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3D Printed Bone Supplement Materials

Azem Khalifa Yahamed

Western Michigan University, azemsoc@hotmail.com

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3D PRINTED BONE SUPPLEMENT MATERIALS

by

Azem Khalifa Yahamed

A dissertation submitted to the Graduate College
in partial fulfillment of the requirements
for the degree of Doctor of Philosophy
Chemical and Paper Engineering
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Doctoral Committee:

Alexandra Pekarovicova, Ph.D., Chair
Paul Dan Fleming, Ph.D.
Pavel Ikonomov, Ph.D.
Three-dimensional (3D) printing is an advanced rapid technology that can be used to make human bone substitutes with exact shape and designed structures, based on models created from actual individual bone medical Digital Imaging and Communications in Medicine (DICOM) images. Biocompatible polymers have been selected for 3D printing of human bone structures. The thermoplastics were 3D printed with Fused Deposition Modeling (FDM) are Acrylate Butadiene Styrene (ABS), Polylactic Acid (PLA) and ULTEM 9085 (a polyetherimide). The polyamide PA 2200 was 3D printed using Selective Laser Sintering (SLS). Digital ABS™ (a crosslinked acrylic polymer) was 3D printed using PolyJet™ Technology. These 3D printing technologies allow precision manufacturing of bone structures for replacement of the missing/broken parts created from actual Magnetic Resonance Imaging (MRI) or Computed Tomography (CT) scan DICOM images. Differential Scanning Calorimetry (DSC) was used to acquire the thermal analysis profiles of these polymers. The thermal analysis results indicate that ABS and ULTEM9085 are amorphous, PLA is partially crystalline, and PA2200 is completely crystalline. To use these materials as a bone replacement, thorough mechanical property testing was performed to evaluate if the 3D printed bone replacement structures can sustain the same loads that human bones experience.

Furthermore, it is important to create bone structures that can accurately mimic the real human bone structures with a solid outer shell that represents the cortical (compact) bone and porous internal volume that represents the trabecular (spongy) bone.
Designing of the proper trabecular bone is one of the most critical steps, because its structure helps support the entire bone, while at the same time keeps the weight low. Due to the low resolution of the DICOM images, the trabecular bone structure cannot be obtained directly from CT and MRI scans.

Therefore, CAD software SolidWorks was used to design special 3D honeycomb structures (hexagonal, triangular, and square). The honeycomb structures are widely used in industry and aerospace applications, because they provide high strength, while reducing the weight, cost, and density.

3D printed samples were designed and produced to test the structure properties with different geometric shapes. Structure property tests, such as: tensile strength test, compressive strength test, and bending test were investigated. We found that the mechanical properties of the designed thermoplastic structures either exceed or fall within the range of the mechanical properties of the human trabecular bones. Therefore, they can be successfully applied for bone structure replacements.
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Azem Khalifa Yahamed
# TABLE OF CONTENTS

ACKNOWLEDGMENTS ............................................................................................................. ii
LIST OF TABLES ...................................................................................................................... vii
LIST OF FIGURES ..................................................................................................................... ix

CHAPTER

1. INTRODUCTION ................................................................................................................ 1
   1.1 Background and General Overview .............................................................................. 1
   1.2 Polymer Advantages ........................................................................................................ 6
   1.3 Polymer Biocompatibility ............................................................................................... 7
   1.4 Tissue Engineering (TE) ............................................................................................... 7
   1.5 Three-dimensional Printing ......................................................................................... 8

2. LITERATURE REVIEW ..................................................................................................... 9
   2.1 Bone Surgical Replacement ......................................................................................... 9
   2.2 Bone Tissue .................................................................................................................. 10
   2.3 Building Bone Structure ............................................................................................. 11
       2.3.1 Anatomical Geometry ......................................................................................... 11
       2.3.2 Internal Structure (Cellular scaffold) ................................................................. 11
       2.3.3 Mechanical Properties ....................................................................................... 12
       2.3.4 Degradation Rates ............................................................................................ 13
       2.3.5 Porosity and Pore Size ....................................................................................... 15
   2.4 Three-dimensional Printing Technology .................................................................... 17
   2.5 Common Methods of 3D Printing Technology ............................................................ 18
       2.5.1 Selective Laser Sintering ................................................................................... 18
       2.5.2 Fused Deposition Modeling (FDM) ..................................................................... 20
       2.5.3 Stereolithography ............................................................................................... 22
       2.5.4 PolyJet Technology ............................................................................................ 23
   2.6 3D Honeycomb Scaffolds ........................................................................................... 24
### Table of Contents–Continued

**CHAPTER**

3. PROBLEM STATMENT AND OBJECTIVES ................................................................. 25

3.1 Tasks .................................................................................................................. 26

3.1.1 Testing the Structure Properties of 3D Printed Samples at 100% Infill .......... 26

3.1.2 Testing the Structure Properties of 3D Printed Samples Designed with Different Internal Structure (Geometric Shape) ......................................................... 27

3.1.3 Testing the Surface Topography of Thin Layers of 3D Printed Samples ...... 27

3.1.4 Thermal Analysis using Differential Scanning Calorimetry (DSC) .......... 28

4. THERMOPLASTICS FOR MEDICAL APPLICATIONS BY 3D PRINTING .......... 29

4.1 Introduction ......................................................................................................... 29

4.1.1 Building Bone Structures ............................................................................. 29

4.1.2 Fused Deposition Modeling ......................................................................... 30

4.1.3 Selective Laser Sintering (SLS) .................................................................. 31

4.1.4 Stereolithography .......................................................................................... 32

4.1.5 PolyJet Technology ....................................................................................... 32

4.2 Experimental ....................................................................................................... 33

4.2.1 3D Printing of Test Samples ........................................................................ 33

4.2.2 Testing Mechanical Properties of 3D Printed Samples using MTS .......... 34

4.2.3 Creating of 3D Bone Structure Model using OsiriX .................................. 36

4.2.4 Cleaning 3D Model using MeshLab ............................................................ 37

4.2.5 Thermal Analysis by Differential Scanning Calorimetry (DSC) ............... 38

4.3 Results and Discussion ....................................................................................... 39

4.3.1 Tensile Strength Tests .................................................................................. 39

4.3.2 Compressive Tests ......................................................................................... 42

4.3.3 Bending Tests ............................................................................................... 46

4.3.4 Compressive Tests for ABS Cubes .............................................................. 48

4.3.5 Thermal Analysis ......................................................................................... 51

4.4 Conclusion ......................................................................................................... 55
Table of Contents–Continued

CHAPTER
5. DESIGNED HONEYCOMB STRUCTURES FOR BONE REPLACEMENT .......... 58
   5.1 Introduction ........................................................................................................ 58
   5.1.1 Honeycomb Structures ............................................................................... 58
   5.1.2 Three Dimensional Printing....................................................................... 58
   5.1.3 Thermoplastics............................................................................................. 59
   5.1.4 Biomaterials................................................................................................. 60
   5.1.5 Bioprinting................................................................................................... 60
   5.2 Experimental .................................................................................................... 61
   5.2.1 3D Printing of Test Samples....................................................................... 61
   5.2.2 Testing Mechanical Properties of 3D Printed Samples using MTS-Machine.. 63
   5.2.3 Calculating Void Volume and Percentage of Infill for Designed Structures .. 63
   5.3 Results and Discussions ................................................................................ 64
   5.3.1 Tensile Strength Tests ................................................................................. 64
   5.3.2 Compressive Strength ............................................................................... 68
   5.3.3 Bending Strength....................................................................................... 73
   5.4 Conclusion........................................................................................................ 78

6. BIOPOLYMERS FOR 3D PRINTED BONE STRUCTURE ................................ 82
   6.1 Introduction ........................................................................................................ 82
   6.1.1 Three–dimensional Printing ...................................................................... 82
   6.1.2 Biomaterials................................................................................................. 82
   6.1.3 Bioprinting................................................................................................... 83
   6.1.4 Fused Deposition Modeling....................................................................... 83
   6.1.5 PolyJet Photopolymerization................................................................... 84
   6.2 Experimental .................................................................................................... 85
   6.2.1 3D Printing of Test Samples....................................................................... 85
   6.2.2 Creating 3D Bone Structure Model............................................................. 88
   6.3 Results and Discussions ................................................................................ 91
   6.4 Conclusion........................................................................................................ 99
CHAPTER

7. CONCLUSIONS AND FUTURE OUTLOOK .......................................................... 102

REFERENCES ........................................................................................................ 111

APPENDICES ........................................................................................................ 122

A. Figures of the Tensile Strength tests for the Materials Printed at 100% Infill ... 122
B. Figures of the Compressive Strength tests for the Materials Printed at 100% Infill .......................................................... 125
C. Figures of the Flexural Strength tests for the Materials Printed at 100% Infill .. 129
D. Figures of the Compressive Strength tests for ABS Cubes Printed at 100% Infill at two different speed rates 0.2 mm/s and 0.05 mm/s ............... 132
E. Figures of the Tensile Strength tests for designed structures ....................... 135
F. Figures of the Compressive Strength tests for designed structures ............... 140
G. Figures of the Flexural Strength tests for designed structures ..................... 145
LIST OF TABLES

1. Selected Properties of Thermoplastic materials from MSDS ................................................. 34
2. Tensile Strength of the Thermoplastics at 100% Infill after testing with
   MTS machine ....................................................................................................................... 41
3. Tensile Strength and Young’s Modulus per unit mass for the Thermoplastics
   at 100% Infill ....................................................................................................................... 41
4. Compressive Strength and Compressive Modulus for selected materials from
   MSDS ................................................................................................................................. 42
5. Compressive Strength and Compressive Modulus after testing with MTS machine .. 45
6. Compressive Strength and Compressive Modulus per unit mass for the
   Thermoplastics at 100% ....................................................................................................... 46
7. Flexural Strength and Flexural Modulus for selected materials from MSDS. ........ 47
8. Flexural Strength and Flexural Modulus after testing with MTS machine
   at 100% Infill ...................................................................................................................... 47
9. Flexural Strength and Flexural Modulus per unit mass for the Thermoplastics
   at 100% Infill ...................................................................................................................... 47
10. Compressive Strength and Compressive Modulus for ABS cubes for
    low strain region ................................................................................................................ 50
11. Compressive Strength and Compressive Modulus for ABS cubes for
    high strain region .............................................................................................................. 51
12. Selected Properties of Thermoplastic Materials. ............................................................... 61
13. Void volume fraction and Percentage of Infill for designed structures. ......................... 63
14. Tensile Strength and Young’s modulus for different geometric structures.
    Standard deviation of Young’s modulus was calculated from the standard error of the
    coefficient of the linear term in a quadratic fit to the tensile data. ................................. 64
15. Tensile Strength and Young’s Modulus per unit mass for designed structures........... 68
16. Compressive Strength and Compressive Modulus for selected Materials
    from MSDS ......................................................................................................................... 69
17. Compressive Strength and Compressive Modulus for various geometries.
    Standard deviation of Young’s Modulus was calculated from the standard error of the
    coefficient of the linear term in a quadratic fit to the compression data. ......................... 69
18. Compressive Strength and Compressive Modulus per unit mass for
    designed structures ............................................................................................................ 73
19. Flexural Strength and Flexural Modulus for selected Materials from MSDS............ 74
20. Flexural Strength and Flexural Modulus for structures. Standard deviation of
    Young’s Modulus was calculated from the standard error of the coefficient of the
    linear term in a quadratic fit to the bending data. ............................................................ 74
List of Tables–Continued

21. Flexural Strength and Flexural Modulus per unit mass for designed structures........ 78
22. Mechanical Properties of Thermoplastic Materials........................................... 85
23. Conditions of the thermoplastic Polymers Printing............................................. 86
24. Thickness and Roughness ABS, PLA and PVA printed in 1-3 layers,
    oriented at 45°...................................................................................................... 92
25. Thickness and Roughness ABS and PVA oriented at 90° ..................................... 94
26. Thickness and Roughness of ABS and PVA Printed at 45° using
    MakerBot Replicator 2X..................................................................................... 96
27. Thickness and Roughness of ABS Printed at 45° using MakerBot
    Replicator 2X and FlashForge Creator Pro.......................................................... 97
28. Thickness and Roughness of digital ABS™ Printed using
    Stratasys Objet 500 Connex3.............................................................................. 98
29. Stratasys 500 Objet Connex3, Maker Bot, and Flash Forge
    Thickness and Roughness.................................................................................... 101
LIST OF FIGURES

1. Selective Laser Sintering. ................................................................. 19
2. Fused Deposition Modeling................................................................. 21
3. Schematic of Stereolithography........................................................... 22
4. 3D printing principle used by Stratasys PolyJet Technology [89]. ........ 23
5. 3D Printing Tensile test Sample on MakerBot. ............................... 34
6. ROI and Segmentation in OsiriX......................................................... 37
7. 3D model created after Segmentation in OsiriX.................................. 37
8. (A) 3D model of vertebra cleaned by MeshLab. ............................... 38
   (B) 3D Printed bone vertebra structure............................................. 38
9. Tensile Stress-Strain calculated from least squares fit to tensile data  for the materials................................................................. 40
10. Compressive Stress-Strain calculated from fits at 100% Infill for the materials in X. 43
11. Compressive Stress-Strain calculated from fits at 100% Infill for the materials in Z. ................................................................. 43
12. Stress-Strain calculated from fit to bending data at 100% Infill for the materials. .... 47
13. ABS cubes Stress-Strain calculated from fit at 100% Infill for high strain in X, Y, Z for compression rate 0.2 mm/s.......................... 49
14. ABS cubes Stress-Strain calculated from fit at 100% Infill for high strain in X, Y, Z for compression rate 0.05 mm/s.......................... 50
15. Thermal Analysis of ABS................................................................. 52
16. Thermal Analysis of PLA................................................................. 53
17. Thermal Analysis of ULTEM9085.................................................... 54
18. Thermal Analysis of PA2200............................................................ 55
19. Hexagonal Honeycomb Structure..................................................... 62
20. Triangular Honeycomb Structure..................................................... 62
21. Square Honeycomb Structure.......................................................... 62
22. Tensile Strength vs. Young’s Modulus............................................. 65
23. ULTEM9085 structures Stress-Strain calculated from fit ................ 66
24. PA2200 structures Stress-Strain calculated from fit......................... 67
25. Digital ABS™ structures Stress-Strain calculated from fit ................ 67
26. Compressive Modulus vs. Compressive Strength.............................. 70
27. ULTEM9085 structures Stress-Strain calculated from fit to compression data. ...... 71
28. PA2200 structures Stress-Strain calculated from fit to compression data. ...... 72
29. Digital ABS™ structures Stress-Strain calculated from fit to compression data. ...... 72
30. Flexural Modulus vs. Flexural Strength of 3D Printed Polymer Structures........ 75
31. ULTEM9085 structures Stress-Strain calculated from fit. .................... 76
List of Figures—Continued

32. PA2200 structures Stress-Strain calculated from fit. .................................................. 77
33. Digital ABSTM structures Stress-Strain calculated from fit. ..................................... 77
34. 3D Printed Specimen one layer of PLA at 45° .............................................................. 85
35. Specimen imported by Makerware Software to be Printed ........................................... 87
36. 3D Printing of the Tensile test Sample ....................................................................... 87
37. Data loading in 3D Slicer [123] .................................................................................. 89
38. ROI and Segmentation in 3D Slicer [123] ............................................................... 89
39. 3D Models Created after Segmentation by 3D Slicer [123] ...................................... 90
40. 3D Printed Bone Femur Structure ............................................................................ 90
41. Topographic map of first layer Abs1 ........................................................................ 92
42. Topographic map of second layer ABS2 ................................................................. 92
43. Topographic map of third layer ABS3 ....................................................................... 93
44. Thickness and Roughness for ABS, PLA and PVA 1-3 layers Printed at 45° ........... 93
45. Thickness and Roughness for ABS (1 or 2 layers) and PVA layers Printed at 90° .... 94
46. ABS Thickness and Roughness for layers Printed at 45° with different designed Thickness using MakerBot Replicator 2X .................................................. 96
47. PVA Thickness and Roughness for layers Printed at 45° with different designed Thickness using MakerBot Replicator 2X .................................................. 97
48. ABS Thickness and Roughness for layers Printed at 45° with different designed Thickness using FlashForge Creator Pro ....................................................... 98
49. Digital ABSTM Thickness and Roughness for layers printed at 45° with different designed Thickness using Stratasys 500 Objet Connex3 ........................................ 99
50. ABS Stress-Strain and calculated (Stress-Strain) at 100% Infill ................................ 122
51. PLA Stress-Strain and calculated (Stress-Strain) at 100% Infill ................................ 122
52. ULTEM9085 Stress-Strain and calculated (Stress-Strain) at 100% Infill ................. 123
53. PA 2200 Stress-Strain and calculated (Stress-Strain) at 100% Infill ....................... 123
54. Digital ABSTM Stress-Strain and calculated (Stress-Strain) at 100% Infill ............ 124
55. ABS Stress-Strain and calculated (Stress-Strain) at 100% Infill in X ....................... 125
56. ABS Stress-Strain and calculated (Stress-Strain) at 100% Infill in Z ....................... 125
57. PLA Stress-Strain and calculated (Stress-Strain) at 100% Infill in X ....................... 126
58. PLA Stress-Strain and calculated (Stress-Strain) at 100% Infill in X ....................... 126
59. Digital ABSTM Stress-Strain and calculated (Stress-Strain) at 100% Infill in X ..... 127
60. Digital ABSTM Stress-Strain and calculated (Stress-Strain) at 100% Infill in Z ..... 127
61. ULTEM9085 Stress-Strain and calculated (Stress-Strain) at 100% Infill in X and Z ................................................................. 128
62. PA 2200 Stress-Strain and calculated (Stress-Strain) at 100% Infill in X and Z .... 128
63. ABS Stress-Strain and calculated (Stress-Strain) at 100% Infill .............................. 129
64. PLA Stress-Strain and calculated (Stress-Strain) at 100% Infill .............................. 129
List of Figures–Continued

65. ULTEM9085 Stress-Strain and calculated (Stress-Strain) at 100% Infill .................. 130
66. PA 2200 Stress-Strain and calculated (Stress-Strain) at 100% Infill .................. 130
67. Digital ABS™ Stress-Strain and calculated (Stress-Strain) at 100% Infill .......... 131
68. ABS cube Stress-Strain and calculated (Stress-Strain) at 100% Infill for high strain in X at speed rate 0.2 mm/s .......................................................... 132
69. ABS cube Stress-Strain and calculated (Stress-Strain) at 100% Infill for high strain in Y at speed rate 0.2 mm/s .......................................................... 132
70. ABS cube stress-strain and calculated (stress-strain) at 100% Infill for high strain in Z at speed rate 0.2 mm/s .......................................................... 133
71. ABS cube Stress-Strain and calculated (Stress-Strain) at 100% Infill for high strain in X at speed rate 0.05 mm/s ......................................................... 133
72. ABS cube Stress-Strain and calculated (Stress-Strain) at 100% Infill for high strain in Y at speed rate 0.05 mm/s ......................................................... 134
73. ABS cube Stress-Strain and calculated (Stress-Strain) at 100% Infill for high strain in Z at speed rate 0.05 mm/s ......................................................... 134
74. ULTEM9085Hexagonal structure Stress-Strain and calculated (Stress-Strain) .... 135
75. ULTEM9085 Triangular structure Stress-Strain and calculated (Stress-Strain) .... 135
76. ULTEM9085 Square structure Stress-Strain and calculated (Stress-Strain) .... 136
77. PA2200 Hexagonal structure Stress-Strain and calculated (Stress-Strain)......... 136
78. PA2200: Triangular structure Stress-Strain and calculated (Stress-Strain) .... 137
79. PA2200 Square structure Stress-Strain and calculated (Stress-Strain) ..... 137
80. Digital ABS™ Hexagonal structure Stress-Strain and calculated (Stress-Strain) ... 138
81. Digital ABS™ Triangular structure Stress-Strain and calculated (Stress-Strain) ... 138
82. Digital ABS Square structure Stress-Strain and calculated (Stress-Strain) .... 139
83. ULTEM9085 Hexagonal structure Stress-Strain and calculated (Stress-Strain) .... 140
84. ULTEM9085 Triangular structure Stress-Strain and calculated (Stress-Strain) .... 140
85. ULTEM9085 Square structure Stress-Strain and calculated (Stress-Strain) .... 141
86. PA2200 Hexagonal structure Stress-Strain and calculated (Stress-Strain) .... 141
87. PA2200 Triangular structure Stress-Strain and calculated (Stress-Strain) .... 142
88. PA2200 Square structure Stress-Strain and calculated (Stress-Strain) .... 142
89. Digital ABS Hexagonal structure Stress-Strain and calculated (Stress-Strain) .... 143
90. Digital ABS Triangular structure Stress-Strain and calculated (Stress-Strain) .... 143
91. Digital ABS Square structure Stress-Strain and calculated (Stress-Strain) .... 144
92. ULTEM9085 Hexagonal structure Stress-Strain and calculated (Stress-Strain) .... 145
93. ULTEM9085 Triangular structure Stress-Strain and calculated (Stress-Strain) .... 145
94. ULTEM9085 Square structure Stress-Strain and calculated (Stress-Strain) .... 146
95. PA2200 Hexagonal structure Stress-Strain and calculated (Stress-Strain) .... 146
96. PA2200 Triangular structure Stress-Strain and calculated (Stress-Strain) .... 147
List of Figures–Continued

97. PA2200 Square structure Stress-Strain and calculated (Stress-Strain).................... 147
98. Digital ABS Hexagonal structure Stress-Strain and calculated (Stress-Strain)........ 148
99. Digital ABS Triangular structure Stress-Strain and calculated (Stress-Strain). ...... 148
100. Digital ABS Square structure Stress-Strain and calculated (Stress-Strain)......... 149
CHAPTER 1
INTRODUCTION

1.1 Background and General Overview

Polymers have been used in medicine for long time. Their use medically varies from conventional applications such as syringes, catheters to matrices for drug delivery, cell encapsulation and tissue engineering. Polymers are categorized according to their chemical backbone, such as condensation polymers, or addition polymers, depending on the reaction by which they were synthetized. Depending on structure, they can be linear or branched. Polymers can be categorized based on whether they are natural (e.g. polypeptides) or synthetic (acrylates). These factors affect their biodegradability, they may be either degradable or non-degradable [1]. The degradable polymers include Polyvinyl alcohol (PVA), Polyglycolic acid (PGA), Polylactic acid (PLA) and Polycaprolactone (PCL), while non-degradable polymers include Polyethylene (PE), Polypropylene (PP), Polytetrafluoroethylene (PTFE or Teflon™), Polymethylmethacrylate, (PMMA or Plexiglass™) or Polyurethane (PU) among others.

The properties of polymers are predetermined by the structure of the polymer backbone and functional groups found on the polymer chain. The monomer units (blocks) and the linkages between monomers are built by various chemical reactions [1] [2]. Generally, carbon-carbon bonds are chemically and biologically inert [1] [3].

Polymer selection is based on many properties such as mechanical strength, simplicity of processing, inertness in a biological environment, blood compatibility, tissue adhesion, sharp resistance, wear-tear traits and permeability to oxygen among others. The main property, which will control the variety of criteria, is determined by the interaction
between these variables. For instance, in selecting a material for facial rebuilding or re-
enhancement purposes, moldability and inertness may be among the dominating factors for consideration [1].

Acceptable mechanical properties and structural features represent some of the requirements needed for skeletal tissue replacement. Synthetic polymers are used to make the articulating surface in joint rebuilding such as the entire hip and knee substitute. The original articulating surface has certain load bearing functions. An artificial substitute should match these requirements [1] [4].

Polyvinyl alcohol (PVA) is a degradable synthetic polymer produced by partial or full hydrolysis of polyvinyl acetate [5]. The physical characteristics, chemical properties, and mechanical properties of the polymer are determined by the degree of hydroxylation [5] [6]. The polymer is soluble in water, but resistant to organic fluids such as blood [5] [7]. Medically, PVA is used as a biomaterial because of its biocompatible, nontoxic, non-
carcinogenic and bio-adhesive characteristics [5] [8]. PVA has been used for damaged cartilage replacement and orthopedic applications because of its elastic and compressive mechanical properties [5].

Polyglycolic acid (PGA) is a rigid thermoplastic polymer that has high crystallinity. The melting temperature of the polymer is 225 °C and, due to its high crystallinity, is not soluble in most organic solvents [9]. PGA is used to make porous scaffolds, but properties and degradation rate and mode are affected by the procedures used during its synthesis.

Polylactic acid (PLA) is more hydrophobic than poly (glycolic acid) (PGA) and more resistant to hydrolytic attack than PGA. For most applications, the L (+) isomer of
lactic acid (LA) is chosen because it is preferentially metabolized in the body. The degradation of PLA, PGA and PLA/PGA copolymers in general involves random hydrolysis of their ester bonds. PLA degrades to form lactic acid, which is naturally found in the body. In the next step, lactic acid enters the tricarboxylic acid cycle and is emitted as water and carbon dioxide [9]. The biocompatibility of PLA and PGA has been determined in vitro and in vivo studies [9] [10].

Polycaprolactone (PCL) is a semicrystalline polymer and has a low melting temperature of 64 °C. The degradation rate of the polymer is lower than PLA and is a useful base for developing long term implantable drug delivery systems [9]. PCL has also been investigated for suitability as a scaffold for tissue repair through tissue engineering. The degradation time of the polymer ranges from two to three years [9] [11] [12] [13]. The degradation process of biodegradable polymers in medical application may result in water and carbon dioxide formation, and they are released from the body through the respiratory system [9] [14].

High density polyethylene (HDPE) is non degradable polymer with very high molecular weight ranges. PE shows good flexural and compressive modulus and an insignificant coefficient of friction. PE is used widely in orthopedic devices [1] [4].

Delrin™ is a synthetic polymer derived from poly (oxymethylene) and it is also known as polyacetal. It has been investigated as an alloplastic material in the rebuilding of mandibular joints [1] [15]. Research on retrieved implants has proven that, while the tissue response to PE and Delrin are similar, changes to the properties of the implant surface were clearly different. Generally, it was obvious the friction in recovered Delrin holes was two
times that of PE holes and the dimensional change was four times larger in Delrin [1] [16]. However, Delrin is used to make heart valve occluders [1]. Research on retrieved implants has shown that, while the tissue responds to PE and Delrin, PE has good enough wear-and-tear features [1] [17].

Polypropylene (PP) is a non degradable synthetic linear polymer, which is also used in some medical applications. Polypropylene mechanical properties are not proper for load bearing applications, but can be used in situations where it’s good fiber forming properties can be applied [1] [18] [19]. Lately, polypropylene (PP) fibers have been investigated for use in the delivery of tetracycline, an antimicrobial agent, to the root canal [1] [20]. The polymer is also now being used in mandibular and malar rebuilding [1] [21].

Polytetrafluoroethylene (PTFE), which is known as Teflon™, is a synthetic linear polymer with exceptional properties due to the greatly polarized C-F bonds along the backbone. Also, this polymer creates highly hydrophobic surfaces, which are biologically inert, non-biodegradable and have low friction properties. The exceptional strength of the fluorine-carbon (C-F) bond gives PTFE great chemical stability. The polymer is very resistant to fouling and because of its very low surface energy, nothing sticks to it. Extended PTFE has very good permeability to oxygen and has been used in many tissue-contact applications [1] [22]. The expansion process generates a microporous structure that gives the product unique mechanical properties. Also, it is used as a barrier membrane in guiding re-growth of bone in periodontal sites with good access [1] [23] [24] [25]. Since both Teflon and extended PTFE have an inert nature, they are used in orbital, re-enactment, and facial reconstruction [1] [26] [27] [28] [29]. The use of extended PTFE has been increased in dental and facial reconstruction. In the future, exponential use of the polymer
is expected to be seen in emerging disciplines such as tissue engineering, where inertness of the scaffold is significant. The bio-inertness of Teflon will continue to push its use in tissue contacting applications such as meshes for abdominal surgery and biliary stents [1][30].

Polymethylmethacrylate (PMMA), which is an addition copolymer of acrylic and methacrylic monomers, can be synthesized via UV curing. The polymer has been used as a bone cement in the fixation of artificial joints [1] [31] [32]. This linear copolymer has also been effectively applied in cranial reconstruction as a bone replacement [1]. The significance of the PMMA bone cement is in its formulation, which can be changed by adding bone supporting fillers such as hydroxyapatite or other tri-calcium salts [1].

Polyurethane (PU) is linear condensation polymer created by condensation of diisocyanates and short chain diols. It is a slow degrading polymer in nature that shows good blood compatibility. Because of its phase separated microstructure [1] [33], PU has been used for the fabrication of small diameter vascular grafts [1] [34] [35]. Since some enhancements in PU stability can be made, the polymer is investigated as a coating for biliary stents [1] [36] and in heart valve prosthesis [1] [37].

Polyaryletherketone (PEEK) is linear polymer with phenylene rings joined together by oxygen bridges. This is a biomaterial that is appropriate for medical implant use, allowing device makers to produce high performance implants with customized properties that are compatible with new medical methods [38].
1.2 Polymer Advantages

Polymers have been considered as a high performance implant material because of their advantages over metals. The main advantage is that the polymers are transparent to X-rays, thus enabling inspecting tissue or bone growth and repair using X-rays, which is impossible with metal parts due to the shadow cast by a metal implant in X-ray images, covering significant area for the physicians, making it hard or impossible to check [38].

Because of PEEK’s transparency to X-rays, no artifacts are created in CT images. MRI technology still can be used with patients that have received a plastic implant because plastics are non-magnetic. Surface modification technologies can be more simply used for organic surfaces, such as PEEK, than to a metal surface, which gives more advantages for parts with direct blood contact. [38].

Another advantage of plastics over metals is clearness of inspecting X-ray images following the progress of healing. Monitoring the healing process by current imaging technologies, such as CT, MRI and X-ray is an important issue. Another advantage when using plastic implants is that no metallic ions are released or react with the allergic tissues. In addition, is the reduced implant stiffness of plastic elements, which is more adapted to the stiffness of the enclosed bone. This decreases stress concentrations that can move to the bone and stimulates the healing process. Plastic processing technology gives more freedom in design and shape [38]. Plastics have low thermal conductivity and this is preferable from the patients’ view. Cranial plates made of titanium, which have great heat conductivity, cause pain when the temperature fluctuates dramatically around them such as, when the patient leaves a well-heated house to go outdoors in winter [39].
Polymers can be fabricated into different forms, by using some processing methods such as extrusion, injection and molding. One of the newest common methods of polymer extrusion is 3D printing technology.

1.3 Polymer Biocompatibility

Generally, any material that can be employed for a period of time as part of a system to treat or to substitute any tissue or organ is a biomaterial [40] [41]. Biomaterials should satisfy several requirements before they can be employed in medical applications [40] [42]. Therefore, different tests are recommended to evaluate biomaterial use and safety in medical application [40] [43]. To prove the biocompatibility of the material, different studies should be performed in vitro and clinical trials. Also, other studying areas including biology, chemistry, toxicology and pharmaceutics. The term biocompatibility includes many characteristics of the material such as mechanical, chemical and physical properties, as well as potential cytotoxic and allergenic effects [40] [43]. Biocompatible materials do not cause infection, irritation or any negative side effects. Surface energy, roughness, and chemistry have an important role in cell material interactions, mainly when studying an absorbable material [40] [44].

1.4 Tissue Engineering (TE)

The main purpose of TE is to replace, repair or renew damaged tissues. The surgical procedure is significant when normal physiologic reactions cannot take place. Presently, two standards are used, namely autografts and allografts. Everyone has some limitations including disease or the risk of disease transmission in both cases. In the scaffold-based TE method, it is significant that the contact of 3D-scaffold materials and cells take place by cell bond, growing, variation and biocompatibility. Scaffolds should be designed with
proper surface chemistry and morphology to support cellular functions with appropriate structural and physical properties such as mechanical strength, porosity and pore sizes [45]. Unlike kinds of organic and inorganic polymers and materials including natural and synthetic polymers and their compounds are used to fabricate biomaterial scaffolds. Scaffold materials should be designed to mimic the 3D structure of the native tissue and can act as delivery agents for growth factors, drugs, and antibiotics depending on the nature of the tissue to be repaired. Biomaterial scaffolds can be pre-manufactured either as solid structure or injectable forms that will be influenced by the nature of particular tissue engineering application [45].

1.5 Three-dimensional Printing

Three-dimensional printing is a new technology that allows generation of individually fitted implants based on medical 3D data. This new technology can produce various scaffolds with proper inner structure from biocompatible materials and with high precision. 3D printing for tissue-engineering application makes possible creating substituted tissues with specific heterogeneity. This is especially applicable for design of bone scaffolds with structural properties compatible with the heterogeneity and mechanical properties of the replaced bone tissue [46]. Biodegradable bone tissue-engineering scaffolds provide a foundation for renewing bone tissue, while supplying temporary mechanical support for improved regeneration. The synthetic materials for bone substitutes are widely used in medical applications. Part of our research is to test and investigate the mechanical properties of biocompatible polymer materials that can be used for 3D printing of human bone structure [46]. The synthetic materials of bone substitutes are widely used in medical applications.
CHAPTER 2
LITERATURE REVIEW

2.1 Bone Surgical Replacement

Bone surgical replacement is needed to help repair or replace damaged or diseased tissues ranging from trauma and degenerative disease, to cancer, and plastic surgery requirements [47]. Bone substitutes are important in such situations [47]. The production of tissue or organ structure needs a scaffold to direct the general shape and three-dimensional grouping of several cell types [47] [48] [49]. The inner architecture of a bone scaffold build is not trivial and different traits need to be considered, such as porosity, pore size, and interconnectivity of the scaffold tissue structure [47]. Tissue-engineering scaffold properties and behavior, such as porosity, surface area, pore size, pore interconnectivity, structural strength, shape and biocompatibility, are important factors in their design and manufacture. [47] [50] [51] [52].

The structure plays an important role in allowing flow of nutrients that would facilitate more vigorous growth of new cells [47]. The conventional process of scaffold manufacture includes solvent casting, fiber bonding, particulate leaching, membrane lamination, melt molding and gas foaming. These techniques pose several problems such as long manufacturing time, poor repeatability, unevenly formed pores, insufficient interconnectivity of pores, and limited form control [53] [54]. These limitations led the way to look for other manufacturing techniques that can provide the user with control over the structure of the scaffolds [53].
2.2 Bone Tissue

Bone tissue-engineering recommends a substitute solution to the traditional techniques of bone substitute, such as autografts and cellular bone replacement. It solves the problem of tissue damage caused by implants and the stress effects of implants that are currently used. More significantly, it can completely replace the missing bone tissue. One of the most advanced tissue-engineering methods that can be used for this purpose is the use of a permeable bioresorbable scaffold, supplied as a 3D template for original cell connection and consequent tissue structure rebuilding both in vitro and in vivo [55] [56] [57]. The target of tissue-engineering is to repair, maintain and enhance tissue functions, which have been lost by harsh pathological conditions, either by recreating tissues or by building up biological replacements.

The common tissue-engineering tactics are (i) inserting cell replacements into the organism, (ii) transporting tissue-inducing substance and (iii) placing cells on the scaffolds. The third tactic is more commonly linked with the idea of tissue-engineering with the use of living cells seeded on a natural or synthetic substrate to generate implantable pieces [58] [59]. Tissue-engineering scaffolds should fulfill three main goals: (i) they must describe a space that forms the renewing tissue; (ii) they should temporarily provide the original function (affected by the defects), while the tissue renews, and (iii) they should facilitate easy ingrowths of tissue and possibly allow for insertion of seeded cells to speed up tissue renewal. Scaffolds must meet health tissue hardness and strength requirements [60] [61] [62]. The scaffold for bone renewal should fulfill specific criteria: (i) The pore size should be greater than 300 micrometers. (ii) Good biocompatibility for scaffold design is required. The bone renewal rate should meet the degradation rate of the scaffold. (iii) The
scaffold should have mechanical properties similar to that of the bone being repaired [63] [64].

2.3 Building Bone Structure

2.3.1 Anatomical Geometry

The initial 3D geometry can be obtained using MRI or CT (Computed Tomography) scans of the actual body parts [65] [66]. Subsequently, 3D modeling software is used to create the new part or the model of the missing bone structure. The 3D model is then imported to the 3D printing software for building the replacement bone structure. Physical properties are considered very significant when scaffolds are used for tissue reconstruction. Scaffolds with suitable physical characteristics are special materials that can mimic the natural extracellular matrix (ECM). The ECM plays an important role in tissue structural design by supplying structural support and tensile strength. The manufacture and design of macro to nano-scale structural architectures have received much attention in medical applications. Three-dimensional scaffolds can renew tissue and organs to their normal physiological form [58].

2.3.2 Internal Structure (Cellular Scaffold)

The inner bone structure has a cellular scaffold structure. Cellular scaffold units, designed with different porosity and inner constructions, can supply tailored mechanical and biological properties. After designing the external bone structure model, the internal structure architecture, including pores, pore sizes and shapes, and their distribution, is engineered. As a result, the essential mechanical and biological properties of the bone structure can be matched to the real ones [47]. The benefits of the cellular scaffolds are as follows: (i) Cellular scaffolds keep their correct anatomical structure; (ii) They keep the
native extracellular matrix ECM architecture; (iii) The decellularization process facilitates similar biomechanical properties to those of native tissues [58].

2.3.3 Mechanical Properties

For proper bone structure replacement, the mechanical properties of the replacement materials need to be calculated and tested. The designed scaffolds should use materials with suitable mechanical properties. The computational analysis of the scaffolds can be used for estimation of their mechanical properties prior to their testing. We can analyze these scaffolds and their capability to maintain the in-growth of bone and demonstrate their potential for application in tissue engineering. For example, a suitable assessment of the mechanical properties of PCL scaffolds produced through SLS (Selective Laser Sintering) is essential to guarantee that the scaffold properties are in the range needed for human trabecular bone. Scaffold mechanical properties meeting those of trabecular bone are significant for estimating practical load, which can be helpful to improve targeted bone structures [67].

For selected materials, the elastic modulus can be calculated as the slope of the preliminary linear area of the stress-strain curve. The compressive modulus of the magnesium phosphate (MP) and polycaprolactone MP/PCL combined scaffold is lower than that of human trabecular bone (50 MPa), which was confirmed by mechanical test results [67]. The combined scaffold is not proper for application in high-load-bearing sites. For instance, materials with highly interconnected porous structures and rapid degradation rates, such as magnesium phosphate and polycaprolactone MP/PCL compound scaffolds, could be applied only for non-load-bearing purposes [55].
The properties of the bone replacement materials, such as scaffold stiffness are selected to match target tissue stiffness. Optimization of the microstructure design is needed. All microstructures should offer a linked path for nutrient flow and cell migration to guarantee renewal of linked tissue. Failure to ensure linkage of pores leads to unlinked tissue that can significantly decrease the mechanical properties [60]. One of the suitable scaffold designs is the one with 45° inclined layers. The purpose is to aid the seeding process and improve cell attachment. Moreover, these scaffolds enable cell production inside the structure without blockage [65].

The purpose of the tissue-engineering field is to develop three-dimensional tissues to replace damaged tissue. Therefore, study of biomaterials for bone engineering represents a crucial area for developing tissue-engineering approaches. Future biomaterials should mix bioactive and biodegradable properties to activate in vivo systems for tissue reproduction, stimulating the body to repair itself and facilitate replacement of the scaffold by the regenerating tissue. Many different biomaterials, including synthetic polymers, ceramics and natural polymers, are being used to make artificial scaffolds that act as guides and lead to three-dimensional tissue growth [68].

2.3.4 Degradation Rates

The strength of biodegradable tissue scaffolds should not decline quickly and should degrade at a rate comparable to the growth of new tissue cells [47]. Sufficient degradation properties include the rate of scaffold degradation, which has to be slow enough for maintaining the structural support for cellular production, and ECM emission, but leaving room for new tissue development by its own degradation. The perfect scaffold
should produce degradation metabolites that are non-toxic and are simply removed by metabolic pathways [55].

Certain synthetic polymers, if synthesized under controlled circumstances from specific monomers, can be biodegradable. Generally, they show expected and reproducible mechanical and physical properties, such as tensile strength, elastic modulus, but they need to exhibit required degradation rate. Biodegradable polymers have transformed the applications of biomaterial into the field of drug delivery and implants for tissue engineering. Scaffold degradation can happen through methods that engage physical, chemical, and biological processes that are mediated by biological agents, such as enzymes in the processes of tissue modification. The biodegradable scaffold slowly degrades through a determined period and is substituted by produced tissue from the adhered cells [58].

There is an optimization method to calculate successful properties that can be simply extended to include middle steps with hybrids of degrading scaffolds and renewing tissue [60]. Sufficient biodegradability is a significant factor that must be considered in designing and fabricating scaffolds for bone tissue. A small weight loss was observed for PCL scaffolds through the total period of incubation. The weight loss of the combined scaffolds was more noticeable than with PCL scaffolds and slowly improved with the incubation time. The low solubility of MgO could be a reason for this result. Also, the weight loss of the combined scaffolds increased with the MP content at each time point. The degradation rate of the combined scaffolds can be tailored to match the rate of tissue renewal by adjusting the MP content in the combination material [63].
Solid free form (SFF) manufacture methods allow design and manufacture of anatomically shaped scaffolds with varying internal architectures, which enable exact control over pore size, porosity, permeability, and stiffness. Directing these features improve cell penetration and mass transfer of nutrients and metabolic waste through the scaffold [67].

2.3.5 Porosity and Pore Size

The design of the scaffold must support growth of regenerative tissue and assist the transport of nutrients and chemical signals. This can be achieved by controlling the porosity of the structure, providing suitable interconnectivity in the structure, and by selecting proper biocompatible materials [47]. The features of scaffold microstructure and properties such as porosity, pore size, pore interconnectivity, structural strength, shape and biocompatibility play a significant role in their design and manufacture. Therefore, the design of microstructures should have the following characteristics: (i) High porosity, which means that more than sixty percent pores are required to create attached cells and transfer pathways, and (ii) High interconnectivity of the pores [53].

Proper porosity, pore size and pore structure will guarantee the nutrition of cells, cell connection, and cell growth within the scaffold, while at the same time providing space for tissue renewal [55].

Porous scaffolds with porosities having uniform interconnected pore networks are very important for tissue engineering. Sponge scaffolds are used in tissue engineering applications, particularly for bone regrowth [58] [69]. The enhanced pore interconnectivity of the scaffold is needed for the growth of new blood vessels or nerve enlargement [58]. Perfect pore sizes differ for different cells and tissues [58] [70]. Porous scaffolds could be
produced with exact pore size, porosity and surface area [58]. The important parameters to be considered for scaffold design are pore size distribution, average pore size, pore volume, pore shape, pore interconnectivity and pore wall roughness. Several research works have shown the importance of porosity [58] [71].

Pore size has an influence on tissue renewal and this has been confirmed by experiments showing optimum pore size of 5 μm for neovascularization, 5–15 μm for fibroblast ingrowth, 20 μm for the ingrowth of hepatocytes, 200–350 μm for osteoconduct, and 20–125 μm for regeneration of adult mammalian skin [58] [72] [73]. Pore interconnectivity is also important to make sure that all cells are within 200 μm from blood supply to contribute for mass transfer of oxygen and nutrients [58] [74].

Scaffolds also must meet healthy tissue hardness and strength requirements. Factors that can improve tissue regrowth include such varied traits as pore size, total porosity, pore nature, pore interconnectivity, material surface chemistry, efficient scaffold permeability, and scaffold stiffness [60].

PCL is a biodegradable material that has good biocompatibility and simple processing ability. It is used to design scaffolds for tissue engineering [63] [75]. The pore size of the scaffold for bone renewal should be at least 100 μm. Pore size greater than 300 μm is preferred to improve the osteogenesis and the formation of capillaries. The combined scaffolds show cubical macropores with pore morphology similar to the geometry of salt particles [63]. Some micropores with size ranging from 1 to 10 μm exist on the walls of macropores. Pore interconnectivity has a significant role in supporting the ingrowth of cells and new tissue. Excellent interconnectivity is useful for the flow transfer of nutrients and removal of waste [63].
2.4 Three-dimensional Printing Technology

Three dimensional printing produces the scaffolds with precise, reproducible inner formation directly from computer data. One of the materials used to manufacture permeable ceramic structures, with engineered inner architecture, is hydroxyapatite (HA) [65][76]. For bone repair and renewal, calcium phosphates have been applied, due to their biocompatibility and osteoinductivity that support the formation of chemical bonds with living tissue by mimicking the apatite phase of the natural bone tissue. Synthetic hydroxyapatite is one of the most significant bone replacement materials, due to its capability after implant to shape chemical bonding with surrounding hard tissues through the formation of a hydroxyapatite interfacial layer. Various tactics have been developed lately, including phase inversion/particulate leaching, quick prototyping, and phase separation [68]. Three dimensional printing is used to replace damaged bones in different parts of the body. The technology can be used to replace the skulls of people damaged by disease or trauma, or in patients with sickness, car accident casualties and injured fighters to replace bone structure [77].

There are situations when the bone structure is damaged and it cannot be repaired by regular noninvasive methods such as casts. At present, damaged bones are repaired with metal parts, but a variety of cases show that the bone cannot be replaced or repaired. However, many successful attempts of using 3D printing to print human bone structures even for most complex shapes, such as skulls and jaws, have been demonstrated [77][78].

Many different biocompatible and biodegradable materials have been studied and tested for application in 3D printed bone structure. There are different 3D printing methods that can be applied for bone tissue-engineering. For this reason, different biocompatible
and biodegradable materials will be evaluated in this PhD work to print bone structure by using different 3D printing methods.

2.5 Common Methods of 3D Printing Technology

2.5.1 Selective Laser Sintering

Selective laser sintering (SLS) is advantageous for making bone tissue engineering builds for sites, such as temporomandibular joint (TMJ), since it provides a technique to build scaffolds to match the anatomical geometry of periodontal structure [67] [79]. SLS constructs the scaffolds from 3-D digital data layer by layer, using a computer controlled scanning laser beam. The powder biomaterial binds using the heat of the laser beam, forming bone scaffolds. PCL is a biodegradable polymer with the following properties suitable for bone and cartilage repair: PCL is stable in ambient circumstances: it is inexpensive, and widely available [67] [80] [81] [82].

The PCL scaffolds manufactured via SLS have been used to construct bone tissue. PCL scaffolds must be precisely built from specific designs that have mechanical characteristics with suitable physiological ranges to be successfully used for bone tissue [67]. Artificial bone substitute materials based on calcium phosphates are generally used in medical applications [65] [83]. An artificial scaffold used for bone tissue engineering needs an internal structure with built in interconnecting pores, similar to the real bone tissue. The pore diameter should exceed 300 μm for good connections of bone cells to allow their growth in all three dimensions [65].
SLS (Fig. 1) can be used for a variety of applications. SLS is rapid, cheap, and it can directly manufacture small projects. Laser sintering is appropriate for various sizes of parts. Using laser sintering technology, elements are built layer by layer. Basically the raw material is powder with particle size near 50 µm. The laser beam scans the surface and selectively binds together the powder particles of cross section of the product. Through the laser contact, the powder temperature increases above the glass transition point and coalescence is initiated [84].

The method uses a high power laser to fuse tiny particles of powder such as plastic, metal, ceramic and glass into a group that has a desired three-dimensional form. The roller above the surface of the build cylinder stretches the powder. To make a room for the new layer of powder, the piston in the cylinder shifts down by one layer thickness. After that, the powder supply piston goes up to provide a fresh amount of powder for the next layer (See Figure 1). The process builds the item layer by layer. SLS is able to generate elements from an extensive variety of powder materials. These materials can contain polymers as
nylon or polystyrene, metals such as steel, titanium, alloy mixtures and green sand. In addition, materials can be used are polyamide (PA), Glass filled polyamide (PA-GF) and Alumide, combination of aluminum and polyamide [84].

2.5.2 **Fused Deposition Modeling (FDM)**

Fused Deposition Modeling is a common technique that deposits a molten plastic filament to construct 3D printed item layer by layer. The initial step to build a 3D printed item is to make a 3D model. Then the 3D modeled item will be converted to STL format by 3D printing software. This format can maintain and adjust the geometry of the 3D model such as scaling and quality [85]. After that the 3D printing software imports the STL file to be ready for printing and it is sliced into multiple thin layers. These slices are the two dimensional paths that the 3D printing process is going to construct and after repeatedly stacking on one another, the 3D object will be built. The thinner is the layer and higher is the accuracy of the deposition process; the higher is the quality that will be performed for the item [62].
FDM is a modern method that uses production-grade thermoplastic materials to manufacture models or end-use parts (Figure 2). The FDM method employs a plastic filament from a coil and provides material to an extrusion nozzle. The plastic is melted by the heated extrusion nozzle and the melt plastic flow can be turned on or off. When the nozzle is moved above the platform, the needed geometry is created by putting down a thin wire of extruded plastic to build every layer [86].

The method runs molten material onto an X, Y coordinate system, sketches of the model one layer at a time and then moves up in the Z direction for the next layer. The plastic solidifies in the air after leaving the nozzle and bonds to the lower layer. The item is constructed on a mechanical phase that shifts down perpendicularly layer by layer when the element is shaped. FDM uses thermoplastics such as Acrylonitrile-Butadiene-Styrene (ABS), ABSi (ABS polymer engineered for higher impact strength), polyphenylsulfone...
(PPSF) and Polycarbonate (PC). These materials are applied because they have the required heat resistance [87].

2.5.3 Stereolithography

![Schematic of Stereolithography](image)

Stereolithography is a developed process using a container of liquid UV-curable monomer and a UV laser to construct layers (Figure 3). For each layer, the laser ray draws a cross-section of the part model on the surface of the liquid resin. The resin is cured by the laser beam that solidifies it, after movement on X-Y direction following the layer pattern the layer of model is created and bonds to the lower layer. When the laser ray hits the surface of the liquid monomer, the photopolymer is created, which rapidly hardens. After one layer is totally drawn the stage is lowered one step down into the container and the second layer will be sketched on top of the first. The material bonds every layer to the prior one, repeating the process over-and-over again till it builds the entire shape of the
three dimensional part. Stereolithography is a fast method that has a high level of precision and good finishing [88].

2.5.4 PolyJet Technology

The working mechanism of Stratasys PolyJet 3D printing technology is similar to inkjet printing. The printer jets layers of curable liquid monomer onto the substrate instead of jetting drops of ink onto paper. A print head with multiple nozzles, jets photopolymer onto the substrate table surface. Simultaneously with the movement of the head (Figure 4), the ink droplets are flattened by the small roller to make the surface even. An ultraviolet light strip follows the head and cures the material instantaneously. Two polymer materials plus a supporting material can be jetted simultaneously. The supporting material provides a base for the main material, especially when there is a cavity or overhand structure. The supporting material can be easily removed mechanically or by water jetting [89] [90].

![Figure 4: 3D printing principle used by Stratasys PolyJet Technology [89].](image-url)
2.6 3D Honeycomb Scaffolds

Nowadays, tissue engineers are trying to design practically all human tissues, including bone, cartilage, heart valves, nerves, muscle, liver, bladder, etc. Also, because of the complex cell microenvironments with unlike biochemical and physical properties, there is no surprise that cell behavior in 3D culture is unexpectedly different as compared to those in 2D culture [91] [92] [93] [94]. Engineering of 3D cell microenvironment is required to mimic neuronal cells and imitate their surrounding original microenvironment, particularly to understand the effect of organized 3D cell microenvironments on neuronal cell development [91].

Generally, different tissue engineering tactics aim on designing 3D porous biomaterial scaffolds to provide a 3D structure to improve nutrient delivery, along with mechanical support for cell behavior and its construction defines the final shape of the lately developed hard or soft tissue [95] [96]. Because of their high porosity and good mechanical performance, 3D honeycomb scaffolds have attracted a lot of attention.

Primary scaffolds were not manufactured with exact porous structural design. The first report of different honeycomb scaffold structures produced by fused deposition modeling (FDM) for tissue engineering applications was given by Hutmacher [51] [61]. The results of the research indicate that the honeycomb scaffolds have good mechanical properties and great biocompatibility with human fibroblast and periosteal cell culture systems [62]. In this work, honeycomb structures will be studied more in depth, with main focus of assessing their mechanical properties as replacement of human trabecular bones.
CHAPTER 3

PROBLEM STATEMENT AND OBJECTIVES

Researchers in the medical field are looking for the best biocompatible materials that can be used as replacements for human bone structures to be inserted into the human body to match the criteria of the bone’s mechanical properties, without causing any negative side effects. Several metals have been studied for many years as implants. These metals include aluminum, copper, zinc, silver, carbon steels, iron, nickel, and magnesium alloys. But most of them were rejected because they release metallic ions in the body during long time implantation. Then, researchers tried to find types of metals that may have less side effects to be used as a replacement for fractured bone. Metals such as titanium, steel and cobalt-chromium have been employed due their specific properties. These materials have been used as implants for the human body to serve for a long time and for heavy load purposes. Now, high-performance plastics have started to be considered as replacements for these metals, because of their more suitable properties, such as reduced weight and stiffness. One solution may be engineered plastics, such as polyetheretherketone (PEEK). These plastic materials are less dense than metals, and because of that, they are X-ray transparent, unlike metals, which are opaque to X-rays. This allows good monitoring of bone growth and healing processes. Another advantage of plastics is the reduced implant stiffness, which is a better match to the stiffness of the surrounding bones. This reduces stress that transfers to the bone and aids the healing process. Because of these advantages, high performance plastics have become known as significant options to metallic implant materials. This fact motivated research on biocompatible polymers applied by using 3D printing technology to create bone implants.

25
The primary objective of this study was to test the mechanical properties of 3D printed human bone structures using biocompatible polymers. We determined how the 3D printing technology affected the mechanical properties of the polymer structures after they had been printed, and then we investigated if they matched the mechanical properties of human bone structures. The main goal of this study was to design a process for building replacement for the fractured part of bones and investigate different technologies and biopolymers for printing 3D structures at 100% of infill and with porous structures that can be applied as trabecular bone tissue replacement.

3.1 Tasks

In order to achieve the main objective of this work, the following tasks were performed:

3.1.1 Testing the Structure Properties of 3D Printed Samples at 100% Infill

We created and designed specific specimens with specific sizes to test the mechanical properties of 3D printed samples of biocompatible polymers. The biocompatible polymers selected to be printed and tested were PLA, ULTEM9085, polyamide (PA2200) and Digital ABS™. Mechanical properties, such as tensile strength test, compressive strength test, and bending test were executed after these specimens had been 3D printed. We compared the obtained results, at 100% of infill (inside filled structure) mechanical properties, with those of the human bone to check if they are close or not. All tested plastic specimens were compared to ABS as well for reference. ABS is one of the most common polymers used in 3D printing and produce good quality models samples.
3.1.2 Testing the Structure Properties of 3D Printed Samples Designed with Different Internal Structure (Geometric Shape)

Since the trabecular bone structure cannot be obtained from a CT scan, due to the low resolution of the DICOM images, we were not able to design it. Therefore, we used CAD software SolidWorks to design special 3D honeycomb structures (hexagonal, triangular, and square). The honeycomb structures provide high strength, while keeping the weight light. The geometry of the honeycomb reduces the amount of material needed, therefore reducing the weight, cost, and density. We designed and produced 3D printed samples to test the structure properties with different geometric shapes. Structure property tests, such as: tensile strength test, compressive strength test, and bending test were investigated. The trabecular bone gives elasticity and support to the cortical bone, which makes the bone structure capable of bearing higher loads without being fractured. That’s why we mimicked the geometry of the trabecular bone structure by designing honeycomb structures to create bone structures closely matching actual ones.

3.1.3 Testing the Surface Topography of Thin Layers of 3D Printed Samples

We designed several samples using SolidWorks software with specific thickness and printed them using MakerBot replicator 2X and FlashForge Creator Pro. Both printers use the Fused Deposition Modeling (FDM) method. We printed two samples of ABS and PVA using MakerBot replicator 2X. We tested the difference in thickness and roughness of the samples to compare them with each other and with the designed thickness. Then we printed ABS using FlashForge Creator Pro. We wanted to test the minimum thickness that each printer can provide and the highest precision it can reach. The thickness of the designed samples ranged from 0.4 mm (400 µm) for the thickest down to 0.05 mm (50 µm)
for the thinnest. The samples were printed at 45°. The measured thickness and roughness were measured using a White Light Interferometer (Bruker).

The samples were also printed by PolyJet™ Technology using Stratasys Objet 500 Connex3 printer with digital ABS™ material and the thickness of the samples this time ranged from 0.4 mm (400 µm) for the thickest down to 0.016 mm (16 µm) for the thinnest. They were printed to investigate if the Stratasys Objet 500 Connex3 can produce the minimum thickness that the manufacturer claimed which is 0.016 mm (16µm) and the highest precision the printer can reach with the smoothness level. Then, compare the results with the previous printers that use the FDM method.

3.1.4 Thermal Analysis using Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) was used to determine the thermal analysis profile of these polymers. It is important to understand material behavior under the influence of thermal loads. Thermal analysis provides important information about the polymer, whether it is amorphous or crystalline. To understand melting, solidification and leveling of the polymers, differential scanning calorimetry (DSC) was performed.
CHAPTER 4

THERMOPLASTICS FOR MEDICAL APPLICATIONS BY 3D PRINTING

4.1 Introduction

Thermoplastics have been used successfully as replacements for certain metals for many years in manufacturing and have been used widely in medical applications [97]. 3D printing of plastics has a significant role in applying these materials, providing high performance, cost efficiency and enhanced resistance to environmental conditions. The low melting temperature used in 3D printing is considered an advantage of the technology to create high quality parts for manufacturing and in medical applications, also allowing precise manufacturing for replacement of tissue, specifically bone structures. The goal of this work is to design and build bone structures from biocompatible plastic materials and investigate their mechanical properties. We studied and tested several biocompatible materials to investigate the possibility of their use in bone structures by using 3D printing.

4.1.1 Building Bone Structures

Initially, Digital Imaging and Communications in Medicine (DICOM) image slices of bones are acquired using MRI or CT scans from actual body organs. Next, 3D modeling software is used to produce a new part or the model of the missing bone structure. The 3D model is then imported into 3D printing software for building the substitute bone structure [65]. Recently, there have been many successful attempts to 3D print items for human bone substitutes, using 3D printing technology [77].
4.1.2 Fused Deposition Modeling

Fused Deposition Modeling (FDM) is a method widely used to produce 3D printed items from thermoplastics [85]. The first step is to create a 3D model and then convert it to STL (Stereolithography) format to produce the 3D object. STL format has some advantages and disadvantages. The advantage of this format is that it facilitates the geometry of the object by reducing it to its initial components and it can maintain and adjust the geometry of 3D model such as shape and size. The disadvantage of this format is that the object loses some of its resolution because it uses only triangles to represent the complex geometry. Once the STL file format is imported to the 3D printing software to be prepared for 3D printing, it is sliced into numerous thin slices that become layers during the 3D printing process.

These layers define the two dimensional planes that the 3D printing process will produce to build the 3D object. When created, the layers are stacked upon one another, thus creating a 3D object directly from the original design. It is obvious that the thinner the layer is, and higher the precision is of the 2D movement; the higher is the precision that can be carried out for an item [62]. The working mechanism of the FDM technique is that it takes a plastic filament from a coil and drives it through an extruder. The plastic is heated and melted by the heat extrusion nozzle, the molten filament flows through the nozzles, and is deposited on the building plate to form a layer. The heads move on the X-Y axes to follow a predefined path to form a specific shape on each layer. Then, the platform moves vertically in the Z direction to produce the next layer [61]. 3D printing with thermoplastics is one of the most common methods to create 3D structures in both medical and industrial fields [86].
4.1.3 Selective Laser Sintering (SLS)

Selective Laser Sintering (SLS) is another rapid prototyping process that can manufacture 3D structures directly from 3D models. Applying laser-sintering technology, objects are built layer by layer [84]. The method uses a high power laser to fuse tiny particles of powders, such as plastic, metal, ceramic and glass, into a structure that has a desired three-dimensional (3D) form. The principle of SLS process is that a thin layer of powder is distributed and leveled by a roller above the flat surface. Then, a laser beam follows a defined profile on the layer and melts the powder that bonds together. To make room for the new layer of powder, the piston in the cylinder shifts down by one layer thickness. Next, the powder supply piston goes up to provide a fresh amount of powder for the subsequent layer. The powder is distributed again on the flat surface. The laser repeats the same process as on the first layer. This process repeats layer by layer until the entire object is built. SLS is capable of producing objects from an extensive variety of powder materials. These materials can contain polymers, such as nylon or polystyrene, or metals, such as steel, titanium, alloy mixtures and green sand. In addition, materials that can be used are polyamide (PA), glass filled polyamide (PA-GF) and alumide, a combination of aluminum and polyamide [84] [98]. For medical purposes, SLS has been used for making bone tissue engineering builds for sites, such as temporomandibular joint (TMJ) using polycaprolactone (PCL), since it provides a technique to build scaffolds to match the anatomical geometry of periodontal structures. The method allows building scaffolds with complicated inner and outer structures [67].
4.1.4 Stereolithography

Stereolithography is a developed process using a container of liquid UV-curable monomer and a UV laser to construct layers. For each layer, the laser ray draws a cross-section of the part model on the surface of the liquid resin. When the resin is cured by the laser beam it solidifies, after movement in the X-Y direction following the layer pattern, the layer of the model is created and bonds to the lower layer. When the laser ray hits the surface of the liquid monomer, the photopolymer is created, which rapidly hardens. After one layer is totally drawn, the stage is lowered one step down into the container and the second layer will be sketched on top of the first. The material bonds every layer to the prior one, repeating the process over-and-over again till it builds the entire shape of the three dimensional part. Stereolithography is a fast method that has a high level of precision and good finishing properties [88].

4.1.5 PolyJet Technology

PolyJet™ technology is a great manufacturing process that can produce smooth, exact parts with a layer resolution of 16 µm and precision of 0.1 mm height. The process can produce thin walls and complex geometric shapes with many materials. PolyJet 3D printing jets layers of curable liquid photopolymer onto a build substrate, which is like inkjet printing that fires drops of ink onto paper. The build preparation software automatically estimates the placement of photopolymers and support material from a 3D CAD file. The 3D printer jets and directly UV-cures small drops of liquid prepolymer. The acceptable layers gather on the build substrate to generate an accurate 3D model. The 3D printer jets a removable gel like support material when the complex shapes are in need for support. Then, the support material can be removed easily by the operator’s hand or
flushing with water. PolyJet 3D printing technology can offer several advantages for rapid prototyping. The technology can make smooth detailed prototypes, produce complex shapes, complicated details and smooth surfaces. In addition, it can combine color and various material properties into one model with the best material versatility obtainable [99].

4.2 Experimental

4.2.1 3D Printing of Test Samples

We used SolidWorks software to design and create 3D models for tensile test, compressive test and bending test samples with specific dimensions according to the standard. Then, using 3D printing technology five different 3D printed samples of thermoplastic materials were printed, with five replicates for each sample for each test. ABS (Acrylonitrile-Butadiene-Styrene) [100], PLA (Polylactic Acid) [101], ULTEM9085, a polyetherimide, [102], PA 2200 (Polyamide) [103], and Digital ABSTM, an acrylic photopolymer [104]. ABS, PLA, ULTEM9085 samples were 3D printed using Fused Deposition Modeling (FDM). ABS samples were 3D printed with Maker Bot replicator 2X. PLA samples were 3D printed with Type A Series 1, and ULTEM9085 samples were 3D printed with Fortus 400 MC. PA 2200 samples were 3d printed using SLS with EOS P 396. Digital ABSTM samples were 3D printed using PolyJet Technology with Stratasys 500 Objet Connex3. Selected mechanical and physical properties of these thermoplastic materials are shown in Table 1.
Table 1: Selected Properties of Thermoplastic materials from MSDS.

<table>
<thead>
<tr>
<th>Material</th>
<th>Tensile strength [MPa]</th>
<th>Young Modulus [MPa]</th>
<th>Melting Point [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABS</td>
<td>44.8</td>
<td>2250</td>
<td>100*</td>
</tr>
<tr>
<td>PLA</td>
<td>57.8</td>
<td>3500</td>
<td>160</td>
</tr>
<tr>
<td>Ultem9085</td>
<td>71.6</td>
<td>2200</td>
<td>186</td>
</tr>
<tr>
<td>PA2200</td>
<td>48</td>
<td>1700</td>
<td>172-180</td>
</tr>
<tr>
<td>Digital ABS™</td>
<td>60</td>
<td>2600-3000</td>
<td>47-53*</td>
</tr>
</tbody>
</table>

*Melting temperature is replaced by the glass transition temperature (T_g) for ABS and Digital ABS™, since these materials cannot be crystalized.

To make 3D printing objects, 3D models need to be created in advance. 3D slicer and OsiriX software were used to design 3D models and then converted to STL format for 3D printing. The sample size and dimensions can be controlled as needed. 3D printing parameters, such as temperature, extruder speed, infill percentage (100% - %void volume), temperature of the heated plate and resolution can be also controlled. Figure 5 shows the 3D printer running while printing the test sample.

![3D Printing Tensile test Sample on MakerBot.](image)

4.2.2 Testing Mechanical Properties of 3D Printed Samples using MTS

After printing 3D samples for tensile tests, compression tests and bending tests, we tested the samples using MTS Bionix Servohydraulic Test Systems-Model 370.02. The
force capacity of the device is 25 kN and it is used to determine the quasistatic mechanical properties for a number of biomaterials. The axial alignments of the system are intended to achieve precise tension, compression and bending tests as well as fatigue and fracture studies. Also, they are used to test durability properties of components such as hip, knee and spine implants [105]. The tested samples were designed according to the standard with specific dimensions for all mechanical property tests. We tested the 3D printed samples at 0.2 mm/s speed rate of the MTS machine at room temperature.
4.2.3 Creating of 3D Bone Structure Model using OsiriX

OsiriX is free open software used to create 3D models of human organs from Computed Tomography (CT), Magnetic Resonance Imaging (MRI) and ultrasound scans. These provide high quality images used for different medical applications including surgeries. To create 3D models for 3D printing bone structures, DICOM images from CT and MRI were acquired by obtaining information from actual patients [46].

For creating 3D models, there are several steps required. The initial step is that the region of interest (ROI) must be selected on each image. After that, the segmentation should be performed to separate the borders of the organ. An example of using OsiriX to make the 3D model is shown in Figure 6. OsiriX aims to view, approximate, read and post process the images. OsiriX software presents highly developed post processing techniques for 2D imaging, database, and 3D models.

Figure 6 illustrates the collection of images used to describe the ROI (region of interest) and segmentation, (highlighted in green color), to create the 3D model. Once the segmentation is finished through all the slices, the volumization is carried out to create the final 3D shape. As shown in Figure 7, the 3D model is visualized by OsiriX. Then the model is exported to 3D format, which is STL in our case, to be printed by a 3D printer. The mechanical properties of the 3D printed samples can be tested, once the samples for the tensile test machine-MTS machine are printed at ambient temperature.
4.2.4 Cleaning 3D Model using MeshLab

Before 3D printing, the mesh model needs to be cleaned and smoothened. We use MeshLab software for cleaning of the mesh, which means removing all the tiny geometrical irregularities that may be found in shell meshes. Common problems that usually occur in
the model are duplicated vertices, unreferenced null faces, self-intersecting faces, non-manifold faces and small holes. For filling holes, we use the hole filler tool that allows us to select holes and edit them in different ways. The basic filling algorithm uses a technique that inserts a face between the two adjacent border edges. This algorithm selects every time the best pair of adjacent border edges into the hole. Then smoothing of the model is performed, as shown in Figure 8(A) [106]. A bone structure sample was printed to test the accuracy of the 3D printer as shown in Figure 8(B). 3D models were exported to STL format to be printed by the 3D printer (MakerBot replicator 2X).

![Figure 8: (A) 3D model of vertebra cleaned by MeshLab. (B) 3D Printed bone vertebra structure.](image)

**4.2.5 Thermal Analysis by Differential Scanning Calorimetry (DSC)**

Differential Scanning Calorimetry (DSC) was used to investigate the amorphous and crystalline behavior of these polymers. This tool is important in thermal analysis to investigate how the heat capacity of materials is changed by temperature. A sample with known weight is heated or cooled and the changes in its heat capacity are tracked as
changes in the heat flow. This can detect transitions, such as glass transition temperatures and melting temperatures [107]. Test samples of 0.045g for all of them were used. For the first cycle the sample was held for 1 minute at 35 ºC, then it was heated from 35 ºC to 260 ºC at 10 ºC/min. After that, it was held for 1 minute at 260 ºC and cooled from 260 ºC to 35 ºC at 60 ºC/min. The same steps were repeated for the second cycle for all the samples.

4.3 Results and Discussion

4.3.1 Tensile Strength Tests

Five different thermoplastic materials were printed and tested using the MTS machine. The Fused Deposition Modeling (FDM) technique was used to print three different thermoplastic materials (See Table 1 for selected properties). Five samples were printed for each material ABS, PLA and ULTEM9085. The Selective Laser Sintering (SLS) method was used to print one thermoplastic material PA2200. PolyJet Technology was used to print digital ABS™. All the samples were printed as a solid at 100% of infill. We used an MTS-machine to test the tensile strength, compression and bending of the 3D printed thermoplastic specimens. Specific equations were used to calculate stress and strain for each test. Figure 9 shows the stress-strain curves of the materials and calculated (stress-strain) by least squares regression of the experimental data using a quadratic polynomial at 100% infill and the MTS machine speed of 0.2 mm/s at room temperature for tensile test.
Figure 9: Tensile Stress-Strain calculated from least squares fit to tensile data for the materials.

The shapes of stress strain curves pinpoint brittle structures, which do not exhibit any dramatic change in elongation prior to rupture. The brittle material ruptures without any obvious prior change in the rate of elongation [108]. Table 2 shows the results of the tensile strength and Young’s modulus after testing with the MTS-machine. By making a comparison between the results of the tensile strength of 3D printed samples, and the values of the material safety data sheet (MSDS) from the manufacturer, both measured tensile strength and Young’s modulus values were slightly less than the ones provided by the manufacturer, which was most likely due to repeated heating and extrusion of the tested thermoplastic samples. For PA2200, which was printed by SLS, they were indistinguishable from the values that obtained from the manufacturer. Figures (10-11) show the stress-strain curves calculated (from least square fits to compression stress-strain data) at 100% infill for compression tests in X and Z directions accordingly, while Figure 12 shows the stress-strain curves and calculated (stress-strain) at 100% infill for bending tests.
Table 2: Tensile Strength of the Thermoplastics at 100% Infill after testing with MTS machine.

<table>
<thead>
<tr>
<th>Material</th>
<th>Tensile Strength [MPa]</th>
<th>SD[MPa]</th>
<th>Young’s Modulus [MPa]</th>
<th>SD[MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABS</td>
<td>44</td>
<td>2</td>
<td>1925</td>
<td>29</td>
</tr>
<tr>
<td>PLA</td>
<td>57</td>
<td>2.1</td>
<td>3333</td>
<td>18</td>
</tr>
<tr>
<td>ULTEM9085</td>
<td>49.7</td>
<td>0.6</td>
<td>1540</td>
<td>3</td>
</tr>
<tr>
<td>PA2200</td>
<td>49.7</td>
<td>0.7</td>
<td>1699</td>
<td>12</td>
</tr>
<tr>
<td>Digital ABS™</td>
<td>55</td>
<td>2.7</td>
<td>2013</td>
<td>12</td>
</tr>
</tbody>
</table>

From Table 2, PLA has the highest values for both Young’s modulus and tensile strength. After that, Digital ABS™ has the second highest values for both Young’s modulus and tensile strength. ULTEM9085 has the lowest value for Young’s modulus and ABS has the lowest value for tensile strength. Cortical bones have a compressive strength in the range of 131-224 MPa, and a Young’s modulus ranging from 17000-20000 MPa, while compressive strength and Young’s modulus for trabecular bones are 5-10 MPa and 50-100 MPa, respectively [109]. The results of the thermoplastics are less than the criteria of the compact bone, but they exceed the criteria of the trabecular bone.

Table 3 shows the tensile strength and Young’s modulus per unit mass for the thermoplastics at 100% infill. PA2200 has the highest values for both tensile strength and Young’s modulus (121kJ/kg) and (3951kJ/kg) consequently. Since the values are dimensions of energy per unit mass, the strength values represent the energy per unit mass that the structure can sustain without breaking, while the modulus per unit mass is the amount of energy.

Table 3: Tensile Strength and Young’s Modulus per unit mass for the Thermoplastics at 100% Infill.

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (kg/m³)</th>
<th>Tensile Strength [kJ/kg]</th>
<th>Young’s Modulus [kJ/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABS</td>
<td>1.04x10³</td>
<td>42.3</td>
<td>1851</td>
</tr>
<tr>
<td>PLA</td>
<td>1.25x10³</td>
<td>45.6</td>
<td>2666</td>
</tr>
<tr>
<td>ULTEM9085</td>
<td>1.34x10³</td>
<td>37.3</td>
<td>1149</td>
</tr>
<tr>
<td>PA2200</td>
<td>0.430x10³</td>
<td>121</td>
<td>3951</td>
</tr>
<tr>
<td>Digital ABS™</td>
<td>1.18x10³</td>
<td>46.6</td>
<td>1706</td>
</tr>
</tbody>
</table>
4.3.2 Compressive Tests

Compression tests give information about the compressive properties of the material of interest. The specimen dimensions were printed according to the standard, and they can be either blocks or cylinders for this test. In our case we made them blocks with the specific dimensions according to ASTM D695. The compressive test properties explain the performance of the material when it is compressed under a load that is relatively low and uniform. The equations used to calculate stress and strain for compressive tests are the same for tensile tests. Figures (10-11) show the relation between stress vs. strain and the fitted points of the samples for each material. For ABS polymer, the curves appear concave as in Figure 10, when the material was printed horizontally along the X axes, and in Figure 11 when it was printed vertically in the Z axis, but the slopes are not the same in both printing directions. This indicates that this material creates anisotropic 3D printed structures, because it has different slopes in different printing directions. Table 4 shows the results of the compressive strength and compressive modulus for selected materials from material safety data sheet (MSDS).

Table 4: Compressive Strength and Compressive Modulus for selected materials from MSDS.

<table>
<thead>
<tr>
<th>Material</th>
<th>Compressive Strength [MPa]</th>
<th>Compressive Modulus [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABS</td>
<td>65</td>
<td>2500</td>
</tr>
<tr>
<td>PLA</td>
<td>80</td>
<td>4000</td>
</tr>
<tr>
<td>ULTEM9085</td>
<td>104</td>
<td>1930</td>
</tr>
<tr>
<td>PA2200</td>
<td>58</td>
<td>1500</td>
</tr>
<tr>
<td>Digital ABSTM</td>
<td>110</td>
<td>2200</td>
</tr>
</tbody>
</table>
For PLA, when it was printed along the X axis, the curve appears concave, while it appears convex when it was printed perpendicularly along the Z axis. This indicates that PLA created anisotropic 3D printed structures, since it has different behavior in different printing directions. The same behavior was found with Digital ABS™, which was printed
by using PolyJet™ technology. When it was printed along the X axes, the curve appears convex, while it appears concave when it was printed vertically along the Z axis. This indicates Digital ABS™ creates anisotropic 3D printed structures, since it has different behavior in different directions.

The rest of the materials showed the same behavior in both directions (Figures 10-11). For ULTEM9085 the curves were concave, while for PA2200 the curves were convex in both printing directions, but the slopes are different in both printing directions for both materials. This is an indicator that ULTEM9085 and PA2200 also form anisotropic 3D printed structures. All of these materials have in common that they are thermoplastic polymers, which means that they form linear polymeric chains, thus it can be expected, that the strength is highest in the direction of polymeric chains, and in other directions the strength will be lower.

Table 5 shows the results of compressive strength and compressive modulus after testing with MTS machine. The table shows the results of the thermoplastic samples that were printed at 100% of infill along both directions X and Z for compression tests. The values of the compressive modulus and compressive strength of the tested samples are lower than the original values from the material safety data sheet (MSDS) (ABS, 2015). It is obvious that by comparing the compressive modulus values of all the printed samples along both directions X and Z from table 5. It was found that for compressive moduli, the values of the convex figures are less than the values of the concave figures regardless of the printing direction, but if the figures have the same shape in both printing directions, then the values of the compressive modulus of the samples that were printed vertically
along the Z axes are less than the ones that were printed horizontally along the X axes and
vice versa for the compressive strength.

Table 5: Compressive Strength and Compressive Modulus after testing with MTS machine.

<table>
<thead>
<tr>
<th>Print Direction</th>
<th>Material</th>
<th>Compressive Strength [MPa]</th>
<th>SD [MPa]</th>
<th>Compressive Modulus [MPa]</th>
<th>SD [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>ABS</td>
<td>30</td>
<td>2</td>
<td>1839</td>
<td>12</td>
</tr>
<tr>
<td>Z</td>
<td>ABS</td>
<td>45</td>
<td>7</td>
<td>1055</td>
<td>20</td>
</tr>
<tr>
<td>X</td>
<td>PLA</td>
<td>24.7</td>
<td>0.6</td>
<td>3077</td>
<td>29</td>
</tr>
<tr>
<td>Z</td>
<td>PLA</td>
<td>74.8</td>
<td>0.37</td>
<td>1610</td>
<td>28</td>
</tr>
<tr>
<td>X</td>
<td>ULTEM9085</td>
<td>69.98</td>
<td>0.05</td>
<td>1870</td>
<td>13</td>
</tr>
<tr>
<td>Z</td>
<td>ULTEM9085</td>
<td>54.98</td>
<td>0.05</td>
<td>1721</td>
<td>10</td>
</tr>
<tr>
<td>X</td>
<td>PA2200</td>
<td>51.9</td>
<td>0.15</td>
<td>1175</td>
<td>23</td>
</tr>
<tr>
<td>Z</td>
<td>PA2200</td>
<td>54.9</td>
<td>0.18</td>
<td>1064</td>
<td>24</td>
</tr>
<tr>
<td>X</td>
<td>Digital ABS™</td>
<td>75</td>
<td>5</td>
<td>2157</td>
<td>20</td>
</tr>
<tr>
<td>Z</td>
<td>Digital ABS™</td>
<td>79.98</td>
<td>0.04</td>
<td>1729</td>
<td>20</td>
</tr>
</tbody>
</table>

From Table 5, PLA has the highest compressive modulus in the X direction and the
second highest compressive strength in Z direction. Digital ABS™ has the highest
compressive strength in the Z direction and the second highest compressive modulus in X
direction. PA2200 has the lowest compressive modulus in the X direction and ABS has the
lowest compressive modulus in the Z direction. The compressive modulus values of human
trabecular bones range from 1 to 5000 MPa, with strength values ranging from 0.10 to 27.3
MPa [67]. The thermoplastics show compressive modulus values ranging from 1175 to
3077 MPa when they were printed horizontally along X axes and from 1055 to 1729 MPa
when they were printed vertically along Z axes. The compressive strength values of the
thermoplastics range from 25 to 75 MPa for the samples that were printed along the X axes
and from 45 to 80 MPa for the ones that were printed along the Z direction. The
compressive modulus values fall within the range of human trabecular bone, while the
compressive strength values exceed the range of human trabecular bones.

Table 6 shows the compressive strength and compressive modulus per unit mass for the
thermoplastics at 100% infill. PA2200 has the highest values for compressive strength and
compressive modulus per unit mass in both printing directions X and Z. Once again these represent the energies per unit mass that can be absorbed without breaking and the energies per unit mass that are absorbed for unit strain.

Table 6: Compressive Strength and Compressive Modulus per unit mass for the Thermoplastics at 100%.

<table>
<thead>
<tr>
<th>Printed Direction</th>
<th>Material</th>
<th>Compressive Strength [kJ/kg]</th>
<th>Compressive Modulus [kJ/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>ABS</td>
<td>28.8</td>
<td>1768</td>
</tr>
<tr>
<td>Z</td>
<td>ABS</td>
<td>43.3</td>
<td>1014</td>
</tr>
<tr>
<td>X</td>
<td>PLA</td>
<td>20.0</td>
<td>2462</td>
</tr>
<tr>
<td>Z</td>
<td>PLA</td>
<td>60.0</td>
<td>1288</td>
</tr>
<tr>
<td>X</td>
<td>ULTEM90</td>
<td>52.0</td>
<td>1396</td>
</tr>
<tr>
<td>Z</td>
<td>ULTEM90</td>
<td>41.0</td>
<td>1284</td>
</tr>
<tr>
<td>X</td>
<td>PA2200</td>
<td>121</td>
<td>2733</td>
</tr>
<tr>
<td>Z</td>
<td>PA2200</td>
<td>128</td>
<td>2474</td>
</tr>
<tr>
<td>X</td>
<td>Digital ABS™</td>
<td>63.6</td>
<td>1828</td>
</tr>
<tr>
<td>Z</td>
<td>Digital ABS™</td>
<td>67.8</td>
<td>1465</td>
</tr>
</tbody>
</table>

4.3.3 Bending Tests

Bending tests measure the force required to bend a beam under three point loading conditions. The purpose of this test is to select materials for parts that support loads without bending. The flexural modulus indicates the stiffness of material when bent. The load is applied to the center generating three point bending at a given rate. The test parameters are the support span, loading rate, and the determined deflection. They all are based on the specimen thickness and are defined by ASTM D790. The equations used to calculate bending stress and bending strain are different from those used to calculate stress and strain for tensile and compressive tests. Figure 9 shows clearly the concave shape of bending stress-strain curves for all materials except Digital ABS™, which appears convex. Table 7 shows the flexural strength and flexural modulus of the selected materials from their material safety data sheet (MSDS).
Table 7: Flexural Strength and Flexural Modulus for selected materials from MSDS.

<table>
<thead>
<tr>
<th>Material</th>
<th>Flexural Strength [MPa]</th>
<th>Flexural Modulus [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABS</td>
<td>69</td>
<td>2300</td>
</tr>
<tr>
<td>PLA</td>
<td>80</td>
<td>4000</td>
</tr>
<tr>
<td>ULTEM9085</td>
<td>115</td>
<td>2500</td>
</tr>
<tr>
<td>PA2200</td>
<td>58</td>
<td>1500</td>
</tr>
<tr>
<td>Digital ABS™</td>
<td>66</td>
<td>1700-2200</td>
</tr>
</tbody>
</table>

Figure 12: Stress-Strain calculated from fit to bending data at 100% Infill for the materials.

Table 8 shows the results of the flexural strength and flexural modulus after testing with the MTS-machine. The values of the flexural modulus and flexural strength in Table 8 after testing with the MTS machine are less than the values of the flexural modulus obtained from material safety data sheet (MSDS) in Table 7. PLA has the highest flexural modulus value after that ULTEM9085 is the second highest value and PA2200 is the third.

Table 8: Flexural Strength and Flexural Modulus after testing with MTS machine at 100% Infill.

<table>
<thead>
<tr>
<th>Material</th>
<th>Flexural Strength [MPa]</th>
<th>Flexural Modulus [MPa]</th>
<th>SD [MPa]</th>
<th>SD [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABS</td>
<td>17.57</td>
<td>1065</td>
<td>0.87</td>
<td>16</td>
</tr>
<tr>
<td>PLA</td>
<td>25</td>
<td>2627</td>
<td>2.0</td>
<td>20</td>
</tr>
<tr>
<td>ULTEM9085</td>
<td>30</td>
<td>2049</td>
<td>1.0</td>
<td>20</td>
</tr>
<tr>
<td>PA2200</td>
<td>29.93</td>
<td>1490</td>
<td>0.14</td>
<td>30</td>
</tr>
<tr>
<td>Digital ABS™</td>
<td>20</td>
<td>1120</td>
<td>4.97</td>
<td>8.0</td>
</tr>
</tbody>
</table>
Table 9 shows the flexural strength and flexural modulus per unit mass for the thermoplastics at 100% infill. PA2200 has the highest flexural strength and flexural modulus per unit mass (69.8 kJ/kg) and (3465 kJ/Kg) accordingly. As before, these represent energies per unit mass absorbed before failure or per unit strain.

Table 9: Flexural Strength and Flexural Modulus per unit mass for the Thermoplastics at 100% Infill.

<table>
<thead>
<tr>
<th>Material</th>
<th>Density [kg/m³]</th>
<th>Flexural Strength [kJ/kg]</th>
<th>Flexural Modulus [kJ/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABS</td>
<td>1.04x10³</td>
<td>17.3</td>
<td>1022</td>
</tr>
<tr>
<td>PLA</td>
<td>1.25x10³</td>
<td>20.0</td>
<td>2102</td>
</tr>
<tr>
<td>ULTEM9085</td>
<td>1.34x10³</td>
<td>22.4</td>
<td>1529</td>
</tr>
<tr>
<td>PA2200</td>
<td>0.430x10³</td>
<td>69.8</td>
<td>3465</td>
</tr>
<tr>
<td>Digital ABS™</td>
<td>1.18x10³</td>
<td>17.0</td>
<td>949</td>
</tr>
</tbody>
</table>

4.3.4 Compressive Tests for ABS Cubes

We designed a cube with 1 in. sides using SolidWorks for compression test and printed several specimens of ABS using MakerBot replicator 2X as a solid at 100% of infill. The cubes were tested in different directions X, Y, and Z at two different speed rates 0.2 mm/s and 0.05 mm/s. We tested two sets of cubes, each set containing six cubes and each couple was tested in a different direction. After testing them with the MTS-machine, we obtained two different strain regions for all the cubes. The low strain region and high strain region. The results of compressive strength and compressive modulus for low strain and high strain regions were compared with the results of the compression tests of the standard samples with the specific dimensions according to ASTM D695. The results of high strain region of ABS cubes approximately match the results of the samples having dimensions according to the standard, while the results of low strain region never match. Figure 13 shows the stress-strain curves calculated from least squares fit to compression.
data for ABS cubes at 100% for the high strain region at a speed of 0.2 mm/s on the MTS-machine.

Figure 13: ABS cubes Stress-Strain calculated from fit at 100% Infill for high strain in X, Y, Z for compression rate 0.2 mm/s.

Figure 14 shows the stress-strain curves calculated from least squares fit to compression data for ABS cubes at 100% infill for the high strain region at a rate of 0.05 mm/s on the MTS-machine.
Figure 14: ABS cubes Stress-Strain calculated from fit at 100% Infill for high strain in X, Y, Z for compression rate 0.05 mm/s.

Tables 10 and 11 show the results of compressive strength and compressive modulus for both regions of strain (low and high) for ABS cubes when they were tested in different directions X, Y, and Z at two different speed rates. The low rate moduli for the X and Y directions are indistinguishable. This should be expected based on how the MakerBot prints each layer in the X and Y directions.

Table 10: Compressive Strength and Compressive Modulus for ABS cubes for low strain region.

<table>
<thead>
<tr>
<th>Print Direction</th>
<th>Speed Rate [mm/s]</th>
<th>Compressive Strength [MPa]</th>
<th>SD [MPa]</th>
<th>Compressive Modulus [MPa]</th>
<th>SD [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>0.2</td>
<td>5</td>
<td>1.0</td>
<td>260</td>
<td>8</td>
</tr>
<tr>
<td>Y</td>
<td>0.2</td>
<td>6.65</td>
<td>0.7</td>
<td>248</td>
<td>3</td>
</tr>
<tr>
<td>Z</td>
<td>0.2</td>
<td>4.5</td>
<td>0.9</td>
<td>330</td>
<td>9</td>
</tr>
<tr>
<td>X</td>
<td>0.05</td>
<td>5</td>
<td>2.0</td>
<td>284</td>
<td>11</td>
</tr>
<tr>
<td>Y</td>
<td>0.05</td>
<td>5.5</td>
<td>0.7</td>
<td>206</td>
<td>3</td>
</tr>
<tr>
<td>Z</td>
<td>0.05</td>
<td>4</td>
<td>0.25</td>
<td>236</td>
<td>7</td>
</tr>
</tbody>
</table>
Table 11: Compressive Strength and Compressive Modulus for ABS cubes for high strain region.

<table>
<thead>
<tr>
<th>Print Direction</th>
<th>Speed Rate [mm/s]</th>
<th>Compressive Strength [MPa]</th>
<th>SD[MPa]</th>
<th>Compressive Modulus [MPa]</th>
<th>SD[MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>0.2</td>
<td>70</td>
<td>16</td>
<td>1375</td>
<td>6</td>
</tr>
<tr>
<td>Y</td>
<td>0.2</td>
<td>90</td>
<td>9</td>
<td>1373</td>
<td>7</td>
</tr>
<tr>
<td>Z</td>
<td>0.2</td>
<td>61</td>
<td>6</td>
<td>1427</td>
<td>4</td>
</tr>
<tr>
<td>X</td>
<td>0.05</td>
<td>60</td>
<td>1.5</td>
<td>1393</td>
<td>3</td>
</tr>
<tr>
<td>Y</td>
<td>0.05</td>
<td>70</td>
<td>8</td>
<td>1396</td>
<td>9</td>
</tr>
<tr>
<td>Z</td>
<td>0.05</td>
<td>55.96</td>
<td>0.08</td>
<td>1241</td>
<td>7</td>
</tr>
</tbody>
</table>

4.3.5 Thermal Analysis

To better understand melting, solidification and leveling of these thermoplastics, differential scanning calorimetry (DSC) was done. It is important to understand material behavior under the influence of thermal loads. Thermal analysis provides important information of use to engineers and designers. The results of thermal analysis for ABS by using DSC are shown in Figure 15. We heated the sample and then cooled it consecutively for two cycles. Figure 15 shows the behavior of ABS during the first and second cycles. A small exothermic peak appeared around 50 ºC, but the graph in general indicates that ABS is an amorphous polymer.
Figure 15: Thermal Analysis of ABS.

Consequently, the thermal analysis results of PLA, ULTEM9085 and PA 2200 were obtained by following the same steps using the DSC under the same conditions. PLA thermal analysis, as plotted in Figure 16, shows that there are two small endothermic peaks. The first peak appeared around 60 °C, which is the glass transition temperature ($T_g$) for the polymer during the first cycle while the second peak was around 160 °C, which is the melting point ($T_m$) of PLA for both cycles. This indicates the polymer is partially crystalline.
Figure 16: Thermal Analysis of PLA.

ULTEM9085 thermal analysis as shown in Figure 17. From Figure 17, we can see there are no peaks appearing during the first or the second cycle and the uniform shape of the curves at the Figure 17 indicates that the ULTEM9085 is an amorphous polymer.
The thermal analysis for PA2200 is shown in Figure 18, showing two sharp peaks. The first peak was exothermic and appeared around 150 ºC and the second one is endothermic around 180 ºC, which is the melting point ($T_m$) of PA2200. These sharp peaks appear clearly during the first and second cycles, which shows crystalline behavior of the PA2200.
4.4 Conclusion

Five thermoplastic materials, ABS, PLA, PA2200, ULTEM9085, and Digital ABS™ were printed and tested for selected properties, tensile strength tests, compressive tests and bending tests. The thermoplastic materials ABS, PLA and ULTEM 9085 were printed at 100% of infill using fused deposition modeling (FDM). Five replicates from each material were printed and tested for each property. ABS samples were 3D printed with MakerBot replicator 2X, PLA samples were 3D printed with Type A Series 1, and ULTEM9085 samples were 3D printed with Fortus 400 MC. PA2200 samples were 3D printed using Selective Laser Sintering (SLS) at 100% of infill with EOS P 396.
Digital ABS™ samples were 3D printed using PolyJet™ technology with Stratasys Objet 500 Connex3. The average tensile strength and Young’s moduli of the 3D printed samples and flexural strength properties were slightly lower than the values of the material safety data sheets (MSDS) that were obtained from the manufacturer. The curves show near linear trends, showing that the rupture occurs without any dramatic change in elongation, which is typical for brittle structures.

Also, the values of the compressive modulus and compressive strength of the tested samples are lower than the original values obtained from the material safety data sheet (MSDS). This was most likely due to the heating and extrusion of the 3D printed tested samples, since they were extruded for a second time. For PA2200, which was printed using SLS, the tensile strength and Young modulus were indistinguishable from the values that obtained from the manufacturer (MSDS). Compression tests show that PLA and Digital ABS™ are anisotropic polymers, because they have different properties in different printing direction. ABS, ULTEM9085, and PA2200 have the same shape in both printing directions, but different slopes.

PLA has the highest values for both Young’s modulus and tensile strength. ULTEM9085 has the lowest Young’s modulus value and ABS has the lowest tensile strength value. PLA has the highest compressive modulus in the X direction and the second highest compressive strength in the Z direction. Digital ABS™ has the highest compressive strength in the Z direction and the second highest compressive modulus in X direction. PA2200 has the lowest compressive modulus in the X direction and ABS has the lowest compressive modulus value in the Z direction. PLA has the highest flexural modulus value, ULTEM9085 has the second highest value and PA2200 is the third highest.
Bending tests show that all the curves of the polymers appear clearly concave except for digital ABSTM that appears convex. The values of the flexural modulus after testing with the MTS-machine are less than the values of the flexural moduli obtained from the material safety data sheet (MSDS), and the values of the flexural strength after testing with the MTS machine are also less than the ones obtained from the material safety data sheet (MSDS). PA2200 has the highest values per unit mass for both tensile test and Young’s modulus (121 kJ/kg) and (3951 kJ/kg) consequently. PA2200 has the highest values for compressive strength and compressive modulus per unit mass in both printing directions X and Z. The compressive strength per unit mass is (121 kJ/kg) in X and (128 kJ/kg) in Z. The compressive modulus values per unit mass are (2733 kJ/kg) in X and (2474 kJ/kg) in Z. PA2200 has the highest flexural strength and flexural modulus per unit mass (69.8 kJ/kg) and (3465 kJ/Kg) accordingly. These values correspond to the energies per unit mass absorbed before failure and per unit strain, respectively.

For ABS cubes, after testing with the MTS-machine, two different strain regions were obtained for all the cubes; low strain region and high strain region. The results of the high strain region of ABS cubes approximately match the results of the samples that have dimensions according to the standard ASTM D695, while the results of low strain region never match. The thermal analyses of these polymers indicate that ABS and ULTEM9085 are amorphous, while PLA is partially crystalline and PA2200 is completely crystalline.

The results of mechanical properties of the thermoplastics are less than the criteria of the compact bones, but they exceed the criteria of the trabecular bones. The compressive modulus values fall within the range of human trabecular bones, while the compressive strength values exceed the range of human trabecular bones.
CHAPTER 5

DESIGNED HONEY COMB STRUCTURES FOR BONE REPLACEMENT

5.1 Introduction

5.1.1 Honeycomb Structures

Honeycomb structures, with their unique design properties providing mechanical strength and light weight, have attracted massive attention lately for both fundamental research and practical applications and progressively have become a hot research area [110]. The honeycomb structure has great properties, such as high mechanical strength, excellent structural stability, large space area, and low density. Therefore, the honeybee comb is one of the natural cellular structures that has been investigated by wide variety of researchers: physicists, mathematicians, and biologists. The microstructure of the walls and the macroscopic properties of honeybee combs have been researched in depth. The natural honeybee comb has been a typical example of interest for engineered cellular structures [110].

5.1.2 Three Dimensional Printing

Three dimensional printing technology is able to create 3D items by using many different materials. The technology is also called rapid prototyping, because it is a programmed process where 3D items are rapidly made [111]. Building 3D models using 3D printing technology saves time and cost because designing, manufacturing, and assembling of separate parts of a product is not required. 3D printing technology can make models of objects either designed with CAD programs or scanned with 3D scanners. The
technology has been widely used in many applications such as industrial design, engineering, architecture, aerospace, dental and medical applications [111].

One of the uses of 3D printing in the medical field is to substitute for damaged bones. For example, the 3d printed technology has been already applied to replace the bone structure of the injured or missing parts of people’s skulls damaged by diseases or trauma [77]. There are many cases when the bone structure is extensively damaged and cannot be recovered with regular methods such as casts. Currently, damaged bones are repaired with metal parts, but many cases show that the bone cannot be properly replaced or repaired. However, there have been several successful attempts of using 3D printing to create and replace human bone structures even for most complex shapes, such as skulls and jaws [77]. Many different biocompatible and biodegradable materials have been studied and tested for 3D printed bone structure. There are different 3D printing methods that can be applied for bone tissue-engineering: Fused Deposition Modeling (FDM), Selective Laser Sintering (SLS), and Stereolithography [112].

5.1.3 Thermoplastics

Thermoplastics have been used successfully as replacements for certain metals for many years in manufacturing, and recently they have been used widely in medical applications. 3D printing of polymers has a significant role in applying these materials, providing high performance, cost efficiency and enhanced resistance to environmental conditions [97].
5.1.4 Biomaterials

The study of biomaterials for bone replacement has progressed significantly over many years [113]. There are many examples of applications of 3D printing in creating implantable organs that are designed for specific patients to enhance accuracy and efficiency of the manufacturing. 3D printing uses computer models to build 3D objects by printing layers of materials, including plastics, metals, powders and liquid layer by layer. The process is also used to build items in the medical field that can exactly match the requirements and sizes of specific patients [114].

5.1.5 Bioprinting

Three-dimensional printing can improve medical care in some processes, and it will also open new opportunities for bone replacement or cure. For example, this technology has been successfully applied in the field of prosthetics and drug printing [115]. 3D models are produced through constructive processes. 3D printing refers to only such technologies that use constructive manufacturing ways. It is likely that more medical professionals will introduce 3D printing technologies into their practices. 3D printing gives enormous benefits for experts to produce only what they need, which can reduce production time. It allows objects from actual human scans to be modeled and built for further applications in a few hours, even inside medical facilities [115]. Several processes can be only accomplished with the use of a 3D printer. Biofabrication is a process that doctors traditionally use to produce organ replacements themselves, or order from specialized companies. However, they can now be more successfully accomplished by using 3D printing technologies [114]. We have been studying and testing several biopolymer produced bone structures using 3D printing technology. In this work, we will describe how
we can optimize the internal bone building structure through engineering them for 3D printing process. The thermoplastics that we have been using for 3D printing processes are: ULTEM9085, Polyamide (PA2200), and Digital ABS™ (a crosslinked acrylic polymer) [99].

5.2 Experimental

5.2.1 3D Printing of Test Samples

Using 3D printing technology three different 3D printed samples of thermoplastic materials were printed. ULTEM9085, PA2200 (Polyamide), and Digital ABS™ were employed. Table 12 shows selected properties of these thermoplastics.

<table>
<thead>
<tr>
<th>Material</th>
<th>Tensile strength [MPa]</th>
<th>Young Modulus [MPa]</th>
<th>Melting point [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ULTEM9085</td>
<td>71.6</td>
<td>2200</td>
<td>186</td>
</tr>
<tr>
<td>PA2200</td>
<td>48</td>
<td>1700</td>
<td>172-180</td>
</tr>
<tr>
<td>Digital ABS™</td>
<td>55-60</td>
<td>2600-3000</td>
<td>47-53</td>
</tr>
</tbody>
</table>

We used SolidWorks software to design the internal engineered honeycomb structure with different geometric shapes (hexagonal, triangular, and square). The samples were printed using different 3D printing methods [112]. The Fused Deposition Modeling (FDM) technique was used to print ULTEM9085, with Stratasys machine Fortus 400 MC. Selective Laser Sintering (SLS) was used to print PA2200 (Polyamide) with an EOSP 396. PolyJet™ technology was used to print digital ABS™ with a Stratasys Objet 500 Connex3. All the samples were printed with designed internal structures with different geometric shapes. Five samples were printed for each category [104]. In this work, we mimic the trabecular (spongy) bone structure with the average pore size of the real one (400 µm). The designed structures are shown at Figures (19-21).
Figure 19: Hexagonal Honeycomb Structure.

Figure 20: Triangular Honeycomb Structure.

Figure 21: Square Honeycomb Structure.
5.2.2 Testing Mechanical Properties of 3D Printed Samples using MTS-Machine

The tested samples were designed according to the standard with specific dimensions for all mechanical properties tests. For tensile strength test ISO 3167 standard, for compression test ASTM D695 standard and for bending test ASTM D790 standard, were employed. An MTS Bionix Servohydraulic Test Systems-Model 370.02 instrument was employed for testing. We tested the 3D printed samples at 0.2 mm/sec speed of MTS-machine at room temperature. The force capacity of the device is 25 KN and it is used to determine the dynamic properties for a number of biomaterials. The axial alignments of the system are intended to achieve precise tension, compression and bending tests as well as fatigue and fracture studies. Also, they are used to test durability properties of components such as hip, knee and spine implants [112].

5.2.3 Calculating Void Volume and Percentage of Infill for Designed Structures

We calculated the void volume and percentage of infill for designed structures with different geometric shapes. Table 13 shows the void volume fraction, fill fraction and percentage of infill for the geometric shapes. We wanted to investigate the influence of the geometric shape on the percentage of infill and the impact of the percentage of infill on the strength. From table 13, we observe that the hexagonal structure has the highest percentage of infill 92.6% followed by the triangular structure 83.6% and the lowest is the square structure 82.9%.

<table>
<thead>
<tr>
<th>Geometric Structure</th>
<th>Void volume fraction</th>
<th>Fill fraction</th>
<th>Infill%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Square Structure</td>
<td>0.172</td>
<td>0.829</td>
<td>82.9</td>
</tr>
<tr>
<td>Triangular Structure</td>
<td>0.164</td>
<td>0.836</td>
<td>83.6</td>
</tr>
<tr>
<td>Hexagonal Structure</td>
<td>0.074</td>
<td>0.926</td>
<td>92.6</td>
</tr>
</tbody>
</table>
5.3 Results and Discussions

5.3.1 Tensile Strength Tests

Table 14 shows the results of the average tensile strength and Young’s modulus for ULTEM9085, PA2200, and Digital ABS™ geometric structures after testing with the MTS machine.

Table 14: Tensile Strength and Young’s modulus for different geometric structures. Standard deviation of Young’s modulus was calculated from the standard error of the coefficient of the linear term in a quadratic fit to the tensile data.

<table>
<thead>
<tr>
<th>Geometric Structure</th>
<th>Tensile Strength [MPa]</th>
<th>SD [MPa]</th>
<th>Young’s Modulus [MPa]</th>
<th>SD [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ULTEM9085 Solid</td>
<td>49.7</td>
<td>0.6</td>
<td>1540</td>
<td>3</td>
</tr>
<tr>
<td>ULTEM9085 Hexagonal</td>
<td>32</td>
<td>3.0</td>
<td>1327</td>
<td>10</td>
</tr>
<tr>
<td>ULTEM9085 Triangular</td>
<td>32</td>
<td>2.0</td>
<td>1480</td>
<td>11</td>
</tr>
<tr>
<td>ULTEM9085 Square</td>
<td>32</td>
<td>1.2</td>
<td>1347</td>
<td>3</td>
</tr>
<tr>
<td>PA2200 Solid</td>
<td>49.7</td>
<td>0.7</td>
<td>1699</td>
<td>12</td>
</tr>
<tr>
<td>PA2200 Hexagonal</td>
<td>43</td>
<td>2.95</td>
<td>1508</td>
<td>17</td>
</tr>
<tr>
<td>PA2200 Triangular</td>
<td>42</td>
<td>2.7</td>
<td>1456</td>
<td>15</td>
</tr>
<tr>
<td>PA2200 Square</td>
<td>43</td>
<td>2.0</td>
<td>1487</td>
<td>4</td>
</tr>
<tr>
<td>Digital ABS™ Solid</td>
<td>55</td>
<td>2.7</td>
<td>2013</td>
<td>12</td>
</tr>
<tr>
<td>Digital ABS™ Hexagonal</td>
<td>24.7</td>
<td>0.57</td>
<td>1124</td>
<td>3</td>
</tr>
<tr>
<td>Digital ABS™ Triangular</td>
<td>23.8</td>
<td>0.48</td>
<td>1036</td>
<td>3</td>
</tr>
<tr>
<td>Digital ABS™ Square</td>
<td>32</td>
<td>2.58</td>
<td>1414</td>
<td>13</td>
</tr>
</tbody>
</table>

ULTEM9085 printed with three different geometries, hexagonal, triangular and square gave the same values of the tensile strength, but different Young’s modulus values [Table 14]. The triangular structure has the highest Young’s modulus. Followed by ULTEM9085 square structure, and the lowest Young’s modulus was found in ULTEM9085 hexagonal structure.

PA2200 hexagonal structure has the highest tensile strength average and Young’s modulus [Table 14], followed by PA2200 square structure, and PA2200 triangular structure. For digital ABS™, the square structure has the highest average value for both tensile strength and Young’s modulus, followed by digital ABS hexagonal structure and
digital ABS triangular structure. Generally, the values are in the same range for all the structures. However, if we look at hexagonal structure, the PA2200 resulted in highest tensile strength (43 MPa) along with highest Young’s modulus (1508 MPa). Similarly, ULTEM9085 resulted in the strongest triangular structure, with Young’s modulus of (1480 MPa) and tensile strength of (32 MPa). ULTEM9085 had slightly higher Young’s modulus of 1480 MPa than PA 2200 (1456 MPa). PA 2200 showed also the strongest square structure with (43 MPa) tensile strength and highest Young’s modulus of (1487 MPa).

Figure 22 shows the tensile strength vs. Young’s modulus for designed structures. Tensile strength is the capacity of the material or structure to withstand loads tending to elongate. The behavior shows that the tensile strength and Young’s modulus shows a strong correlation. 3D printed polymer structures show particular trend in values. There is significant relation between tensile strength and Young’s modulus and the correlation is nearly linear.

Figure 22: Tensile Strength vs. Young’s Modulus.
Figure 23 shows the stress-strain curves calculated from the least squares fit to the tensile data for ULTEM9085 hexagonal, triangular, and square structures at the MTS-machine speed of 0.2 mm/sec and room temperature.

Similarly, the stress-strain curves calculated from the least squares fit to the tensile data for polyamide (PA2200), and digital ABS™ (a crosslinked acrylic polymer) structures were obtained (Figures 24-25). The curves show near linear trend, showing that the rupture occurs without any dramatic change in elongation, which is typical for brittle structures [108]. Figure 24 shows the stress-strain curves for PA2200 structures. The shape of stress strain curves pinpoints brittle structures, which do not exhibit any dramatic change in elongation prior to rupture. Figure 25 shows the stress-strain curves for digital ABS™ geometric structures, which show a stress-strain trend of brittle structures. The brittle material ruptures without any obvious prior change in the rate of elongation.
Figure 24: PA2200 structures Stress-Strain calculated from fit.

Figure 25: Digital ABSTM structures Stress-Strain calculated from fit.

Table 15 shows the tensile strength and Young’s modulus per unit mass for different geometric structures of the materials.
Table 15: Tensile Strength and Young’s Modulus per unit mass for designed structures.

<table>
<thead>
<tr>
<th>Geometric Structure</th>
<th>Tensile Strength [kJ/kg]</th>
<th>Young’s Modulus [kJ/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ULTEM9085 Solid</td>
<td>37.3</td>
<td>1149</td>
</tr>
<tr>
<td>ULTEM9085 Hexagonal</td>
<td>25.9</td>
<td>1070</td>
</tr>
<tr>
<td>ULTEM9085 Triangular</td>
<td>28.6</td>
<td>1321</td>
</tr>
<tr>
<td>ULTEM9085 Square</td>
<td>28.8</td>
<td>1203</td>
</tr>
<tr>
<td>PA2200 Solid</td>
<td>121</td>
<td>3951</td>
</tr>
<tr>
<td>PA2200 Hexagonal</td>
<td>108</td>
<td>3789</td>
</tr>
<tr>
<td>PA2200 Triangular</td>
<td>117</td>
<td>4044</td>
</tr>
<tr>
<td>PA2200 Square</td>
<td>119</td>
<td>4130</td>
</tr>
<tr>
<td>Digital ABS™ Solid</td>
<td>46.6</td>
<td>1706</td>
</tr>
<tr>
<td>Digital ABS™ Hexagonal</td>
<td>23.0</td>
<td>1028</td>
</tr>
<tr>
<td>Digital ABS™ Triangular</td>
<td>24.0</td>
<td>1050</td>
</tr>
<tr>
<td>Digital ABS™ Square</td>
<td>33.0</td>
<td>1446</td>
</tr>
</tbody>
</table>

From table 15, PA2200 square has the highest value for both Young’s modulus per unit mass (4130 kJ/kg), and strength per unit mass (119 kJ/kg). After that PA2200 triangular is the second (4044 kJ/kg) and (117 kJ/kg) respectively. Then PA2200 hexagonal is the third (3789 kJ/kg) and (108 kJ/kg). The PA2200 strength values for both triangular and square are virtually indistinguishable from the 100% infill case for this polymer. This is an indication that these two structures can absorb about the same tensile energy per unit mass as the corresponding solid structure without failing. This could have a profound effect in using this polymer for replacements of original components in many applications. Digital ABS™ hexagonal has the lowest values for both Young’s modulus (1028 kJ/kg) and tensile strength (23 kJ/kg).

5.3.2 Compressive Strength

Compressive strength tests provide information about the compressive properties of geometric structures. The compressive test properties explain the performance of the material with its internal engineered structure when it is compressed under a load that is relatively low and uniform. Compressive strength of trabecular bones is in the range of 5-
The specimen dimensions were printed as blocks according to ASTM D695 standard. Table 16 shows the results of the compressive strength and compressive modulus for selected materials from material safety data sheets (MSDS).

**Table 16: Compressive Strength and Compressive Modulus for selected Materials from MSDS.**

<table>
<thead>
<tr>
<th>Material</th>
<th>Compressive Strength [MPa]</th>
<th>Compressive Modulus [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ULTEM9085</td>
<td>104</td>
<td>1930</td>
</tr>
<tr>
<td>PA2200</td>
<td>58</td>
<td>1500</td>
</tr>
<tr>
<td>Digital ABS™</td>
<td>70</td>
<td>2200</td>
</tr>
</tbody>
</table>

Table 17 shows the average compressive strength and compressive modulus for ULTEM9085, PA2200, and Digital ABS™ structures after testing with the MTS-machine.

**Table 17: Compressive Strength and Compressive Modulus for various geometries. Standard deviation of Young’s Modulus was calculated from the standard error of the coefficient of the linear term in a quadratic fit to the compression data.**

<table>
<thead>
<tr>
<th>Geometric Structure</th>
<th>Compressive Strength [MPa]</th>
<th>SD [MPa]</th>
<th>Compressive Modulus [MPa]</th>
<th>SD [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ULTEM9085 Solid</td>
<td>69.98</td>
<td>0.05</td>
<td>1870</td>
<td>13</td>
</tr>
<tr>
<td>ULTEM9085 Hexagonal</td>
<td>42.9</td>
<td>0.017</td>
<td>1068</td>
<td>13</td>
</tr>
<tr>
<td>ULTEM9085 Triangular</td>
<td>50.98</td>
<td>0.024</td>
<td>1293</td>
<td>16</td>
</tr>
<tr>
<td>ULTEM9085 Square</td>
<td>49.99</td>
<td>0.015</td>
<td>1216</td>
<td>4</td>
</tr>
<tr>
<td>PA2200 Solid</td>
<td>54.93</td>
<td>0.15</td>
<td>1175</td>
<td>23</td>
</tr>
<tr>
<td>PA2200 Hexagonal</td>
<td>49.99</td>
<td>0.012</td>
<td>763</td>
<td>10</td>
</tr>
<tr>
<td>PA2200 Triangular</td>
<td>49.7</td>
<td>0.6</td>
<td>476</td>
<td>4</td>
</tr>
<tr>
<td>PA2200 Square</td>
<td>49.65</td>
<td>0.7</td>
<td>962</td>
<td>13</td>
</tr>
<tr>
<td>Digital ABS™ Solid</td>
<td>75</td>
<td>5</td>
<td>2157</td>
<td>20</td>
</tr>
<tr>
<td>Digital ABS™ Hexagonal</td>
<td>25</td>
<td>2.6</td>
<td>1298</td>
<td>10</td>
</tr>
<tr>
<td>Digital ABS™ Triangular</td>
<td>29.99</td>
<td>0.005</td>
<td>1153</td>
<td>11</td>
</tr>
<tr>
<td>Digital ABS™ Square</td>
<td>39</td>
<td>1.0</td>
<td>716</td>
<td>7</td>
</tr>
</tbody>
</table>

Table 17 shows that all the materials have compressive strength sufficient for replacement of trabecular bones. The compressive modulus is the highest for Digital ABS™ hexagonal structure, followed by ULTEM 9085 triangular, and square structure. On the other hand, compressive strength values were indistinguishable among PA2200 structures and ULTEM9085 square and triangular structures. The least compressive strength was found for digital ABS™ hexagonal structures, which had the highest
compressive modulus. For brittle materials, the eventual strength in compression is much higher than the eventual strength in tension. This refers to the existence of microscopic cracks or cavities, which tend to deteriorate the material in tension, while not significantly affecting its resistance to compressive failure [108].

Figure 26 shows compressive strength vs. compressive modulus for the designed structures. Compressive strength is the capacity of the material or structure to resist loads tending to decrease size different than tensile strength, which resists loads tending to elongate. Roughly, Figure 26 shows a random relation between compressive strength and compressive modulus of chosen polymer 3D structures, as confirmed by statistical analysis.

![Figure 26: Compressive Modulus vs. Compressive Strength.](image)

Compressive modulus values of human trabecular bone range from 1 to 5000 MPa, with strength values ranging from 0.10 to 27.3 MPa [67]. The thermoplastics structures show compressive modulus values ranging from 476 to 1298 MPa. The strength values of the thermoplastic structures range from 25 to 60 MPa. The compressive moduli values fall within the range of human trabecular bone, while the compressive strength values exceed
the range of human trabecular bone. Figure 27 shows the stress-strain curve calculated from least squares fit to compression data for ULTEM9085 geometric structures.

![Calculated Stress vs. Calculated Strain](image)

**Figure 27:** ULTEM9085 structures Stress-Strain calculated from fit to compression data.

Figure 28 shows the stress-strain curve and calculated (stress-strain) of PA2200 geometric structures for compression test. The hexagonal and square PA2200 structures appear to have convex trends, while triangular PA2200 structure shows concave trend.
Figure 28: PA2200 structures Stress-Strain calculated from fit to compression data.

Figure 29 shows the stress-strain curve calculated from least squares fit to compression data for digital ABSTM geometric structures.

Figure 29: Digital ABSTM structures Stress-Strain calculated from fit to compression data.
Table 18 shows the compressive strength and compressive modulus per unit mass for different geometric structures of the materials.

<table>
<thead>
<tr>
<th>Geometric Structure</th>
<th>Compressive Strength [kJ/kg]</th>
<th>Compressive Modulus [kJ/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ULTEM9085 Solid</td>
<td>52.0</td>
<td>1396</td>
</tr>
<tr>
<td>ULTEM9085 Hexagonal</td>
<td>34.7</td>
<td>861</td>
</tr>
<tr>
<td>ULTEM9085 Triangular</td>
<td>45.5</td>
<td>1155</td>
</tr>
<tr>
<td>ULTEM9085 Square</td>
<td>45.0</td>
<td>1096</td>
</tr>
<tr>
<td>PA2200 Solid</td>
<td>121</td>
<td>2733</td>
</tr>
<tr>
<td>PA2200 Hexagonal</td>
<td>126</td>
<td>1917</td>
</tr>
<tr>
<td>PA2200 Triangular</td>
<td>139</td>
<td>1322</td>
</tr>
<tr>
<td>PA2200 Square</td>
<td>140</td>
<td>2702</td>
</tr>
<tr>
<td>Digital ABS™ Solid</td>
<td>63.6</td>
<td>1828</td>
</tr>
<tr>
<td>Digital ABS™ Hexagonal</td>
<td>23.0</td>
<td>1188</td>
</tr>
<tr>
<td>Digital ABS™ Triangular</td>
<td>30.0</td>
<td>1168</td>
</tr>
<tr>
<td>Digital ABS™ Square</td>
<td>40.0</td>
<td>732</td>
</tr>
</tbody>
</table>

From table 18, PA2200 square has the highest compressive modulus value per unit mass (2702 kJ/kg). Then, PA2200 hexagonal is the second (1917 kJ/kg), PA2200 triangular is the third (1322 kJ/kg) and Digital ABS™ square has the lowest compressive modulus per unit mass (732 kJ/kg). PA2200 square has the highest compressive strength per unit mass (140 kJ/kg) and Digital ABS™ hexagonal has the lowest compressive strength value per unit mass (23 kJ/kg). All of void structures for PA2200 seem to be able to absorb more compressive energy per unit mass than the corresponding solid structure.

### 5.3.3 Bending Strength

Bending strength tests measure the force required to bend a beam under three point loading conditions. The goal of this test is to select materials for parts that support loads without flexing. A homogeneous material would have tensile and bending strengths identical. More flexible polymers have lower bending strength values than stiffer ones [116]. However, printed 3D polymer structures are not expected to be homogenous, the
polymer chains may be oriented in the print direction, which ultimately gives non-homogenous character to the structure. On the macroscopic level, non-homogeneity is created by selection of the particular honeycomb structure. The flexural modulus indicates the stiffness of material depending on its internal honeycomb structure when bent. Flexural or bending modulus would ideally have the same value as compressive or tensile modulus, but it often differs, especially for polymers. The load is applied to the center generating three point bending at certain rate. The test parameters are the support span, loading rate, and the determined deflection. They all are based on the specimen thickness and are defined by ASTM D790 Standard. Table 19 shows the flexural strength and flexural modulus of the selected materials from their material safety data sheets (MSDS).

<table>
<thead>
<tr>
<th>Material</th>
<th>Flexural Strength [MPa]</th>
<th>Flexural Modulus [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ULTEM9085</td>
<td>115</td>
<td>2500</td>
</tr>
<tr>
<td>PA2200</td>
<td>58</td>
<td>1500</td>
</tr>
<tr>
<td>Digital ABS™</td>
<td>66-75</td>
<td>1700-2200</td>
</tr>
</tbody>
</table>

Table 19: Flexural Strength and Flexural Modulus for selected Materials from MSDS.

Table 20 shows the average flexural strength and flexural modulus for ULTEM9085, PA2200, and Digital ABS™ structures after testing with the MTS-machine.

<table>
<thead>
<tr>
<th>Geometric Structure</th>
<th>Flexural Strength [MPa]</th>
<th>SD [MPa]</th>
<th>Flexural Modulus [MPa]</th>
<th>SD [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ULTEM9085 Solid</td>
<td>30</td>
<td>1.0</td>
<td>2049</td>
<td>20</td>
</tr>
<tr>
<td>ULTEM9085 Hexagonal</td>
<td>19.89</td>
<td>0.22</td>
<td>767</td>
<td>3</td>
</tr>
<tr>
<td>ULTEM9085 Triangular</td>
<td>12</td>
<td>2.0</td>
<td>1390</td>
<td>5</td>
</tr>
<tr>
<td>ULTEM9085 Square</td>
<td>13.9</td>
<td>0.005</td>
<td>983</td>
<td>4</td>
</tr>
<tr>
<td>PA2200 Solid</td>
<td>29.93</td>
<td>0.14</td>
<td>1490</td>
<td>30</td>
</tr>
<tr>
<td>PA2200 Hexagonal</td>
<td>7.99</td>
<td>0.008</td>
<td>1400</td>
<td>15</td>
</tr>
<tr>
<td>PA2200 Triangular</td>
<td>13.64</td>
<td>0.73</td>
<td>1331</td>
<td>13</td>
</tr>
<tr>
<td>PA2200 Square</td>
<td>15.96</td>
<td>0.08</td>
<td>1270</td>
<td>12</td>
</tr>
<tr>
<td>Digital ABS™ Solid</td>
<td>20</td>
<td>4.97</td>
<td>1120</td>
<td>8</td>
</tr>
<tr>
<td>Digital ABS™ Hexagonal</td>
<td>7.87</td>
<td>0.26</td>
<td>465</td>
<td>8</td>
</tr>
<tr>
<td>Digital ABS™ Triangular</td>
<td>8.89</td>
<td>0.21</td>
<td>915</td>
<td>10</td>
</tr>
<tr>
<td>Digital ABS™ Square</td>
<td>8.84</td>
<td>0.32</td>
<td>590</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 20: Flexural Strength and Flexural Modulus for structures. Standard deviation of Young’s Modulus was calculated from the standard error of the coefficient of the linear term in a quadratic fit to the bending data.
Figure 30 shows relationship between flexural strength and flexural modulus of 3D printed polymer structures, showing no particular trend in values. The behavior between flexural strength and flexural modulus follows a random relation. There is no significant relation between flexural strength and flexural modulus, as confirmed by statistical analysis. Hexagonal Digital ABS™ and square Digital ABS™ structure with 8 MPa bending strength have a much lower flexural modulus (465 and 590 MPa) than PA2200 hexagonal structure with the same bending strength, but much higher flexural modulus of 1400 MPa. Overall, all PA2200 structures had flexural modulus over 1000 MPa. Figure 31 shows the stress-strain curve calculated fit to bending data for ULTEM9085 geometric structures at an MTS machine speed of 0.2 mm/sec at room temperature. The hexagonal honeycomb structure appears convex for ULTEM9085, while triangular and square honeycomb structures appear concave.
Figure 31: ULTEM9085 structures Stress-Strain calculated from fit.

Figure 32 shows the stress-strain curve calculated least squares fit to bending data for PA2200 geometric structures. All the structures appear to have concave trend. Figure 33 shows the stress-strain curve calculated from least squares fit to bending data for digital ABS™ structures.
Figure 32: PA2200 structures Stress-Strain calculated from fit.

Figure 33: Digital ABSTM structures Stress-Strain calculated from fit.
Table 21 shows the flexural strength and flexural modulus per unit mass for different geometric structures of the materials.

**Table 21: Flexural Strength and Flexural Modulus per unit mass for designed structures**

<table>
<thead>
<tr>
<th>Geometric Structure</th>
<th>Flexural Strength [kJ/kg]</th>
<th>Flexural Modulus [kJ/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ULTEM9085 Solid</td>
<td>22.4</td>
<td>1529</td>
</tr>
<tr>
<td>ULTEM9085 Hexagonal</td>
<td>16.0</td>
<td>619</td>
</tr>
<tr>
<td>ULTEM9085 Triangular</td>
<td>10.7</td>
<td>1241</td>
</tr>
<tr>
<td>ULTEM9085 Square</td>
<td>12.6</td>
<td>886</td>
</tr>
<tr>
<td>PA2200 Solid</td>
<td>69.8</td>
<td>3465</td>
</tr>
<tr>
<td>PA2200 Hexagonal</td>
<td>20.0</td>
<td>3517</td>
</tr>
<tr>
<td>PA2200 Triangular</td>
<td>39.0</td>
<td>3697</td>
</tr>
<tr>
<td>PA2200 Square</td>
<td>45.0</td>
<td>3576</td>
</tr>
<tr>
<td>Digital ABSTM Solid</td>
<td>17.0</td>
<td>949</td>
</tr>
<tr>
<td>Digital ABSTM Hexagonal</td>
<td>7.32</td>
<td>425</td>
</tr>
<tr>
<td>Digital ABSTM Triangular</td>
<td>9.12</td>
<td>927</td>
</tr>
<tr>
<td>Digital ABSTM Square</td>
<td>8.18</td>
<td>603</td>
</tr>
</tbody>
</table>

From table 21, PA2200 triangular has the highest flexural modulus value per unit mass (3697 kJ/kg). After that PA2200 square has the second highest flexural modulus value per unit mass (3576 kJ/kg) and PA2200 hexagonal is the third (3517 kJ/kg). Digital ABSTM hexagonal has the lowest values for both flexural modulus per unit mass (425 kJ/kg) and flexural strength per unit mass (7.32 kJ/kg). The Flexural strength per unit mass for the PA2200 square is not quite as much as the corresponding solid structure, but it is stiffer on a mass basis than the solid structure. This indicates that as long as the structure doesn't fail, it will bend less under moderate forces than the corresponding solid structure having the same mass.

### 5.4 Conclusion

The 3D printed samples with internal designed honeycomb structures (Hexagonal, Triangular, and Square) were printed for three different materials (ULTEM9085, PA2200, and Digital ABSTM), using three different methods. The 3D printing methods are Fused
Deposition Modeling (FDM), Selective Laser Sintering (SLS), and PolyJet technology, accordingly. The mechanical properties of the honeycomb structures that were tested are tensile strength test, compressive test, and bending test. From the obtained results we observed that the highest Young’s modulus for ULTEM 9085 was obtained with triangular honeycomb structure and the lowest value was obtained with hexagonal honeycomb structure. The tensile strength test values are the same for all three structures of ULTEM9085, but lower than the solid value. For PA2200 hexagonal honeycomb has the highest value of Young’s modulus, while the triangular structure has the lowest, although they are not that much different from one another. For digital ABS the square honeycomb structure has the highest values for both Young’s modulus and tensile strength, while the triangular structure has the lowest values for both. The relationship between tensile strength and Young’s modulus is one of strong correlation. This relationship is nearly linear.

For compressive test and compressive modulus, the highest values are obtained with the triangular structure and the lowest ones are obtained with the hexagonal structure for ULTEM9085. For PA2200, the square structure has the highest compressive modulus and the triangular has the lowest compressive modulus, but the tensile strengths are the same for all three structures. For digital ABS™ the hexagonal structure has the highest compressive modulus value but the lowest compressive strength. The square structure has the lowest compressive modulus, but the highest compressive strength. This indicates that the compressive modulus is acting contrary with compressive strength for this polymer.

The eventual strength in compression is higher than the eventual strength in tension for brittle materials. This is because the existence of microscopic cracks or cavities, which tend to deteriorate the material in tension, while not significantly affecting its resistance to
compressive failure. However, the microcracked compressed sample will likely not return to its original shape, which would likely compromise its behavior to additional stresses.

For bending test and flexural modulus. ULTEM9085 triangular structure has the highest value of flexural modulus and the lowest bending strength value. ULTEM9085 hexagonal structure has the lowest value of flexural modulus but the highest bending strength. PA2200 hexagonal structure showed the highest flexural modulus value but the lowest bending strength. The square structure showed the lowest flexural modulus value but the highest bending strength. Digital ABS triangular structure has the highest flexural modulus value and the highest bending strength. The hexagonal honeycomb structure for digital ABSTM has the lowest flexural modulus. The highest bending strength was obtained with the triangular structure, while the hexagonal and square structures have the same bending strength values. The behavior between flexural strength and flexural modulus follow random relation. There is no significant relation between flexural strength and flexural modulus for the 3D printed structures.

PA2200 square has the highest values for both Young’s modulus per unit mass and tensile strength per unit mass. After that PA2200 triangular is the second and PA2200 hexagonal is the third. The PA2200 strength values for both triangular and square are virtually indistinguishable from the 100% infill case for this polymer. This is an indication that these two structures can absorb about the same tensile energy per unit mass as the corresponding solid structure without failing. Digital ABSTM hexagonal has the lowest values for both Young’s modulus.

PA2200 square has the highest compressive modulus value per unit mass. Then, PA2200 hexagonal is the second PA2200 triangular is the third and Digital ABSTM square
has the lowest compressive modulus per unit mass. PA2200 square has the highest compressive strength per unit mass and Digital ABST™ hexagonal has the lowest compressive strength value per unit mass. All of void structures for PA2200 seem to be able to absorb more compressive energy per unit mass than the corresponding solid structure.

PA2200 triangular has the highest flexural modulus value per unit mass. After that PA2200 square has the second highest flexural modulus value per unit mass and PA2200 hexagonal is the third. Digital ABST™ hexagonal has the lowest values for both flexural modulus per unit mass and flexural strength per unit mass. The Flexural strength per unit mass for the PA2200 square is not quite as much as the corresponding solid structure, but it is stiffer on a mass basis than the solid structure. This indicates that as long as the structure doesn't fail, it will bend less under moderate forces than the corresponding solid structure having the same mass.

With the obtained results it is hard to realize which structure is the strongest and has the best mechanical properties. This is because the 3D printed samples of the structures were printed using different 3D printing methods of the printed materials. The results of the thermoplastic designed structures either exceed or fall within the range of the mechanical properties of the human trabecular bone. However, the PA2200 shows the most promise for all of the void structures. It would be even more interesting if the behavior reported here could be replicated using other printing methods such as FDM or inkjet.
CHAPTER 6

BIOPOLYMERS FOR 3D PRINTED BONE STRUCTURE

6.1 Introduction

6.1.1 Three–dimensional Printing

Three-dimensional printing is a new technology that creates 3D items using a wide range of materials. This technology is also called rapid prototyping, because it is a programmed process where 3D items are rapidly made. A 3D model can be scaled and sized according to the desired shape from 3D printer software. Making 3D models by using inkjet technology can save time and cost because designing, printing and assembling disconnected parts of the model is not needed. 3D printing technology can make models of objects either designed with a CAD program or scanned with a 3D scanner. The technology is used widely in many applications as industrial design, engineering, architecture, construction, aerospace, automotive, dental and medical applications [111].

6.1.2 Biomaterials

The study of biomaterials for bone replacement has progressed significantly over many years [113]. There are many examples of applications of 3D printing in creating implantable organs that are designed for specific patients to enhance accuracy and efficiency of the manufacturing.

3D printing uses computer models to build three-dimensional objects by printing layers of materials, including plastics, metals, powders and liquids layer by layer. The process is also used to build items in the medical field that meet the exact requirements and dimensions of specific patients [117]. We are studying and testing several biocompatible and biodegradable materials to print bone structures using the Fused Deposition Modelling
technique [85] and PolyJet™ [99] technology. In this project, we will optimize the inside bone building structure through modifying the printing process. Some of thermoplastics that have been tested so far are Acrylonitrile butadiene styrene (ABS) [100], Polylactic Acid (PLA) [101], Polyvinyl Alcohol (PVA) [118], and Digital ABSTM [104].

6.1.3 Bioprinting

Three-dimensional printing can improve medical care in some processes, and it will also open new opportunities for bone replacement or cure. The technology has been used in the field of prosthetics and drug printing. 3D models are produced through constructive processes. 3D printing refers to only such technologies that use constructive manufacturing ways. It is very likely that more medical professionals will introduce 3D printing technologies into their practices. 3D printing gives enormous benefits for experts to produce only what they need, which can reduce production time. It allows objects from actual human scans to be modelled and built for further application in a few hours, even inside medical facilities. Several processes can be only accomplished with use of a 3D printer. Biofabrication is a process that doctors conventionally do by hand, or ask specialized companies to produce. However, they can now be more successfully accomplished by using 3D printing technologies [115].

6.1.4 Fused Deposition Modeling

Fused Deposition Modelling (FDM) is chosen as a method to make 3D printed items from thermoplastics, because it enables high precision when working with many biocompatible polymers. During the printing process, a plastic filament is heated until it reaches the melting point. Then, the extruder drives the molten plastic through the extrusion nozzle and puts it on the plate to build an object layer by layer. First, a 3D model is created
by using special software, and then the model is converted to Stereo Lithography (STL) format to produce a 3D printed object. This format simply maintains the shape of the 3D model and modifies its geometry including scaling and quality [85].

Once the STL file is imported to the FDM software, it is sliced into multiple parallel thin slices that become layers prepared for 3D printing. These slices represent 2D profiles that the FDM process will produce, which, when stacked on top of each other, will be built into the 3D object that matches the original design. Thinner layers enable higher precision for objects to be printed [62].

Stepper motors move the head on the X-Y plane to structure a specific shape of the layer and the extrusion nozzle puts down the material in accordance with the sliced information taken from the STL file. Once the layer is produced, the plate moves vertically in the z direction to start building a new layer on the top of the previous. The process keeps repeating until the entire object is totally built [62].

6.1.5 PolyJet Photopolymerization

The PolyJet printer is manufactured by Stratasys [99] and its working mechanism is similar to an inkjet printer. Generally, it has the same principle, it jets layers of curable liquid onto a build plate instead of jetting drops of ink onto paper. The build platform moves vertically to leave a space for the following layers. The layers gather on the build platform to produce the desired part. The process can produce smooth, exact parts with a layer resolution of 16 µm, which means the finishing of the 3D printed part is quite good. Also, it can produce thin walls and complex geometric shapes with many materials. To avoid deflection, because movement by the printing mechanism and to allow the printing of complex objects, 3D printers need support structures. The software of the printer
automatically adds supports through the printing process. PolyJet printers use support resin structures that can be removed easily by flushing with water [89] [90] [119].

6.2 Experimental

6.2.1 3D Printing of Test Samples

Using 3D printing technology, three different samples of thermoplastic materials were printed. These were ABS (Acrylonitrile-Butadiene-Styrene, manufacturer), PVA (Polyvinyl Alcohol, manufacturer) and PLA (Polylactic Acid, manufacturer). Some of the mechanical properties and melting points of these thermoplastic materials are shown in Table 22 [100] [120] [121].

*Table 22: Mechanical Properties of Thermoplastic Materials.*

<table>
<thead>
<tr>
<th>Material</th>
<th>Tensile [MPa]</th>
<th>Elongation [%]</th>
<th>Melting Point [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABS</td>
<td>42.5-44.8</td>
<td>25</td>
<td>100*</td>
</tr>
<tr>
<td>PVA</td>
<td>65-120</td>
<td>3</td>
<td>191-224</td>
</tr>
<tr>
<td>PLA</td>
<td>70</td>
<td>3.8</td>
<td>170</td>
</tr>
</tbody>
</table>

*Melting temperature equals the glass transition temperature (Tg), for ABS, since this material cannot be crystalized.

Solid Works software was used to design and make specific sample files [122]. These files were then converted to STL format for 3D printing. Figure 34 shows PLA specimen after printing at 45° print head orientation.

*Figure 34: 3D Printed Specimen one layer of PLA at 45°.*
After printing, a white light interferometer was employed to measure the roughness and thickness of each sample. The surface topography was measured for an ABS tensile test specimen before and after the sample being tested to check how the tensile strength test affects surface topography. For testing the tensile strength, a standard specific dimension test specimen was printed by using CAD software. The model was converted to STL format to be printed by an FDM 3D printer (MakerBot Replicator 2x).

Figure 35 shows the test sample after it was imported from the STL data file to the MakerWare software. 3D printing operation process parameters can be controlled and adjusted according to the mechanical properties of the material. These parameters are melting temperature, extruding speed, resolution, infill percentage (100 – void percentage), build plate temperature, etc.

Table 23: Conditions of the thermoplastic Polymers Printing.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Extruding Temperature [°C]</th>
<th>Extruding Speed [mm/s]</th>
<th>Infill [%]</th>
<th>Resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABS</td>
<td>230</td>
<td>90</td>
<td>100</td>
<td>High</td>
</tr>
<tr>
<td>PVA</td>
<td>230</td>
<td>90</td>
<td>100</td>
<td>High</td>
</tr>
<tr>
<td>PLA</td>
<td>220</td>
<td>90</td>
<td>100</td>
<td>High</td>
</tr>
</tbody>
</table>
After importing of the 3D model and setting the parameters, the test sample was printed automatically by the FDM machine. Figure 36 shows the MakerBot in the process of printing the tensile test sample. The next step is building and printing bone structures.

Figure 35: Specimen imported by Makerware Software to be Printed.

Figure 36: 3D Printing of the Tensile test Sample.
6.2.2 Creating 3D Bone Structure Model

To enable the printing of actual bone structures, models need to be made from authentic human body scans. 3D models of genuine bone structures are built from CT and MRI scan DICOM medical images. Magnetic Resonance Imaging (MRI), CT (Computerized Tomography), DICOM (Digital Imaging and Communications in Medicine) and Ultrasound scans are methods used in radiology for medical procedures. The same DICOM images used by doctors in their medical practice to build 3D models of bone structures were employed. Since DICOM images are only two dimensional images, slices of a 3D body, “3D Slicer” software was engaged to create high quality 3D models.

Several software applications were applied to create the 3D models, one of these being “3D Slicer”, open source software that is widely used in the medical field [123]. 3D Slicer allows doctors and biomedical researchers to focus on applications, such as data communication, visualization and analysis. 3D Slicer is open source that is being constantly upgraded and optimized by the actual users, providing important feedback. 3D slicer provides a common set of base functionalities to assist progress and support of medical image computing techniques, simplifies the doctors work and does not require users to understand or modify complicated computational algorithms [124]. To create a model using 3D Slicer, there are several steps that need to be performed. The first step is to load CT scan data as shown from Figure 37.
After the images are loaded, the Region of Interest (ROI) is determined on each image and then segmentation is performed on the organ, in our case bone structure. Figure 38 shows three cross slices of a chest image (3 planes) used to determine ROI and segmentation to make the 3D model. Further, segmentation through all images on each slice is produced within the ROI by thresholds. When the segmentation is finished on all the slices, a volumization is performed to produce a 3D shape.
The 3D slicer software can visualize the 3D model (Figure 39). The user can then modify the 3D bounding box, rotate and export the model to several 3D formats. After the model is created, it is exported to STL format to be visualized, simulated and finally printed by the 3D printer. The mechanical properties of the samples were tested, once they are printed, by using a tensile test machine or special equipment built for this purpose. The tensile test of the samples was performed by a tensile test machine, MTS system, at ambient temperature 20°C. The results of this tests are reported elsewhere [112].

![Figure 39: 3D Models Created after Segmentation by 3D Slicer [123].](image)

We printed a sample of bone structure designed with 3D Slicer from MRI and CT scan data to test the precision of the 3D printer (MakerBot) as shown in Figure 40.

![Figure 40: 3D Printed Bone Femur Structure.](image)

In addition, we designed some samples using SolidWorks software with specific thickness and printed them using MakerBot replicator 2X and FlashForge Creator Pro. We
printed two materials ABS and PVA using MakerBot replicator 2X. We wanted to test the difference in thickness and roughness after these materials were printed to compare them with each other and with the designed thickness. Then we printed ABS using FlashForge Creator Pro. We wanted to test the minimum thickness that each printer can provide and the highest precision it can reach.

The thickness of the designed samples ranges from 0.4 mm (400µm) for the thickest up to 0.05mm (50µm) for the thinnest. The samples were printed at 45°. The measured thickness and roughness were measured using a White Light Interferometer (Bruker). After that, the samples were printed by PolyJet Technology using a Stratasys Objet 500 Connex3 printer with digital ABST™ material and the thickness of the samples this time ranged from 0.4 mm (400 µm) for the thickest down to 0.016 mm (16µm) for the thinnest. They were printed to investigate if the Stratasys Objet 500 Connex3 can produce the minimum thickness that the manufacturer claimed, 0.016 mm (16µm), and the highest precision the printer can reach with the smoothness level. Then, we compared the results with the previous printers that use the FDM method (MakerBot replicator 2X and FlashForge Creator Pro).

6.3 Results and Discussions

The FDM method to print three different thermoplastic samples ABS (Acrylonitrile-Butadiene-Styrene), PVA (Polyvinyl Alcohol), PLA (Polylactic Acid) was chosen. The samples were printed using two different print-head orientations 45° and 90° to better understand the influence of orientation on specimen roughness. Three different samples of ABS were printed with different number of layers: one, two or three layers at 45°. Also, one layer of both PLA and PVA were printed at 45° and measured. The thickness
and roughness were measured each time and the results are shown in Table 24. The surface
topography for ABS1, ABS2 and ABS3 prints are shown in Figures 41-43.

Table 24: Thickness and Roughness ABS, PLA and PVA printed in 1-3 layers, oriented at 45°.

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness (µm)</th>
<th>Roughness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABS1</td>
<td>78</td>
<td>7.4</td>
</tr>
<tr>
<td>ABS2</td>
<td>83</td>
<td>13.3</td>
</tr>
<tr>
<td>ABS3</td>
<td>118</td>
<td>18.0</td>
</tr>
<tr>
<td>PLA1</td>
<td>105</td>
<td>8.0</td>
</tr>
<tr>
<td>PVA1</td>
<td>77</td>
<td>5.7</td>
</tr>
</tbody>
</table>

Figure 41: Topographic map of first layer ABS1.

Figure 42: Topographic map of second layer ABS2.
Figures 41-43 clearly show that these printed surfaces display both macro roughness and micro roughness. The macro roughness clearly corresponds to the spacing between lines of print (see Figure 34). This results since the ABS hardens on the support plate before it can level. This is because the support plate is held at 100 ° C, which is the Tg of ABS.

Figure 44: Thickness and Roughness for ABS, PLA and PVA 1-3 layers Printed at 45°.
Two samples of ABS with one and two layers were printed at 90° and PVA with one layer was printed also at 90°. The results are shown in Table 25.

Table 25: Thickness and Roughness ABS and PVA oriented at 90°.

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness (µm)</th>
<th>Roughness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABS1</td>
<td>80</td>
<td>3.7</td>
</tr>
<tr>
<td>ABS2</td>
<td>87</td>
<td>10.4</td>
</tr>
<tr>
<td>PVA1</td>
<td>62</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Note that ABS printed at 90° is both thicker and smoother than at 45°. This is expected since more material is deposited when printed along raster lines in 2 dimensions. The second layer at 90° is also thicker and smoother than at 45°. However, it is much less than twice the thickness of the first layer, indicating that the second layer fills in between the previous lines.

On the other hand, the first layer of PVA is thinner than at 45°, but still smoother. This may be due to better leveling of the PVA, since its Tg is 85°C [121]. What is clear is that for FDM to succeed at producing uniform smooth layers, an annealing step (raising the temperature of the build platform following initial deposition) is needed.

Figure 45: Thickness and Roughness for ABS (1 or 2 layers) and PVA layers Printed at 90°.
From Figures 44-45 and Tables 24 and 25, it is obvious that the 90° creates smoother specimen surfaces than the 45° orientation. From Table 24, it may also be seen that for ABS material, increasing the thickness also increases the roughness at 45°. At the thickness of 78 μm, the roughness was 7.4 μm. For the two layers of ABS the thickness is 83 μm and the roughness is 13.3 μm. Finally, when printing three layers, the thickness became 118 μm with a roughness of 18 μm (Table 24). This increase in roughness for successive printed layers is consistent with observations for multilayer printing of functional materials in printed electronics applications [125]. To achieve higher smoothness, higher platform temperature may be necessary, or annealing may be needed.

Figure 44 shows ABS and the relation between thickness and roughness for layered samples when the material was printed at different levels of thickness, one two and three layers consecutively, printed at 45° head orientation. The standard deviations of thickness for ABS1, ABS2 and ABS3 (Fig.44-45) are quite similar, which may show that the layer structure eventually conforms after a certain number of layers.

The difference in standard deviation was not significant among the different materials (ABS, PLA, PVA), which points out that difference is due to the printer rather than due to the material being printed. Table 26 shows the specific thickness of the designed samples using SolidWorks software compared with the thickness and roughness after the samples were printed using MakerBot replicator 2X. The samples were printed using ABS and PVA. Then they were measured using White Light Interferometer (Bruker).
Table 26: Thickness and Roughness of ABS and PVA Printed at 45° using MakerBot Replicator 2X.

<table>
<thead>
<tr>
<th>Nominal Thickness (µm)</th>
<th>ABS Thickness (µm)</th>
<th>ABS Roughness (µm)</th>
<th>PVA Thickness (µm)</th>
<th>PVA Roughness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>400</td>
<td>43</td>
<td>400</td>
<td>34</td>
</tr>
<tr>
<td>300</td>
<td>300</td>
<td>29</td>
<td>305</td>
<td>27</td>
</tr>
<tr>
<td>200</td>
<td>198</td>
<td>15</td>
<td>222</td>
<td>22</td>
</tr>
<tr>
<td>100</td>
<td>101</td>
<td>13</td>
<td>127</td>
<td>20</td>
</tr>
<tr>
<td>80</td>
<td>100</td>
<td>8</td>
<td>69</td>
<td>17</td>
</tr>
<tr>
<td>50</td>
<td>70</td>
<td>8</td>
<td>58</td>
<td>17</td>
</tr>
</tbody>
</table>

Figures 46-47 show the thickness and roughness for ABS and PVA printed using MakerBot replicator 2X. The samples were printed at 45° with specific designed thickness that ranges from 400 µm for the thickest sample down to 50 µm for the thinnest one. The minimum thickness that MakerBot can achieve is 50 µm. From the figures it is obvious there is a consistency between the thickness and roughness of the samples.
Figure 47: PVA Thickness and Roughness for layers Printed at 45° with different designed Thickness using MakerBot Replicator 2X.

Table 27 shows the original thickness of the designed samples using SolidWorks software compared with the thickness and roughness after the samples were printed using ABS with two different printers, MakerBot replicator 2X and FlashForge Creator Pro.

Table 27: Thickness and Roughness of ABS Printed at 45° using MakerBot Replicator 2X and FlashForge Creator Pro.

<table>
<thead>
<tr>
<th>Nominal Thickness(µm)</th>
<th>MakerBot Thickness(µm)</th>
<th>MakerBot Roughness (µm)</th>
<th>FlashForge Thickness (µm)</th>
<th>FlashForge Roughness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>400</td>
<td>43</td>
<td>482</td>
<td>50</td>
</tr>
<tr>
<td>300</td>
<td>300</td>
<td>29</td>
<td>364</td>
<td>35</td>
</tr>
<tr>
<td>200</td>
<td>198</td>
<td>15</td>
<td>145</td>
<td>30</td>
</tr>
<tr>
<td>100</td>
<td>101</td>
<td>13</td>
<td>100</td>
<td>28</td>
</tr>
<tr>
<td>80</td>
<td>100</td>
<td>8</td>
<td>88</td>
<td>13.8</td>
</tr>
<tr>
<td>50</td>
<td>70</td>
<td>8</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Figure 48 shows the thickness and roughness for ABS samples printed using the FlashForge Creator Pro. The samples were printed at 45° with specifically designed thicknesses that range from 400 µm for the thickest sample down to 50 µm for the thinnest one. The minimum thickness that MakerBot can reach is 50 µm while the lowest thickness that FlashForge can do is 80 µm. There is a consistency between the thickness and
roughness of the samples for both printers, but it is obvious that MakerBot samples are smoother than FlashForge ones. On the other hand, in terms of precision MakerBot seems more accurate or precise than FlashForge because the thickness of samples that produced by MakerBot better matches the designed thickness than FlashForge.

Figure 48: ABS Thickness and Roughness for layers Printed at 45° with different designed Thickness using FlashForge Creator Pro.

Table 28 shows the specific thickness of the designed samples using SolidWorks software compared with the thickness and roughness after the samples were printed using a Stratasys Objet 500 Connex3. The samples were printed using digital ABS™. Then they were measured using White Light Interferometer (Bruker).

Table 28: Thickness and Roughness of digital ABS™ Printed using Stratasys Objet 500 Connex3.

<table>
<thead>
<tr>
<th>Nominal Thickness (µm)</th>
<th>Stratasys Objet 500 Thickness</th>
<th>Stratasys Objet 500 Roughness</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>400</td>
<td>7.0</td>
</tr>
<tr>
<td>300</td>
<td>300</td>
<td>5.0</td>
</tr>
<tr>
<td>200</td>
<td>200</td>
<td>3.9</td>
</tr>
<tr>
<td>100</td>
<td>105</td>
<td>3.1</td>
</tr>
<tr>
<td>80</td>
<td>85</td>
<td>2.7</td>
</tr>
<tr>
<td>50</td>
<td>57</td>
<td>2.0</td>
</tr>
<tr>
<td>25</td>
<td>30</td>
<td>1.7</td>
</tr>
<tr>
<td>16</td>
<td>22</td>
<td>1.6</td>
</tr>
</tbody>
</table>
Figure 49 shows the thickness and roughness for digital ABS™ samples printed using Stratasys Objet 500 Connex3. The samples were printed with specifically designed thicknesses that range from 400 µm for the thickest sample down to 16 µm for the thinnest one. There is great consistency between the thickness and roughness of the samples. From the obtained results it is obvious that the samples produced by Stratasys 500 Objet Connex3 are smoother than MakerBot replicator 2X and FlashForge Creator Pro that use FDM technique. Also, Stratasys 500 Objet Connex3 is more accurate or precise, and can produce thinner layers.

6.4 Conclusion

We are interested in smoothness because the implants inside the human bodies need to be smooth. Otherwise, they may be rejected by the human body or the resulted friction can cause infection or other negative side effects. ABS, PLA and PVA were printed by using the FDM method. ABS was printed at 45° with different levels of thickness applying one, two or three layers. Roughness and thickness of the samples were measured each time.
by using a White Light Interferometer. One layer of PLA was printed at 45° and both thickness and roughness were measured. Two other samples of ABS were printed with one and two layers at 90°. Two samples, one layer each of PVA, were printed at 45° and 90°. Then both roughness and thickness were measured using the White Light Interferometer. The results show that the roughness of ABS at 45° and 90° increased with increasing thickness, as observed in printing multilayer devices for printed electronics [125]. In addition, the results show that the samples printed at 90° were smoother than 45°, which means the orientation had a significant influence on roughness, but little on thickness. Additional studies are needed to target more realistic and smoother structures for bone replacement. Later, bones created according to actual CT and MRI scans will be printed and tested to loads experienced by humans.

For the designed layers using SolidWorks software, different specific thickness ranging from 400 µm down to 50 µm were printed. We printed these samples with both materials ABS and PVA using MakerBot. We found there is a consistency between thickness and roughness for both materials, but the thickness of ABS better matches the designed one than PVA. For the comparison between ABS samples that were printed using both printers (MakerBot and FlashForge). We can obviously notice that there is a consistency between the thickness and roughness of the samples for both printers. But MakerBot samples are still smoother than FlashForge ones. In terms of precision, MakerBot seems more precise, because the thickness of the samples that were produced by MakerBot better matches the designed thickness than FlashForge.

The minimum thickness that MakerBot can reach is 50 µm, while FlashForge it is 80 µm. For the samples that were printed by using Stratasys 500 Objet Connex3, it is
obvious that they are smoother than MakerBot replicator 2X and FlashForge Creator Pro. Also, Stratasys 500 Objet Connex3 is more precise than either and it can reach thinner levels than both of them.

<table>
<thead>
<tr>
<th></th>
<th>Stratasys Objet Connex3 Roughness (µm)</th>
<th>Stratasys Objet Connex3 Thickness (µm)</th>
<th>MakerBot Roughness (µm)</th>
<th>MakerBot Thickness (µm)</th>
<th>Nominal Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>482</td>
<td>43</td>
<td>400</td>
<td>7.0</td>
<td>400</td>
</tr>
<tr>
<td>35</td>
<td>364</td>
<td>29</td>
<td>300</td>
<td>5.0</td>
<td>300</td>
</tr>
<tr>
<td>30</td>
<td>145</td>
<td>15</td>
<td>198</td>
<td>3.9</td>
<td>200</td>
</tr>
<tr>
<td>28</td>
<td>100</td>
<td>13</td>
<td>101</td>
<td>3.1</td>
<td>105</td>
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<tr>
<td>13.8</td>
<td>88</td>
<td>8</td>
<td>70</td>
<td>2.7</td>
<td>85</td>
</tr>
<tr>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>1.7</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>22</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>16</td>
</tr>
</tbody>
</table>
CHAPTER 7

CONCLUSIONS AND FUTURE OUTLOOK

Three dimensional printing of biomaterials have an important role in bone tissue-engineering. A wide range of different types of biomaterials has been applied in the bone tissue-engineering area. The mechanical properties of biomaterials can affect the success of bone tissue engineering applications. The biomaterial must be suitable to the host environment. Tissue-engineering is a new field that seeks to grow complex three-dimensional tissues to substitute for injured tissues. Therefore, 3D printing technology has attracted a lot of attention in the medical field specifically using biomaterials as implants to replace fractured or damaged bones. This work demonstrated that several thermoplastic materials could be 3D printed with three different methods and tested for their selected mechanical properties; tensile strength, compressive strength, and bending tests. These thermoplastics are ABS, PLA, PA2200, ULTEM9085, and Digital ABSTM. Currently, due to limitations in existing 3D printing technology, it is not possible to print all the materials with the same method using the same device. They were 3D printed using different methods and different printing machines.

The thermoplastics that were 3D printed using Fused Deposition Modeling (FDM) technique are: ABS samples were 3D printed using MakerBot replicator 2X, PLA samples were 3D printed using Type A Series 1, and ULTEM9085 samples were 3D printed using Fortus 400 MC. PA2200 samples were 3D printed using Selective Laser Sintering (SLS) with EOS machine EOSP 396. Digital ABSTM samples were 3D printed using PolyJet™ technology with Stratasys Objet 500 Connex3. To assess use of these materials as bone
replacements, mechanical properties testing was performed to evaluate if the 3D printed bone replacement structures can sustain the same loads that human bones experience.

All 3D printed samples were tested using an MTS Bionix Servohydraulic Test Systems-Model 370.02 for all the selected properties. The results of the 3D printed samples at 100% of infill were slightly lower than the values of the material safety data sheets (MSDS) that were obtained from the manufacturer for all the selected properties, which was most likely due to repeated heating and extrusion of the tested thermoplastic samples. PLA has the highest tensile and Young’s modulus values, followed by Digital ABST™ has the second highest values for both. ABS has the lowest value for tensile strength and ULTEM9085 has the lowest value for Young’s modulus. The results show the compressive modulus values of the samples that were printed vertically in Z less than the ones printed horizontally in X. PLA has the highest compressive modulus in the X direction and the second highest compressive strength in the Z direction. Digital ABST™ has the highest compressive strength in the Z direction and the second highest compressive modulus in X direction. PA2200 has the lowest compressive modulus in the X direction and ABS has the lowest compressive modulus value in the Z direction. PLA has the highest value for flexural modulus, followed by ULTEM9085 and the ABS is the lowest. The mechanical properties of the 3D printed samples at 100% of infill are less than the criteria of cortical bones, but they exceed the criteria of trabecular bones. These results were discussed in Chapter 4.

Currently, because of the low resolution of the DICOM images, the trabecular bone structure cannot be obtained directly from CT and MRI scans. To create bone structures that can exactly mimic the real human bone structures with a solid outer shell that
represents the cortical bone and porous internal volume that represents the trabecular bone, CAD software SolidWorks was used to design special 3D honeycomb structures (Hexagonal, Triangular, and Square).

The designed 3D printed samples with internal structures have a pore size of 400 µm and the thickness of the walls is 160 µm, were based on the averages sizes of the bone trabecular structures. The samples were 3D printed with three different materials (ULTEM9085, PA2200, and Digital ABS™) using three different methods. Fused Deposition Modeling (FDM) with Fortus 400 MC machine, Selective Laser Sintering (SLS) with an EOSP 396 device, and PolyJet technology with Stratasys Objet 500 Connex3, were used. All the designed 3D printed samples were tested for the selected mechanical properties. The results of the 3D printed samples with designed internal structures are close to each other. The mechanical properties of the 3D printed samples with designed internal structures either exceed or fall within the range of the mechanical properties of the human trabecular bones. These results were discussed in Chapter 5.

The void volume fraction, fill fraction and percentage of infill for the designed structures were calculated. The purpose of this was to investigate the influence of the geometric shape on the percentage of infill and the impact of the percentage of infill on the strength. The hexagonal structure has the highest percentage of infill, followed by triangular structure, and the lowest is the square structure. 3D printed polymer structures show there is significant relation between tensile strength and Young’s modulus.

The tensile strength test values are the same for all three structures of ULTEM9085, but lower than the solid value. PA2200 hexagonal has the highest value of Young’s modulus.
modulus, while the triangular has the lowest, although they are not that much different from one another. Digital ABS™ square has the highest values for both Young’s modulus and tensile strength, while the triangular structure has the lowest values for both. The relationship between tensile strength and Young’s modulus is strong and it is almost linear.

ULTEM9085 triangular has the highest values for both compressive test and compressive modulus, while ULTEM9085 hexagonal has the lowest ones. PA2200 square has the highest compressive modulus and the triangular has the lowest compressive modulus, but the tensile strengths are the same for all three structures. Digital ABS™ hexagonal has the highest compressive modulus value but the lowest compressive strength. Digital ABS™ square has the lowest compressive modulus, but the highest compressive strength. This indicates that the compressive modulus is acting contrary with compressive strength for this polymer. The eventual strength in compression is higher than the eventual strength in tension for brittle materials. This is because the existence of microscopic cracks or cavities, which tend to deteriorate the material in tension, while not significantly affecting its resistance to compressive failure.

PA2200 hexagonal structure showed the highest flexural modulus value but the lowest bending strength. The square structure showed the lowest flexural modulus value but the highest bending strength. ULTEM9085 triangular structure has the highest value of flexural modulus and the lowest bending strength value. ULTEM9085 hexagonal structure has the lowest value of flexural modulus but the highest bending strength. Digital ABS triangular structure has the highest flexural modulus value and the highest bending strength. Digital ABS™ hexagonal structure has the lowest flexural modulus. The highest bending strength was obtained with the triangular structure, while the hexagonal and square
structures have the same bending strength values. The behavior between flexural strength and flexural modulus follow a random relation. There is no significant relation between flexural strength and flexural modulus for the 3D printed structures. These results were discussed in Chapter 5.

Further, to investigate the properties of the 3D printed materials, Differential Scanning Calorimetry (DSC) was used to obtain the thermal analysis profile of these polymers. The thermal analysis results indicate that ABS and ULTEM9085 are amorphous, PLA is partially crystalline, and PA2200 is completely crystalline. The difference between them is that the chain molecules of the amorphous material is in a randomly structured, and the chain molecules of semi-crystalline material is orderly structured in some regions. On the other hand, an amorphous and semi-crystalline materials have different thermal properties, which determine the manufacturing parameters. Amorphous materials have no specific melting temperature. They soften over a wide range of temperature, as demonstrated in Chapter 4.

Energy per unit mass was calculated for all the selected mechanical properties, tensile strength tests, compressive tests, and bending tests. For 3D printed samples at 100% of infill, PA2200 has the highest values for energy per unit mass (kJ/kg) for all selected properties. The tensile strength and Young’s modulus values per unit mass are (121 kJ/kg) and (3951 kJ/kg) consequently. The compressive strength per unit mass is (121 kJ/kg) in X and (128 kJ/kg) in Z. The compressive modulus values per unit mass are (2733 kJ/kg) in X and (2474 kJ/kg) in Z. The flexural strength and flexural modulus values per unit mass are (69.8 kJ/kg), and (3465 kJ/kg) consequently. These all represent the energy absorbed per unit mass to failure or unit strain.
Results of 3D printed samples with designed internal structures show that PA2200 square has the highest value for both Young’s modulus per unit mass (4130 kJ/kg), and tensile strength per unit mass (119 kJ/kg). After that PA2200 triangular is the second (4044 kJ/kg) and (117 J/kg) respectively. Then PA2200 hexagonal is the third (3789 kJ/kg) and (108 kJ/kg). PA2200 square has the highest compressive modulus value per unit mass (2702 kJ/kg) and the highest compressive strength (140 kJ/kg). PA2200 hexagonal is the second (1917 J/kg) and PA2200 triangular is the third (1322 kJ/kg). PA2200 triangular has the second highest compressive strength per unit mass (139 kJ/kg) and the lowest compressive modulus per unit mass (1322 kJ/kg). PA2200 triangular has the highest flexural modulus value per unit mass (3697 kJ/kg). After that PA2200 square has the second highest flexural modulus value per unit mass (3576 kJ/kg) and PA2200 hexagonal is the third (3517 kJ/kg). PA2200 square has the highest flexural modulus per unit mass (45 kJ/kg).

With the obtained results it is hard to realize which structure is the strongest and has the best mechanical properties. This is because the 3D printed samples of the structures were printed using different 3D printing methods of the printed materials. The results of the thermoplastic designed structures either exceed or fall within the range of the mechanical properties of the human trabecular bone. However, the PA2200 shows the most promise for all of the void structures. These results were discussed in Chapter 5.

There are problems in printing thin layers of thermoplastics using 3D printing technology with different methods and different machines. We investigated the highest precision and the thinnest thickness each printer can reach as well as the influence of printing orientation on the surface topography of the layers. White Light Interferometer
(Bruker) was used to measure thickness and roughness. The samples were printed with two different printing orientations 45° and 90° using 3D printer - MakerBot replicator 2X. The results show that increasing the number of layers (thickness) increases the roughness as is seen elsewhere in multilayer printing [125]. The samples printed at 90° were smoother than 45°, which means the orientation had a significant influence on roughness. These results were discussed in Chapter 6.

A number of layers with different specific thickness ranging from 400 µm down to 50 µm were designed using SolidWorks software. ABS and PVA layers were printed using MakerBot replicator 2X. A consistency was found between thickness and roughness of the printed layers for both ABS and PVA, but the thickness of ABS layers better matches the designed thickness than PVA layers. Another set of ABS layers were printed using FlashForge 3D printer to investigate the difference between these FDM printers. A consistency between the thickness and roughness of the printed samples was clearly obvious for both printers, but MakerBot printed samples are still smoother than FlashForge ones. MakerBot is also more precise than FlashForge, because the thickness of the samples that produced by MakerBot better matches the designed thickness better than FlashForge. MakerBot can also reach thickness thinner than FlashForge.

For the samples that were printed by using PolyJet technology method with Stratasys 500 Objet Connex3, it is obvious that they are smoother than MakerBot replicator 2X and FlashForge Creator Pro. Also, Stratasys 500 Objet Connex3 is more precise than either and it can reach thinner levels of thickness than both of them. The performance of FDM technique with MakerBot and FlashForge and PolyJet technology with Stratasys 500 Objet Connex3 and their impact on the surface characteristics were discussed in Chapter
6. We are interested in smoothness, because the implants inside the human bodies need to be smooth. Otherwise, they may be rejected by the human body or the resulted friction can cause infection, blood clotting, or other negative side effects.

**Future work**

Medical studies keep searching for possible new scientific solutions for treating, curing, and avoiding maladies. Major progress has been made in the use of medical implants. At present, significant efforts have been put on the design of biopolymer implants. There are several benefits of using biopolymers over metals as implants in bone tissue engineering. However, these new developments show that the mechanical properties, porosity, and bioactivity of biopolymer implants, require future researchers to overcome several remaining limitations in the manufacturing process. No single material can suit all there requirements in all applications, but a wide variety of materials will find a range of uses in different bone tissue engineering applications.

According to the work presented here, there are variety of characteristics and certain concerns that could be solid bases for significant and relevant future work, including:

1. Currently, due to the low resolution of the DICOM images, the trabecular bone structure cannot be obtained from a CT scans with existing technology. Therefore, the model from Biersteker research [126] can be used. After designing the cortical bone shape from CT scan, the trabecular bone structure can be added inside the bone, thus creating bone structure closely matching the actual ones. After that the mechanical properties of the entire 3D printed bone structure need to be tested by using special designed fixtures.
2. Design new honeycomb structures with bigger pore sizes and thicker walls, with interconnections between cavities for blood flow, using CAD software to investigate the influence of the permeability and thickness on the stiffness, strength, and other mechanical properties.

3. Investigating the mechanical properties of other biopolymers that have higher melting temperatures and stronger mechanical properties such as Polyetheretherketone (PEEK).

4. Since the results were lower than the values of the cortical bone. An alternative solution is needed to determine a way to strengthen biopolymers to get better results that match the cortical bone values. For example, using fibers or other fillers to reinforce polymers in 3D printing or investigating other polymers could be stronger than the ones that have already been investigated.

5. After reaching the best mechanical properties of the 3D printed biopolymers in specific design that replaces the missing bony part, animal trials need to be conducted to investigate the influence of the implants on the tissue healing process or recovery.
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APPENDICES

APPENDIX A

Figures of the Tensile Strength tests for the Materials Printed at 100% Infill

Figure 50: ABS Stress-Strain and calculated (Stress-Strain) at 100% Infill.

Figure 51: PLA Stress-Strain and calculated (Stress-Strain) at 100% Infill.
Figure 52: ULTEM9085 Stress-Strain and calculated (Stress-Strain) at 100% Infill.

Figure 53: PA 2200 Stress-Strain and calculated (Stress-Strain) at 100% Infill.
Figure 54: Digital ABS\textsuperscript{TM} Stress-Strain and calculated (Stress-Strain) at 100% Infill.
APPENDIX B

Figures of the Compressive Strength tests for the Materials Printed at 100% Infill

**Figure 55**: ABS Stress-Strain and calculated (Stress-Strain) at 100% Infill in X.

**Figure 56**: ABS Stress-Strain and calculated (Stress-Strain) at 100% Infill in Z.
Figure 57: PLA Stress-Strain and calculated (Stress-Strain) at 100% Infill in X.

Figure 58: PLA Stress-Strain and calculated (Stress-Strain) at 100% Infill in Z.
**Figure 59:** Digital ABS\textsuperscript{TM} Stress-Strain and calculated (Stress-Strain) at 100% Infill in X.

**Figure 60:** Digital ABS\textsuperscript{TM} Stress-Strain and calculated (Stress-Strain) at 100% Infill in Z.
Figure 61: ULTEM9085 Stress-Strain and calculated (Stress-Strain) at 100% Infill in X and Z.

Figure 62: PA 2200 Stress-Strain and calculated (Stress-Strain) at 100% Infill in X and Z.
APPENDIX C

Figures of the Flexural Strength tests for the Materials Printed at 100% Infill

Figure 63: ABS Stress-Strain and calculated (Stress-Strain) at 100% Infill.

Figure 64: PLA Stress-Strain and calculated (Stress-Strain) at 100% Infill.
Figure 65: ULTEM9085 Stress-Strain and calculated (Stress-Strain) at 100% Infill.

Figure 66: PA 2200 Stress-Strain and calculated (Stress-Strain) at 100% Infill.
Figure 67: Digital ABS™ Stress-Strain and calculated (Stress-Strain) at 100% Infill.
APPENDIX D

Figures of the Compressive Strength tests for ABS Cubes Printed at 100% Infill at two different speed rates 0.2 mm/s and 0.05 mm/s.

*Figure 68: ABS cube Stress-Strain and calculated (Stress-Strain) at 100% Infill for high strain in X at speed rate 0.2 mm/s.*

*Figure 69: ABS cube Stress-Strain and calculated (Stress-Strain) at 100% Infill for high strain in Y at speed rate 0.2 mm/s.*
Figure 70: ABS cube stress-strain and calculated (stress-strain) at 100% Infill for high strain in Z at speed rate 0.2 mm/s.

Figure 71: ABS cube Stress-Strain and calculated (Stress-Strain) at 100% Infill for high strain in X at speed rate 0.05 mm/s.
Figure 72: ABS cube Stress-Strain and calculated (Stress-Strain) at 100% Infill for high strain in Y at speed rate 0.05 mm/s.

Figure 73: ABS cube Stress-Strain and calculated (Stress-Strain) at 100% Infill for high strain in Z at speed rate 0.05 mm/s.
APPENDIX E

Figures of the Tensile Strength tests for designed structures

Figure 74: ULTEM9085 Hexagonal structure Stress-Strain and calculated (Stress-Strain).

Figure 75: ULTEM9085 Triangular structure Stress-Strain and calculated (Stress-Strain).
Figure 76: ULTEM9085 Square structure Stress-Strain and calculated (Stress-Strain).

Figure 77: PA2200 Hexagonal structure Stress-Strain and calculated (Stress-Strain).
Figure 78: PA2200: Triangular structure Stress-Strain and calculated (Stress-Strain).

Figure 79: PA2200 Square structure Stress-Strain and calculated (Stress-Strain).
Figure 80: Digital ABS™ Hexagonal structure Stress-Strain and calculated (Stress-Strain).

Figure 81: Digital ABS™ Triangular structure Stress-Strain and calculated (Stress-Strain).
Figure 82: Digital ABS Square structure Stress-Strain and calculated (Stress-Strain).
APPENDIX F

Figures of the Compressive Strength tests for designed structures

Figure 83: ULTEM9085 Hexagonal structure Stress-Strain and calculated (Stress-Strain).

Figure 84: ULTEM9085 Triangular structure Stress-Strain and calculated (Stress-Strain).
Figure 85: ULTEM9085 Square structure Stress-Strain and calculated (Stress-Strain).

Figure 86: PA2200 Hexagonal structure Stress-Strain and calculated (Stress-Strain).
Figure 87: PA2200 Triangular structure Stress-Strain and calculated (Stress-Strain).

Figure 88: PA2200 Square structure Stress-Strain and calculated (Stress-Strain).
Figure 89: Digital ABS Hexagonal structure Stress-Strain and calculated (Stress-Strain).

Figure 90: Digital ABS Triangular structure Stress-Strain and calculated (Stress-Strain).
Figure 91: Digital ABS Square structure Stress-Strain and calculated (Stress-Strain)
APPENDIX G

Figures of the Flexural Strength tests for designed structures

Figure 92: ULTEM9085 Hexagonal structure Stress-Strain and calculated (Stress-Strain).

Figure 93: ULTEM9085 Triangular structure Stress-Strain and calculated (Stress-Strain).
Figure 94: ULTEM9085 Square structure Stress-Strain and calculated (Stress-Strain).

Figure 95: PA2200 Hexagonal structure Stress-Strain and calculated (Stress-Strain).
Figure 96: PA2200 Triangular structure Stress-Strain and calculated (Stress-Strain).

Figure 97: PA2200 Square structure Stress-Strain and calculated (Stress-Strain).
Figure 98: Digital ABS Hexagonal structure Stress-Strain and calculated (Stress-Strain).

Figure 99: Digital ABS Triangular structure Stress-Strain and calculated (Stress-Strain).
Figure 100: Digital ABS Square structure Stress-Strain and calculated (Stress-Strain).