1.2. It is also seen that the damping of the system increases with the increase of the tougher epoxy component. This can be seen by the broadening of the tan delta peak with
increasing epoxy. This is the opposite phenomena as observed by Wang et al. [37], who reported observing increased damping with the increase of the soft component of the polyurethane and epoxy system tested.

In every case, a single peak is observed, indicating good compatibility between the two components. In the case of the 20/80 acrylic/epoxy sample, however, the peak appears to be very broad with a flat peak. This may indicate that the interpenetration at this composition is not as high as for compositions consisting of higher amounts of the acrylic component. Additional testing on other samples including the acrylic/epoxy compositions of 30/70 and 10/90 would help in verifying this conclusion.

A combination sweep of temperature step and frequency sweep was performed on the control system samples in order to generate master curves of each composition using a reference of 20°C. The storage modulus, loss modulus, and tan delta master curves can be seen in the appendix, section A.9. From the master curves, the lower and upper storage modulus limits can be observed with the change of system composition. This can be seen plotted in Figure 44.

Figure 44: Storage modulus limits with composition at 20°C.
This figure shows that as the acrylic component increases in the system composition, both the upper and lower storage modulus limits decrease. The upper modulus limit decreases from around 10,000 MPa to 6,000 MPa while the lower limit decreases from around 40 MPa to 10 MPa with increasing acrylic component. Both limits appear to be following an exponential curve. It is also important to know the frequency range that is included within the upper and lower onsets of the storage modulus of each system composition. The lower and upper frequency onsets with changing system composition can be seen in Figure 45 below.

![Figure 45: Onset frequency limits for lower and upper modulus limits at 20°C.](image)

The lower frequency limit represents the onset of the lower modulus limit of the master curve. Likewise, the upper frequency limit represents the onset of the upper modulus of the master curve. At 20°C, all frequency values higher than the upper frequency onset, represented as red squares in Figure 45, will achieve the upper modulus limit. All frequency values lower than the lower frequency onset, represented as blue diamonds, will achieve the lower modulus limit. Frequency values between the lower and upper frequency onset curves represent the modulus...
transition area of the system. Figure 44 and Figure 45 can be used together to aid in the IPN system composition selection for a modulus needed for a particular engineering application. This similar approach can be used in the loss modulus and tan delta of the material as well.

9.1.5 Tensile Testing

Each sample was tested twice to check for reproducibility. All sample tests were proven to be reproducibly. The resulting stress-strain curves of the non-post cured, 90°C post cured, and 150°C post cured samples can be seen in section A.10. The young’s modulus, ultimate strain, and ultimate stress values obtained from the stress-strain curves are summarized in Table 6.

<table>
<thead>
<tr>
<th>Composition acrylic/epoxy</th>
<th>Young’s Modulus (GPa)</th>
<th>Ultimate Strain (%)</th>
<th>Ultimate Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Non-post cured</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100/0</td>
<td>0.015</td>
<td>11.2</td>
<td>1.41</td>
</tr>
<tr>
<td>80/20</td>
<td>0.012</td>
<td>7</td>
<td>0.65</td>
</tr>
<tr>
<td>50/50</td>
<td>0.229</td>
<td>10.6</td>
<td>6.2</td>
</tr>
<tr>
<td>20/80</td>
<td>1.28</td>
<td>2.6</td>
<td>27.1</td>
</tr>
<tr>
<td>0/100</td>
<td>3.44</td>
<td>1.26</td>
<td>38.6</td>
</tr>
<tr>
<td><strong>90°C post cured</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100/0</td>
<td>0.015</td>
<td>10.6</td>
<td>1.4</td>
</tr>
<tr>
<td>80/20</td>
<td>0.0104</td>
<td>7.7</td>
<td>0.77</td>
</tr>
<tr>
<td>50/50</td>
<td>0.16</td>
<td>13.5</td>
<td>6.63</td>
</tr>
<tr>
<td>20/80</td>
<td>1.62</td>
<td>4.97</td>
<td>39.6</td>
</tr>
<tr>
<td>0/100</td>
<td>3.31</td>
<td>1.32</td>
<td>38.8</td>
</tr>
<tr>
<td><strong>150°C post cured</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100/0</td>
<td>0.012</td>
<td>6.9</td>
<td>0.86</td>
</tr>
<tr>
<td>80/20</td>
<td>0.008</td>
<td>10.2</td>
<td>0.95</td>
</tr>
<tr>
<td>50/50</td>
<td>0.12</td>
<td>12.9</td>
<td>5.77</td>
</tr>
<tr>
<td>20/80</td>
<td>1.49</td>
<td>5.3</td>
<td>32.9</td>
</tr>
<tr>
<td>0/100</td>
<td>2.98</td>
<td>1.7</td>
<td>42.2</td>
</tr>
</tbody>
</table>
For the non-post cured samples, it can be seen that the epoxy homopolymer has the highest stress before failure while the acrylic homopolymer has the highest strain percentage. Once the samples encounter some post curing, there is a change in this. For the 90°C post cured samples, the ultimate stress level of the 20/80 sample increases higher than that of the epoxy homopolymer. The maximum strain percentage for the 50/50 sample increases to be greater than that of the acrylic homopolymer. When the samples are post cured at 150°C, the epoxy homopolymer sample gets stronger and achieves the greatest ultimate stress level. The stress of the 50/50 sample is still obtaining the highest level of strain percentage.

Because post curing at 150°C results in the most stable epoxy component, as seen in TGA results in section 9.1.1, it is important to look in more detail at the ultimate stress and ultimate strain trends with relationship to composition. A graphical view of this can be seen in Figure 46.

**Figure 46:** Ultimate stress and strain in 150°C post cured samples.
As discussed before, the ultimate strain increases with increased amount of the tough epoxy component. The ultimate strain is expected to decrease with decreasing epoxy component as found in studies conducted by Atawale et al. [36] and wang et al. [37]. It is seen instead that the ultimate strain has a maximum value for the 50% epoxy component. A similar phenomenon is seen in a study of an IPN composed of polyurethane and acrylate components conducted by Hourston et al. [49]. It was discovered that a maximum ultimate strain occurred at a composition of 80/20 polyurethane to acrylate components along with a maximum toughness.

The introduction of the epoxy component into the acrylic homopolymer causes the ultimate strain to increase. This could be because the epoxy component adds enough strength to delay failure while the acrylic component is able to contribute to the mobility of the system. With a greater than 50% epoxy component present in the IPN system, the epoxy strength is too high to enable the mobility of the acrylic component. In future studies, it would also be interesting to see if the toughness is also at a maximum at the 50/50 composition as well.

9.2 RP Samples

The characterization of the RP samples will help in identifying them as an IPN system. The characterization will be done with several methods including TGA, DSC, and AFM. Tensile testing could not be done with these samples because of their small size and non-uniform shape. The results of the machine system analysis will be compared to the control system for an overall analysis of the acrylic and epoxy system. The machine samples were prepared by the procedure described in section 5.3.1.
9.2.1 Thermogravimetric Analysis

TGA was performed two times on each machine made samples to ensure reproducible results. All compositions were concluded to be reproducible. The mass degradation curve of all RP IPN compositions of acrylic/epoxy can be seen in Figure 47.

![Figure 47: TGA of machine samples: acrylic/epoxy.](image)

From the figure, it can be seen that the epoxy homopolymer is the most thermally stable while the acrylic being the least thermally stable. The other compositions degrade at temperatures that are between the acrylic and epoxy degradation temperatures. This is what was expected because it follows the same trend as the 150°C post cured control samples. The machine IPN samples were post cured at 150°C so it is important that they are compared to the
150°C post cured control samples. Figure 48 shows a close up of the mass degradation curves of all RP made samples in comparison to the 150°C post cured control samples.

![TGA comparison of machine and control IPN samples: acrylic/epoxy.](image)

**Figure 48:** TGA comparison of machine and control IPN samples: acrylic/epoxy.

In this figure, each composition is represented by a different color where the composition made in the machine is represented by a solid line and the same control composition sample is represented by a hatched line of the same color. Each machine sample appears to be less thermally stable than its corresponding control sample. This can be more clearly seen in Figure 49 where each composition is separated from the others for a better degradation analysis.
Figure 49: TGA comparison of acrylic/epoxy RP and control samples.
Figure 49 shows a close up view of the mass degradation of each RP made sample in comparison to the same control sample composition. When looking at these curves, it can be seen that the acrylic homopolymer RP sample is just slightly less thermally stable than the control sample. With the increase in epoxy component to the system, the thermal stability decreases in the RP samples as seen in the 80/20, 50/50, and 20/80. The epoxy homopolymer RP sample in comparison to its control sample is much less stable than the acrylic homopolymer in comparison to its control sample.

The thermal stabilities of the RP samples in comparison to the control system samples suggest that the introduction of the epoxy component to the system affects the thermal stability. This could be the result of the low light source power of the machine in comparison to the power of the polychromatic light source used to cure the control samples. This does not lead to the belief that the 80/20, 50/50, and 20/80 samples are not IPNs. The samples in the machine follow the same trends as the control system, common to those of IPN systems.

### 9.2.2 Differential Scanning Calorimetry

DSC analysis was conducted on the RP samples. Each sample was run once to finish any post curing and a second time to gather the Tg and ΔCp values from the resulting curves. The DSC curves can be found in section A.4. The Tg and ΔCp results for each RP sample in comparison to the control samples are summarized in Table 7.

<table>
<thead>
<tr>
<th>Composition</th>
<th>RP Samples</th>
<th>Control Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>acrylic/epoxy</td>
<td>Tg, C</td>
<td>ΔCp, J/gC</td>
</tr>
<tr>
<td>100/0</td>
<td>-37</td>
<td>0.835</td>
</tr>
<tr>
<td>80/20</td>
<td>-36</td>
<td>0.572</td>
</tr>
<tr>
<td>50/50</td>
<td>-28</td>
<td>0.441</td>
</tr>
<tr>
<td>20/80</td>
<td>63</td>
<td>0.356</td>
</tr>
<tr>
<td>100/0</td>
<td>82</td>
<td>0.302</td>
</tr>
</tbody>
</table>
Because the RP samples were post cured at 150°C after photo curing, the control samples used for comparison are of the 150°C post cured system. In every case, the glass transition temperatures of the RP samples are much lower than those of the control samples with the same composition. A graphical view of the glass transition temperature comparison can be seen in Figure 50.

![Graph showing Tg comparison between RP samples and control samples.]

**Figure 50:** Tg comparison between RP samples and control samples.

It can be seen that both the Tg RP samples follow the same trends as the control samples. Like the control system, there is only one Tg observed for every sample composition. The Tg values increase with increasing epoxy component, suggesting that the 80/20, 50/50, and 20/80 compositions made in the RP machine are in fact IPNs.

The ΔCp values of the RP samples on the other hand, tend to be much greater than those of the control samples with the same composition. A graphical view of the ΔCp comparison between the RP and the control samples can be seen in Figure 51.
Figure 51: ΔCp comparison between RP samples and control samples.

It can be seen that the ΔCp values of the RP samples are much larger but follow the same trends as the control samples, similar to the Tg of the RP samples.

Similar to the TGA results, the same trends are seen from the DSC analysis for both the RP and control samples, but the values are much different. This again leads to the conclusion that there is a different curing kinetics occurring in the RP environment than in the controlled environment. It is a possibility that the low powered light source in the RP machine is not fully curing the material and the post curing is responsible for a larger percentage of curing than in the control system. Analysis on only thermal curing the homopolymers in comparison to photo curing will give more insight to this as seen in section 9.3.

9.2.3 Atomic Force Microscopy

AFM was performed on the samples produced in the RP machine including the homopolymers and the acrylic/epoxy composition samples of 20/80, 50/50, and 80/20. The topographical and phase contrast images can be seen in Figure 52.
Figure 52: AFM results of acrylic/epoxy compositions, 1μm square; Topographical image on left, phase contrast image on right.
In the figure, the topographical images are on the left while the phase contrast images are on the right for every sample. In the topographical images, the brighter regions represent the higher regions of the surface in comparison to the darker regions. In the phase contrast images, the epoxy component is represented as the brighter regions while the acrylic component is represented as the darker regions.

By comparing the phase contrast images of the different compositions it can be seen that the 50/50 sample has very little property variation for much of the square area. Very subtle grain boundaries can be observed in the 20/80 sample where spots of bright epoxy areas are separated from one another. In the 80/20 sample, much larger property variations are observed where both the acrylic and epoxy areas are separated from one another. This is the same trend as observed in the control sample AFM analysis as seen in section 9.1.3.

This leads to the conclusion that the 50/50 composition is the most homogeneous of the three samples tested. However, all samples have a phase distribution not exceeding ±4° suggesting that all samples are to be considered homogeneous. This is further concluded when comparing the pure epoxy sample to the 20/80 acrylic/epoxy and the pure acrylic to the 80/20 acrylic/epoxy sample in which similarities of the phase contrast images are observed. The pure epoxy sample is observed to have similar phase boundary characteristics as the 20/80 acrylic/epoxy sample and the pure acrylic sample is observed to have similar phase clustering as the 80/20 acrylic/epoxy sample.

The phase contrast images of the RP machine samples as seen in Figure 52 have a slightly different and less pronounced look with the phase changes than in the control samples. Because the machine samples are small in comparison to the control samples, the sample surfaces were prepared in a slightly different way. This may be contributing to this difference in the images.
9.2.4 Dynamic Mechanical Analysis

Temperature sweep DMA testing was performed on non-post cured RP samples of the acrylic/epoxy compositions of 80/20, 50/50, and 20/80. The results can be found in the appendix, section A.8. The tan delta curves of the 80/20 and 50/50 samples can be seen in Figure 53 below.

![Figure 53: DMA temperature sweep of RP acrylic/epoxy samples at 10 Hz.](image)

In the figure, the 20/80 acrylic/epoxy sample is not shown because it was too fragile to complete the testing of the DMA. The 80/20 and 50/50 acrylic/epoxy samples however, can give a good idea of the trends of the system. The 50/50 sample has one large peak and another smaller peak. This would suggest that the RP system is not as highly interpenetrated as the control system. The 50/50 peak is broader than the 80/20 peak indicating that the damping of the system increases with the increase of the stiffer epoxy component. This is the same trend as seen with the control system. The curve differences between the RP system and the control system can be analyzed by directly comparing the two as shown in Figure 54 below.
Figure 54: DMA temperature sweep of non-post cured acrylic/epoxy RP and control samples.

In this figure, it can be seen in both cases the RP sample has a higher and narrower peak than that of the control sample. This indicates that there is less of an effect of the epoxy component within the RP system. This could be the result of lack of curing of the epoxy component within the RP machine which further supports the conclusions resulting from the DSC results. However, because the DMA was performed on non-post cured samples and decreasing and widening tan delta peak occurring with increasing epoxy component is still observed, it can be concluded that the RP machine is capable of partially photo curing the epoxy component.

9.3 Thermal Cured Samples

Because of the difference in characteristics seen between the control and RP machine samples, acrylic and epoxy thermally cured homopolymer samples were analyzed. The samples were made by thermally curing the homopolymers at 150°C for 16 hours in a dark, oxygen free environment. TGA and DSC were used to help in the characterization of these thermally cured samples. The results will help in understanding the difference between the control and RP machine samples seen in the previous sections of this chapter.
9.3.1 Thermogravimetric Analysis

TGA was performed on the acrylic and epoxy homopolymers cured thermally. Each of the homopolymers was tested twice to check for reproducible results. In each case, the results were reproducible. The mass degradation of the thermal cured epoxy sample can be seen in Figure 55 along with the UV cured epoxy samples for comparison.

![Graph showing mass degradation comparison](image)

**Figure 55: Mass degradation comparison of thermal and UV curing of epoxy homopolymer.**

It can be seen that the thermal curing has an effect on the mass degradation of the epoxy component. Degradation starts to occur around 200°C for thermal curing in comparison to 350°C for the UV-cured samples with and without post curing. While the thermal stability of the epoxy homopolymer is weakened by thermal curing, the acrylic homopolymer is strengthened. The mass degradation of the thermally cured acrylic component in comparison to the UV-cured samples can be seen in Figure 56.
Figure 56: Mass degradation comparison of thermal and UV curing of acrylic homopolymers.

Figure 56 shows that the UV-cured, non-post cured acrylic homopolymer has the highest thermal stability while the UV-cured, 150°C post cured has the lowest. It is interesting to see that while post curing the UV-cured acrylic homopolymer the thermal stability decreases but by only thermal curing the homopolymer, the thermal stability is improved.

The TGA results of the thermally cured homopolymers help to explain why the thermal stability of the RP machine made samples are weaker than the control samples. The results support the theory that the low power of the machine UV light source is not capable of fully curing the epoxy component of the IPN samples resulting in a higher percentage of thermal curing conversion from post curing. Because the thermal stability is decreased in the epoxy homopolymer by thermal curing, it is possible that full curing is not occurring.

9.3.2 Differential Scanning Calorimetry

DSC was performed on the thermal cured homopolymers in order to evaluate the differences in Tg and ΔCp between thermal curing and UV-curing. The DSC curves can be
found in section A.5. The Tg and ΔCp results of the thermal cured homopolymers in comparison to the UV-cured homopolymers are summarized in Table 8.

Table 8: Tg comparison of thermal and UV curing.

<table>
<thead>
<tr>
<th></th>
<th>Thermal Curing</th>
<th>UV Curing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tg, C  ΔCp, J/gC</td>
<td>Non-post cured</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tg, C  ΔCp, J/gC</td>
</tr>
<tr>
<td>Epoxy</td>
<td>30 0.37</td>
<td>135 0.48</td>
</tr>
<tr>
<td>Acrylic</td>
<td>-42 0.66</td>
<td>-31 0.65</td>
</tr>
</tbody>
</table>

The most surprising result from the DSC curves is the Tg of the thermal cured epoxy homopolymer. By thermal curing the epoxy homopolymer a very low Tg of 30°C results in comparison to the 150°C Tg of the UV-cured sample. The thermal cured acrylic homopolymer also has a low Tg of -42°C compared to the UV-cured sample with a Tg of -27°C.

Two different possibilities can be concluded from the DSC and TGA results. The first is that the curing kinetics is quite different between the thermal and UV curing of the epoxy component resulting in different characteristics. The second possibility is that the curing of the epoxy component is not completed in the thermal curing environment. In either case, the results help to support the theory that increased thermal curing from the post curing process is taking place in the machine samples due to the inability of the low powered light source of the machine to fully cure the epoxy component.
10 Summary

This thesis was a study of interpenetrating polymer network systems (IPNs) and rapid prototyping in the attempt to combine the two. With the ability to produce gradient IPNs within a rapid prototyping system, property control on a molecular level could be theoretically obtained. This would be highly beneficial to progressing technologies of rapid prototyping and to the manufacturing industry as a whole. The benefit of achieving property gradient prototyped objects is the ability to eliminate the need for an interface between two properties and/or materials.

There were two main purposes to this thesis. The first purpose was to build a rapid prototyping machine capable of producing IPNs. The second purpose was to characterize the acrylic and epoxy based system used and to identify it as an IPN system. A rapid prototyping machine was made using the stereo-lithography (SL) rapid prototyping concept. A basic SL machine was manufactured which was capable of making complex three-dimensional shapes. Modifications were made to this machine in order to successfully produce the acrylic and epoxy homopolymers of the IPN system. Once this was accomplished, modifications were made to the machine to produce IPNs of varying compositions of the homopolymers. By conducting thermal, mechanical and phase distribution analysis on the system, it was characterized and identified as an IPN system.

10.1 Experimental Analysis

A control system was made outside of the machine with a high powered polychromatic light source. Samples were made with varying compositions of the acrylic and epoxy compositions. Three different sets of samples were analyzed; non-post cured samples, 90°C post cured samples, and 150°C post cured samples. These systems were characterized by using the methods of TGA, DSC, AFM, DMA and tensile testing. The characteristics of the control system included increasing thermal stability with composition, a single glass transition temperature
changing with composition, homogeneous phase distributions, damping properties changing with composition, and changing of mechanical properties. Because the control system had characteristics similar to those of other IPN systems seen in literature, it was concluded that it can be identified as an IPN system.

Two sets of samples were made in the RP machine with one post cured at 150°C after photo curing and the other not-post cured. The RP system was characterized by using the methods of TGA, DSC, AFM, and DMA. The TGA, DSC, and AFM results of the 150°C post cured control system were compared to those of the 150°C post cured samples made within the RP machine. The DMA results of the non-post cured control system were compared to those of the non-post cured samples made within the RP machine. The characteristics of the RP samples included increasing thermal stability with composition, a single glass transition temperature changing with composition, homogeneous phase distributions, and damping properties changing with composition. All of the trends observed with the RP machine system were the same as with the control system. However, the RP samples had thermal stabilities and glass transition temperatures much lower than those of the control samples. The light source of the machine has a lower output power than that of the polychromatic light source used to cure the control system. Because of this, the machine may not be able to cure a high percentage of the system. A higher percentage of curing may be occurring during the thermal curing during the post curing process.

TGA and DSC analysis were done on the epoxy and acrylic homopolymers thermally cured to see if a higher percentage of thermal curing could have an effect on the overall properties. The results were compared to those of the photo cured control system. It was found that thermal curing resulted in a small decrease in thermal stability and glass transition temperature in the acrylic homopolymer and a large decrease in the epoxy homopolymer. This leads to the conclusion that the weaker light source within the rapid prototype machine was not capable of curing a large percentage of the epoxy component of the system resulting in a higher percentage of curing occurring in the thermal post curing process. The post curing process either
has different curing kinetics in comparison to photo curing, or it is not capable of completing the curing process. These are the two possible reasons for the property change seen between the thermal and photo cured homopolymers and between the RP system and control system. However, because the RP machine samples had the same characteristic trends as the control system, it can be concluded that the rapid prototyping machine is capable of producing IPNs.

10.2 Future Work

The preliminary goal of producing an IPN within a rapid prototyping machine was accomplished. However, progress will continue to be made to accomplish the overall goal of producing a gradient IPN within a rapid prototyping machine with properties changing on the molecular level.

A new machine will be built to increase the accuracy and speed of printing. This will be done by introducing a new light source with an increased level of power. Ideally, this light source would enable the ability to change and control the wavelength and the output power. This will help in the curing rate of the resin and will also be a parameter of control when producing a gradient IPN. The future machine design is described in more detail in section 6 including the initial machine weaknesses that need to be changed.

Determining how to vary and control the properties of the IPN system to form a gradient is the most important next step in the continuation of this project. Variation between photo and thermal curing and uncured material removal are a couple of ideas of how to proceed with this. Because the curing kinetics of the radical acrylic component is so fast, both ideas involve fully curing the acrylic component while having control over the percentage of curing within the cationic epoxy component.

As seen in the RP machine system analysis, property variation may have been taking place by varying the amount UV curing taking place in comparison to the thermal post curing. The acrylic component of the system would likely always fully cure because of its rapid curing
kinetics while only a desired percentage of the epoxy component would photo cure. Additional studies will need to be conducted to see if the property variations seen in this thesis are because of a difference in the curing kinetics between the UV and thermal curing or if the property variations seen are because the reaction time of the thermal curing is too slow to complete the curing. Depending on the results, this could be a good idea for property variation and control.

Another idea for property control is similar to the previous one in that the acrylic component would be completely cured under a UV light source and a controlled percentage of the epoxy component would be cured. Instead of thermally curing the remaining uncured resin of the epoxy component, it would be washed away with a solvent such as acetone. This would result in a compositional change between the acrylic and epoxy components within the interpenetrating polymer network system. These are just some of the challenges that will be faced in the near future of this project.

The fields of rapid prototyping and material science are continually growing. The accomplishment of rapid prototyping gradient IPNs for the purpose of property variation within an object will open the door to new ideas in these continually evolving fields of study.
References


[46] *Photopolymerization of 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate and tri (ethylene glycol) methyl vinyl ether.* Kim, Young-Min, Kostanski, Kris and MacGregor, John F. 2003, Polymer 44, pp. 5103-5109.


Appendices

A.1 Linear Displacement per Revolution of Acme Rod

The following are the motor stepping calculations used for the programming of the sanguino. The results are also useful in understanding the accuracy of the different stepping options of the motor. This is found referenced in section 4.2.

\[
\frac{1 \text{ in}}{16 \text{ rev}} = \frac{25.4 \text{ mm}}{1 \text{ in}} \times \frac{1 \text{ in}}{16 \text{ rev}} = 1.5875 \text{ mm/rev}
\]

Motor steps per revolution:

\[
\text{Full step} = 200 \frac{\text{steps}}{\text{rev}} \quad \frac{1}{2}\text{ step} = 400 \frac{\text{steps}}{\text{rev}} \quad \frac{1}{8}\text{ step} = 1600 \frac{\text{steps}}{\text{rev}}
\]

1/2 step linear displacement per step:

\[
\frac{1.5875 \text{ mm}}{\text{rev}} \times \frac{\text{rev}}{200 \text{ steps}} = 0.00794 \text{ mm/step}
\]

1/2 step linear displacement per step:

\[
\frac{1.5875 \text{ mm}}{\text{rev}} \times \frac{\text{rev}}{400 \text{ steps}} = 0.00397 \text{ mm/step}
\]

1/8 step linear displacement per step:

\[
\frac{1.5875 \text{ mm}}{\text{rev}} \times \frac{\text{rev}}{1600 \text{ steps}} = 0.00099 \text{ mm/step}
\]
A.2 Theoretical Curing Time Analysis Example

The following calculation is an example of determining the theoretical curing time of the acrylic resin given the diameter of the cured spot, the light wavelength, the light source power, the thickness of the resin layer being cured and the density of the photo initiator molecules within the resin. This is found referenced in section 5.1.

\[ d = 863 \mu m \quad \lambda = 355 \text{nm} \quad P = 500 \mu W \quad t = 1 \text{m} \quad \rho = 4.42 \times 10^{19} \text{molecules/mL} \]

\[ V = \pi \left( \frac{d}{2} \right)^2 \quad t = \pi \left( \frac{0.863 \text{mm}}{2} \right)^2 \times 1 \text{mm} = 0.585 \text{mm}^3 \]

\[ 0.001 \text{mL} = 1 \text{mm}^2 \quad V = 0.000585 \text{mL} \]

\[ \text{Molecules} = \frac{V}{\rho} = \frac{0.000585 \text{mL}}{4.42 \times 10^{19} \text{molecules/mL}} = 2.585 \times 10^{16} \text{Molecules} \]

\[ E = \frac{hc}{\lambda} \]

\[ h = \text{Planck's constant} = 6.626 \times 10^{-34} \text{Js} \quad c = \text{speed of light} = 300 \times 10^6 \text{m/s} \]

\[ E = \frac{6.626 \times 10^{-34} \text{J sec} \times 300 \times 10^6 \text{m sec}}{355 \times 10^{-9} \text{m}} = 5.599 \times 10^{-19} \text{J photon} \]

\[ \text{Emission} = \frac{P}{E} = \frac{0.0005 \text{W}}{5.599 \times 10^{-19} \text{J photon}} = 8.929 \times 10^{14} \text{photons/sec} \]

\[ \text{time} = \frac{\text{Molecules}}{\text{Emission}} = \frac{2.585 \times 10^{16} \text{Molecules}}{8.929 \times 10^{14} \text{photons/sec}} = 28 \text{seconds} \]
A.3 **Control System DSC Curves**

The following are the DSC curves of the non-post cured and 150°C post cured control system. In every case, the blue dotted line represents the 1st run and the green solid represents the 2nd run. These are found referenced in section 9.1.2.

![DSC curve of non-post cured 100/0 acrylic/epoxy control sample](image1)

**Figure A-1:** DSC curve of non-post cured 100/0 acrylic/epoxy control sample.

![DSC curve of non-post cured 90/10 acrylic/epoxy control sample](image2)

**Figure A-2:** DSC curve of non-post cured 90/10 acrylic/epoxy control sample.
Figure A-3: DSC curve of non-post cured 80/20 acrylic/epoxy control sample.

Figure A-4: DSC curve of non-post cured 70/30 acrylic/epoxy control sample.
Figure A-5: DSC curve of non-post cured 60/40 acrylic/epoxy control sample.

Figure A-6: DSC curve of non-post cured 50/50 acrylic/epoxy control sample.
Figure A-7: DSC curve of non-post cured 40/60 acrylic/epoxy control sample.

Figure A-8: DSC curve of non-post cured 30/70 acrylic/epoxy control sample.
Figure A-9: DSC curve of non-post cured 20/80 acrylic/epoxy control sample.

Figure A-10: DSC curve of non-post cured 10/90 acrylic/epoxy control sample.
Figure A-11: DSC curve of non-post cured 0/100 acrylic/epoxy control sample.

Figure A-12: DSC curve of 90°C post cured 100/0 acrylic/epoxy control sample.
Figure A-13: DSC curve of 90°C post cured 90/10 acrylic/epoxy control sample.

Figure A-14: DSC curve of 90°C post cured 80/20 acrylic/epoxy control sample.
Figure A-15: DSC curve of 90°C post cured 70/30 acrylic/epoxy control sample.

Figure A-16: DSC curve of 90°C post cured 60/40 acrylic/epoxy control sample.
Figure A-17: DSC curve of 90°C post cured 50/50 acrylic/epoxy control sample.

Figure A-18: DSC curve of 90°C post cured 40/60 acrylic/epoxy control sample.
Figure A-19: DSC curve of 90°C post cured 30/70 acrylic/epoxy control sample.

Figure A-20: DSC curve of 90°C post cured 20/80 acrylic/epoxy control sample.
Figure A-21: DSC curve of 90°C post cured 10/90 acrylic/epoxy control sample.

Figure A-22: DSC curve of 90°C post cured 0/100 acrylic/epoxy control sample.
Figure A- 23: DSC curve of 150˚ C post cured 100/0 acrylic/epoxy control sample.

Figure A- 24: DSC curve of 150˚ C post cured 90/10 acrylic/epoxy control sample.
Figure A-25: DSC curve of 150°C post cured 80/20 acrylic/epoxy control sample.

Figure A-26: DSC curve of 150°C post cured 70/30 acrylic/epoxy control sample.
Figure A-27: DSC curve of 150°C post cured 60/40 acrylic/epoxy control sample.

Figure A-28: DSC curve of 150°C post cured 50/50 acrylic/epoxy control sample.
Figure A- 29: DSC curve of 150°C post cured 40/60 acrylic/epoxy control sample.

Figure A- 30: DSC curve of 150°C post cured 30/70 acrylic/epoxy control sample.
Figure A-31: DSC curve of 150°C post cured 20/80 acrylic/epoxy control sample.

Figure A-32: DSC curve of 150°C post cured 10/90 acrylic/epoxy control sample.
Figure A-33: DSC curve of 150°C post cured 0/100 acrylic/epoxy control sample.
A.4  RP System DSC Curves

The following are the DSC curves of 150°C post cured RP samples. In every case, the blue dotted line represents the 1\textsuperscript{st} run and the green solid represents the 2\textsuperscript{nd} run. These are found referenced in section 9.2.2.

![Figure A-34](image)

Figure A-34: DSC curve of 150°C post cured 100/0 acrylic/epoxy RP sample.

![Figure A-35](image)

Figure A-35: DSC curve of 150°C post cured 80/20 acrylic/epoxy RP sample.
Figure A-36: DSC curve of 150°C post cured 50/50 acrylic/epoxy RP sample.

Figure A-37: DSC curve of 150°C post cured 20/80 acrylic/epoxy RP sample.
Figure A-38: DSC curve of 150°C post cured 0/100 acrylic/epoxy RP sample.
A.5 Thermally Cured Homopolymer DSC Curves

The following are the DSC curves of the thermally cured system with no previous photo curing. In every case, the blue dotted line represents the 1\textsuperscript{st} run and the green solid represents the 2\textsuperscript{nd} run. These are found referenced in section 9.3.2.

Figure A-39: DSC curve of thermal cured acrylic homopolymer.

Figure A-40: DSC curve of thermal cured epoxy homopolymer.
A.6 Control System Isothermal DMA Testing

The following figures are the isothermal DMA results of the control system. The preload was varied in order to find the preload at which the modulus was maximized. These are found referenced in section 9.1.4.

Figure A-41: DMA isothermal testing of 100/0 acrylic/epoxy control sample.

Figure A-42: DMA isothermal testing of 80/20 acrylic/epoxy control sample.
Figure A-43: DMA isothermal testing of 50/50 acrylic/epoxy control sample.

Figure A-44: DMA isothermal testing of 20/80 acrylic/epoxy control sample.
Figure A-45: DMA isothermal test of 0/100 acrylic/epoxy control sample.
A.7 Control System Temperature Sweep DMA Testing

The following figures are the DMA temperature sweep curves of the control system. The data includes the storage modulus, loss modulus and tan delta results. In every case, a preload of 0.02 N was used with an oscillating frequency of 10 Hz with a heating rate of 1° per minute. The amplitude was selected to be a value resulting from 1/3rd of the preload force of each sample composition by using theoretical modulus information obtained from tensile testing results. These are found referenced in section 9.1.4.

Figure A-46: DMA temperature sweep of 100/0 acrylic/epoxy control sample with an amplitude of 1.5 μm.
Figure A-47: DMA temperature sweep of 80/20 acrylic/epoxy control sample with an amplitude of 1.7 μm.

Figure A-48: DMA temperature sweep of 50/50 acrylic/epoxy control sample with an amplitude of 0.10 μm.
Figure A- 49: DMA temperature sweep of 20/80 acrylic/epoxy control sample with an amplitude of 0.02 μm.

Figure A- 50: DMA temperature sweep of 0/100 acrylic/epoxy control sample with an amplitude of 0.007 μm.
A.8 RP System Temperature Sweep DMA Testing

The following figures are the DMA temperature sweep curves of the RP system. The data includes the storage modulus, loss modulus and tan delta results. In every case, a preload of 0.02 N was used with a oscillating frequency of 10 Hz with a heating rate of 1˚ per minute. The amplitude was selected to be scaled from the corresponding control sample to fit the geometry difference. These are found referenced in section 9.2.4.

Figure A- 51: DMA temperature sweep of 80/20 acrylic/epoxy RP sample with an amplitude of 1.3 μm.
Figure A-52: DMA temperature sweep of 50/50 acrylic/epoxy RP sample with an amplitude of 0.1 μm.
A.9 Control System Combination Sweep DMA Testing

The following figures are the master curves of the control system resulting from the TTS of the combination sweep of the DMA. The storage modulus, loss modulus, and tan delta curves are shown for the acrylic/epoxy compositions of 100/0, 80/20, 50/50, 20/80, and 0/100. For every curve, the reference temperature of 20°C was used. These are found referenced in section 9.1.4.

Figure A- 53: DMA storage modulus master curve of 100/0 acrylic/epoxy control sample.
Figure A-54: DMA storage modulus master curve of 80/20 acrylic/epoxy control sample.

Figure A-55: DMA storage modulus master curve of 50/50 acrylic/epoxy control sample.
Figure A- 56: DMA storage modulus master curve of 20/80 acrylic/epoxy control sample.

Figure A- 57: DMA storage modulus master curve of 0/100 acrylic/epoxy control sample.
Figure A- 58: DMA loss modulus master curve of 100/0 acrylic/epoxy control sample.

Figure A- 59: DMA loss modulus master curve of 80/20 acrylic/epoxy control sample.
Figure A-60: DMA loss modulus master curve of 50/50 acrylic/epoxy control sample.

Figure A-61: DMA loss modulus master curve of 20/80 acrylic/epoxy control sample.
Figure A-62: DMA loss modulus master curve of 0/100 acrylic/epoxy control sample.

Figure A-63: DMA tan delta master curve of 100/0 acrylic/epoxy control sample.
Figure A- 64: DMA tan delta master curve of 80/20 acrylic/epoxy control sample.

Figure A- 65: DMA tan delta master curve of 50/50 acrylic/epoxy control sample.
Figure A-66: DMA tan delta master curve of 20/80 acrylic/epoxy control sample.

Figure A-67: DMA tan delta master curve of 0/100 acrylic/epoxy control sample.
A.10 Control Sample Stress-Strain Curves

The following figures are the results from the tensile testing of the control system. The non-post cured, 90°C post cured, and 150°C post cured samples are shown. These are found referenced in section 9.1.5.

**Figure A- 68:** Stress-strain curve of non-post cured samples: acrylic/epoxy

**Figure A- 69:** Stress-strain curve of 90°C post cured samples: acrylic/epoxy
Figure A-70: Stress-strain curve of 150°C post cured samples: acrylic/epoxy