ADDITIVE MANUFACTURING OF STRETCHABLE TACTILE SENSORS:

PROCESSES, MATERIALS, AND APPLICATIONS

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ADDITIVE MANUFACTURING OF STRETCHABLE TACTILE SENSORS: PROCESSES, MATERIALS, AND APPLICATIONS

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ABSTRACT

3D printing technology is becoming more ubiquitous every day especially in the area of smart structures. However, fabrication of multi-material, functional, and smart structures is problematic because of the process and material limitations. This thesis sought to develop a Direct Print Photopolymerization (DPP) fabrication technique that appreciably extends the manufacturing space for the 3D smart structures. This method employs a robotically controlled micro-extrusion of a filament equipped with a photopolymerization process. The ability to use polymers and ultimately their nanocomposites in this process is the advantage of the proposed process over the current fabrication methods in the fabrication of 3D structures featuring mechanical, physical, and electrical functionalities.

In addition, this study focused to develop a printable, conductive, and stretchable nanocomposite based on a photocurable and stretchable liquid resin filled with multi-walled carbon nanotubes (MWNTs). This nanocomposite exhibited piezoresistivity, means its resistivity changes as it deforms. This property is a favorable factor in developing resistance based tactile sensors. They were also able to resist high tensile strains while they showed conductivity.

Furthermore, this study offered a possible and low-cost method to have a unique and highly stretchable pressure sensitive polymer. This disruptive pressure sensitive polymer composed of an Ionic Liquid (IL) and a stretchable photopolymer embedded
between two layers of Carbon Nanotube (CNTs) based stretchable electrodes. The developed IL-polymer showed both field effect property and piezoresistivity that can detect large tensile strains up 30%.

In summary, this research study focused to present feasible methods and material for printing a 3D smart structure especially in the context of flexible tactile sensors. This study provides a foundation for the future efforts in fabrication of skin like tactile sensors in three-dimensional motifs. This thesis sought to (1) present a capable manufacturing method to fabricate (3D) smart structures from polymers and their nanocomposites, (2) develop a stretchable, printable, and conductive Carbon Nanotube (CNT) based nanocomposite, (3) develop a stretchable, piezoresistive, and printable ionic based photopolymer
DEDICATION

This dissertation is dedicated to my mother and father for all of their supports, love, and sacrifice.
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# TABLE OF CONTENTS

| LIST OF FIGURES | ........................................................................................................... xii |
| LIST OF TABLES | ......................................................................................................... xxi |
| **CHAPTER** |  |
| **I. BACKGROUND AND LITERATURE REVIEW** | .................................................. 1 |
| 1.1 Advancing 3D printing process | ................................................................. 1 |
| 1.2 Sense of touch through flexible tactile sensors | ........................................ 11 |
| 1.2.1 Developing flexible tactile sensors | .................................................. 13 |
| 1.2.2 Designing a fully polymeric flexible tactile sensor | ....................... 15 |
| 1.3 A novel pressure sensitive polymer for the 3D printing of tactile sensors using ionic liquid based photopolymer | ................................................................. 17 |
| 1.3.1 Developing a conductive ionic liquid polymer | ................................. 20 |
| 1.3.2 Properties of several ionic liquids for the electrochemical applications | ................................................................. 22 |
| 1.4 Introducing conductivity into the nonconductive polymers | ......................... 24 |
| 1.4.1 Conductive nanocomposites developed by dispersion conductive nanoparticles into a polymer matrix | ................................................................. 26 |
| 1.5 Challenges in front of the dispersion of CNTs into the polymers | ............... 34 |
| 1.5.1 Ultrasonication an effective dispersion method | ..................................... 36 |
| 1.5.2 Ultrasonication with the aid of a long-term shear mixer | .......................... 39 |
| 1.6 Noncovalent functionalization of CNTs in the presence of solvent | ............... 45 |
1.6.1 Selection of a proper solvent for the zippering mechanism .......... 47
1.6.2 Selection of a proper surfactant for zippering mechanism .......... 48
1.7 Thesis organization .................................................................................. 53

II DIRECT PRINT PHOTOPOLYMERIZATION (DPP) PROCESS ............... 54
2.1 Introduction ............................................................................................... 54
2.2 Direct Print Photopolymerization (DPC) machine ................................. 55
  2.2.1 Adjusting the printing parameters in planner printing ............... 58
  2.2.2 Experimental Results: Manufacturing Parameters ..................... 61
  2.2.3 Conformal printing algorithm for adjusting gap height .......... 64
2.3 Viscoelastic photopolymers used in the DPC process ......................... 71
  2.3.1 Introducing viscoelastic property using Fumed Silica (SiO2) ... 72
2.4 Conclusion ................................................................................................ 80

III STRETCHABLE ELECTRODES AND SENSORS USING CARBON NANOTUBES-POLYMER MATRIX ................................................. 81
3.1 Introduction ............................................................................................... 81
3.2 Preparation of a SWCNT/Prepolymer solution ................................... 83
3.3 Fabrication and characterization of the flexible conductive wires .... 84
3.4 Results and discussion ............................................................................ 86
  3.4.1 Resistance measurement ............................................................. 87
3.5 Conclusion ................................................................................................ 90

IV A MULTI-LAYER COMPLIANT TACTILE SENSOR FOR DETECTION OF THE POSITION, DIRECTION, AND SPEED OF SLIDING CONTACT ......... 91
4.1 Introduction ............................................................................................... 91
4.2 Tactile sensors ........................................................................................ 92
5.3.1 Preparation of a photocurable CNT/Prepolymer .......................... 124

5.4 Fabrication of multi-layer tactile sensors .......................................................... 124

5.4.1 Sensor type I: hybrid manufacturing process including the multi-material 3D printing and injection processes ................. 124

5.4.2 Sensor type II: hybrid manufacturing process including multi-material 3D printing and DPC process ............................ 126

5.4.3 Sensor type III: hybrid manufacturing process including the PSL and DPC processes ................................................ 127

5.5 Contact point detection experiment .......................................................... 130

5.6 Discussion .................................................................................................. 132

5.7 Conclusion .................................................................................................. 132

VI FLEXIBLE POLYMERIC PRESSURE SENSOR .......................................................... 134

6.1 Introduction .................................................................................................. 134

6.2 Material and method .................................................................................. 137

6.3 Sensor fabrication ....................................................................................... 139

6.4 Sensor evaluation ....................................................................................... 140

6.4.1 Field effect property .............................................................................. 140

6.4.2 Pressure test .......................................................................................... 143

6.5 Conclusion .................................................................................................. 147

VII CONCLUSIONS AND FUTURE WORK .......................................................... 149

7.1 Conclusion .................................................................................................. 149

7.2 Future work .................................................................................................. 151

VIII REFERENCES .................................................................................................. 153
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1. Application of 3D printing technology in simple prototypes [3].</td>
<td>1</td>
</tr>
<tr>
<td>1-3. An integrated process including Stereolithography and Direct Printing was used to fabricate a magnetic flux sensor. The structure was built by stereolithography process. Through the process interruption, the electrical components were inserted into the structure. The direct print process was used to deposit the conductive traces [4].</td>
<td>2</td>
</tr>
<tr>
<td>1-4. Schematic of a 3D printed battery using Direct Print technology [13].</td>
<td>3</td>
</tr>
<tr>
<td>1-5. Direct Printing with (a) one dispenser [16], (b) multiple dispenses [23]. Copyright © 2003 Elsevier Science Ltd. All rights reserved.</td>
<td>4</td>
</tr>
<tr>
<td>1-6. Different successful approaches used by direct print technology. (a) Planner printing [29]. Copyright © 2010, Royal Society of Chemistry (b) conformal printing [31]. Copyright © 2011 WILEY-VCH Verlag GmbH &amp; Co. KGaA, Weinheim (c) free standing printing [26]. Copyright © 2013 WILEY-VCH Verlag GmbH &amp; Co. KGaA, Weinheim.</td>
<td>5</td>
</tr>
<tr>
<td>1-7. Application of direct printing technology. (a)-(b) printing circuitry [35]. (c) bio printing [18]. (d) sensor printing [15,16,34].</td>
<td>5</td>
</tr>
<tr>
<td>1-8. An ideal 3D printed structure where the shape of deposited filament is retained by the progress of the process [36].</td>
<td>6</td>
</tr>
<tr>
<td>1-9. Rheological property of several viscoelastic inks developed by the dispersion of graphene and silica into the polymer matrix. (a) The apparent viscosity of a viscoelastic ink decreases in the presence of shear stresses. (b) Viscoelastic inks have a storage modulus ($G'$) greater than loss modulus ($G''$). A strong ink exhibit larger values for both the $G'$ and $G''$ [36].</td>
<td>7</td>
</tr>
<tr>
<td>1-10. Rheological behavior of a fugitive ink used in direct print technology. (a) ink has a viscoelastic behavior where its shear storage ($G'$) is greater than its loss moduli ($G''$) [39]. (b) An optimized rheological property of an ink by considering its deposition through the nozzle. A very strong ink with large $G'$ cannot be deposited through the nozzle [38].</td>
<td>8</td>
</tr>
</tbody>
</table>
1-11. A direct printed periodic structure using the fugitive ink [38] Copyright © 2005 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.................................................... 8


1-13. Schematic of proposed Direct Print Photopolymerization system .................................. 10

1-14. A large area tactile sensor helps the robot to interact with the environment [47]. Copyright © 2006, IEEE ................................................................................................... 12

1-15 A highly flexible optical fiber tactile sensor. [61]. Copyright © 2008, IEEE......... 13

1-16. Schematic of a soft tactile sensor with orthogonal microchannels. [53]. Copyright © 2005, IEEE ........................................................................................................................ 14

1-17. Using elastomer material in the fabrication of flexible tactile sensors to detect slip [16]. ................................................................................................................................... 15

1-18. A fully polymeric resistance based tactile sensor .................................................... 16

1-19. The configuration of a taxel ..................................................................................... 17

1-20. Schematic procedures for synthesizing functionalized MWCNTs using ionic liquid [78]. Copyright © 2012 Elsevier Ltd. ........................................................................................................ 18

1-21. SEM fracture images of composites without BMIMBF4 dispersion. Individual nanotubes are randomly distributed on the fractured surface showing no interfacial compatibility between the matrix and the nanotubes. (d) Composites with BMIMBF4 as the dispersion–curing agent. MWCNTs are dispersed well within the matrix showing excellent adhesion [77]. Copyright © 2013 Royal Society of Chemistry .......... 18

1-22. Application of Ion gel gated polymer in thin film transistor (Right). The structure of ionic liquid and triblock copolymer ion gel components (Right). Reprinted with permission from [71]. Copyright © 2007, American Chemical Society .................................................. 18

1-23. Application of ionic liquid in printable actuators. (a) Ion migration mechanism. (b) Schematic of a printed actuator using Bucky-gel electrodes. Reprinted with permission from [79]. Copyright © 2014 American Chemical Society ............................................ 19
1-24. Schematic illustration of developing IL-based conductive polymer based on the different mechanism. Reprinted with permission from [80]. Copyright © 2012, Royal Society of Chemistry................................................................. 21

1-25. Cation stability [85]..................................................................................................... 22

1-26. Anion stability [85]..................................................................................................... 23

1-27. Electron conductance mechanism in the elastomeric piezoresistive nanocomposite [114]: (a) Carbon nanotubes inside the polymer matrix form conductive networks. (b) When deformed by an object, the polymer matrix projects the deformation to the conductive networks. (c) The resistivity of these networks can be modeled by the intrinsic conductance of nanotubes (RCNTs), direct contact conductance of nanotubes (RContact) and electron tunneling conductance between the conducting nanotubes in close proximity (RTunneling)..................................................................................................................... 27

1-28. The electrical conductivity of an MWNT- Polyoxymethylene composite as a functional weight loading of the CNTs. Reprinted from [115]. Copyright © 2010 Elsevier Ltd. .................................................................................................................................... 28

1-29. A well-dispersed MWNT swirling the polymer matrix results in a higher conductivity. CNT load: 1 wt%, Dispersion method: Three Roll Milling. Shear intensity of three roll milling increases from left to right. Reprinted with permission from [142]. Copyright © 2009 Elsevier Ltd................................................................. 32

1-30. The dependence of conductivity on the distribution and dispersion of CNTs. Different type of MWNTs (NLIG: Length 0.2 µm, Diameter: 3.4 nm, NL15L: Length 0.3 µm, Diameter: 3 nm, C100: Length 0.1 µm, Diameter: 5 nm, C150P: Length 0.08 µm, Diameter: 4.5 nm) were dispersed into the epoxy resin using three roll milling machine under different shear intensity. A higher shear intensity results in a better dispersion but lower conductivity due to the lower connection between adjacent CNTs. Reprinted with permission from [142]. Copyright © 2009 Elsevier Ltd................................................................. 33

1-31. Dispersion of MWNT in polypropylene. (a) 5 wt% of non-treated MWNTs were dispersed into the polypropylene. The MWNTs were functionalized using Triton X-100 as surfactant in an ethanol solution. Agglomerations of MWNTs are obvious in the dispersion. (b) Individual MWNTs are obvious in a well-dispersed solution. Printed with permission from [159]. Copyright © 2011, SAGE Publications................................................................. 35

1-32. A horn sonicator with the controller. (Q700, Qsonica, Newtown, CT, USA) .......... 37

1-33. Cavitation process and inducing the intensive shock waves into the solution. The intensity and power of cavitation depend on the solution properties, and system set up [161]................................................................................................................................. 38

1-34. Disorders are introduced into the CNTs as a result of sonication. Reprinted with permission from [155]. Copyright © 1996 Published by Elsevier Ltd................................. 40
1-35. Induced defects in the CNTs under the sonication process. (a) bend with buckling, (b) fracture of graphene layers, (c) stripping of the outer layer. (d) The outer layer of graphene sheet stripped off. Reprinted with permission from [155]. Copyright © 1996 Published by Elsevier Ltd. ................................................................. 40

1-36. Effect of sonication time on the length of nanofillers. Reprinted with permission from [163]. Copyright © 2009 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim .......... 41

1-37. Histogram of length distribution MWNTs after the (a) 1 h, and (b) 10 h horn sonication treatment. Reprinted from [152]. ......................................................... 42

1-38 combination of ultrasonic horn and ultrasonic bath [165]. ........................................... 43

1-39. Sonicator with the magnetic stirrer for the dispersion of CNTs: (a) magnetic stirrer, (b) material container, (c) sonicator horn, and (d) sonicator controller. ......................... 44

1-40. Dispersion of nanotubes into the solution in the presence of surfactant and ultrasonication [168]. ........................................................................................................ 46

1-41. Schematic of (a) single surfactant molecule (Triton X-100) with the hydrophilic region and hydrophobic region. (b) Attachment of the surfactant to the CNT through its hydrophobic end. Reprinted with permission from [174]. Copyright © 2008 Elsevier ... 49

1-42. Bridging and flocculation mechanism as a result of surfactants. Reprinted with permission from [175]. Copyright (c) 2008 Elsevier Inc. ........................................... 50

1-43. Effect of different content of Triton X-100 on the dispersion and electrical conductivity. Printed with permission from [159]. Copyright © 2011, SAGE Publications .................................................................................................... 51

1-44. Electrical conductivity of functionalized MWNT with TRITON X-100 and dispersed into the Polypropylene. Increasing the Titon-X100 increases the conductivity but decreases the conductivity after an optimum content. Printed with permission from [159]. Copyright © 2011, SAGE Publications .................................................................................. 51

1-45. SEM images of dispersed MWNTs into the Polypropylene. The MWNTs were functionalized using Triton X-100 in the presence of ethanol. (a) 1 wt% of functionalized CNT dispersed into the Polypropylene. (b) 5wt% of functionalized CNT dispersed into the Polypropylene. (c) 1 wt% of non-treated CNT dispersed into the Polypropylene. (d) 5wt% of non-treated CNT dispersed into the Polypropylene Printed with permission from [159]. Copyright © 2011, SAGE Publications. .................................................................................. 52

2-1. Schematic of the DPC process. (a) Schematic of a multi-dispenser DPP machine. (b) Light intensity profile of a beam light around the tip. (c) Light distribution around the nozzle. ............................................................................... 56
2-2. Placing the light guide near the nozzle to minimize the light intensity near the nozzle. ........................................................................................................................................... 58

2-3. Adjusting dispensing parameters in direct printing. (a) Leading in the deposited material. (b) Lagging in the deposited material ........................................................................................................................................... 59

2-4. Rheology of 4% CNT nanocomposite. The viscosity of nanocomposite without any shear force is about ~7×10^6 cps........................................................................................................................................... 60

2-5. Effects of dispensing parameters on the line widths. (a) line width variation according to the fluid flow rate, (b) inconsistent and non-continuous line widths due to the too low fluid flow rate........................................................................................................................................... 62

2-6. Line width variation with respect to the fluid flow rates at fixed translation speed. (Tip diameter: 437µm; translation speed: 20 mm/s; gap height: 300–350 µm).................................. 62

2-7. Line width variation with respect to the translation speed at fixed fluid flow rate. (Tip diameter: 437µm; fluid flow rate: 1V; gap distance: 300–350 µm).................................. 63

2-8. Leading and lagging phenomena in the inclined printing. (a) leading in the downward printing, (b) lagging in the upward printing. The angle of the inclined surface is 35 degrees, printing speed is 10 mm/s, and nozzle has an outside diameter of 635 µm with an inside diameter of 535 µm. ........................................................................................................................................... 65

2-9. Conformal printing algorithm - an optimized tool location to adjust the gap height in the downward printing (left column) and upload printing (right column) on the inclined surface. The Final gap heights (third row) were set by having the two translation vectors along the normal direction (second row) of the surface and the horizontal direction (third row). ........................................................................................................................................... 67

2-10. Effect of applying conformal printing algorithm in creating a uniform gap height. (a) Downward, (b) upward, and (c) a 2D view of printing filaments before applying the conformal algorithm. (d) Downward, (e) upward, and (f) a 2D view of printing filaments after applying the conformal algorithm. (Nozzle outside diameter: 635 µm, inside diameter: 535 µm, gap height: 350 µm, and scale bar, if it has not been mentioned, is 500 µm).... 68

2-11. Filament width variations in upward and downward printing. (a) Before and (b) after applying the algorithm. ........................................................................................................................................... 70

2-12. Schematic representation of the formation of hydrogen bonding between the surface hydroxyl groups to form a gel. [34] ........................................................................................................................................... 72

2-13. Rheological behavior of the test sample (TS0) as received with a loss modulus (G”) higher than its storage modulus (G’). ........................................................................................................................................... 73

2-14. An example of a viscoelastic ink. (SR150 with 10 wt% fumed silica) ............... 76
2-15. The effect of fumed silica on the rheological behavior of the photocurable resin. 77
2-16. The effect of stabilizer on the rheological behavior of the photocurable resin. 77
2-17. The effect of stabilizer on viscosity behavior of a viscoelastic photocurable resin. 78
2-18. 3D printed structures using the DPC process. (a,b) a thin-wall micro blade fabricated with ink1 (Table 2-4). (c,d) an object fabricated with the ink2 (Table 2-4). (e) a 3D printed hand with ink3 (Table 2-4). (f) a 3D printed part with embedded connectors fabricated with ink2 (Table 2-4). The scale bars in (c,d) are 500 µm. 79
3-1 Schematic of the entire process to fabricate the stretchable sensors 85
3-2 Schematic of the resistance measurement 86
3-3 fabricated sensors: (a) conductive wires deposited on the polyurethane substrate; (b) a folded sensor 87
3-4, Photos of the specimen for the resistance measurement while tensioning 89
3-5 Resistance changes according to the applied strain 89
4-1. Electron conductance mechanism in the elastomeric piezoresistive nanocomposite [114]: (a) Carbon nanotubes inside the polymer matrix form conductive networks. (b) When deformed by an object, the polymer matrix projects the deformation to the conductive networks. (c) The resistivity of these networks can be modeled by the intrinsic conductance of nanotubes (RCNTs), direct contact conductance of nanotubes (RContact) and electron tunneling conductance between the conducting nanotubes in close proximity (RTunneling). 94
4-2. Multi-layer compliant tactile sensor structure. Two layers of orthogonal sensing elements are separately embedded into an elastomeric body in the two orthogonal directions. The juxtaposition of sensing elements in I and J directions forms taxels that can be used to detect the two-dimensional location of a force applied to the surface of the sensor. 95
4-3. Schematic of the developed sensor. The sensor was built layer by layer to embed the sensing patterns into the elastomeric structure. The sensing patterns are printed using a DP process on the soft-molded compliant layer. 97
4-4. Developed Direct-Print Cure system 98
4-5. Hybrid manufacturing process to build multi-layer compliant tactile sensor. Manufacturing process follows the steps (a) to (h). Steps (a), (d), and (g) are used to build the base (bottom), intermediate, cover (top) insulating layers, respectively. In step (b), the first layer of the sensing patterns is printed onto the base molded layer. In step (e) the orthogonal sensor pattern is printed onto the layer that has been built in step (d). First and
second layers of sensing material are cured in steps (c) and (f) with UV light before being covered, respectively. After all steps (a) to (g), the final sensor (h) is ready.

4-6. Fabricated compliant multi-layer tactile sensor. The sensor is comparably stretchable in both body structure and sensing elements. There are two orthogonal layers of 16 sensing elements that make a 64-taxel tactile sensor.

4-7 Wiring diagram: (a) all the sensing elements are wired in a half Wheatstone bridge circuit supplied with a DC voltage. (b) Schematic of a single sensing element in a half Wheatstone bridge measures the change in electrical impedance resistivity as a result of an external force.

4-8 Signal processing algorithm. The signal from each element is first passed through a filter to attenuate high-frequency noise. Then to accentuate the signal, its derivative is passed through a nonlinear gain with power P. The signals are then compared with the threshold values to detect the location a force is applied. As a force is translated along the surface of the sensor, the direction and speed of motion is calculated by referencing the time and distance between detected contacts in adjacent strips in each direction.

4-9 Contact force detection experiment: the test probe was automatically placed on the predefined positions at A (I7, J7), B (I5, J5), and C, a position between the J2 and J3 strips along the I3 sensing element.

4-10 Evaluation of the sensor to detect the motion of applied force. (a) A rubber probe was manually slid from the start point (I8, J8) to the end point (I2, J1). (b) A rubber probe was slid purely in the J direction from the start point (I6, J1) to the end point B (I6, J8). (c) A rubber cylinder was slid purely in the I direction from the start point (I8, J3) to the end point (I1, J3).

4-11 Sensor signals in the contact point detection experiments. (a) Output signals from sensing elements that lay in the I direction. (b) Output signals from sensing elements that lay in the J direction.

4-12 Contact point detection. (a), (b), and (c) show contact point detection of points A, B, and C as depicted in Figure 9, respectively. When the relays are triggered in orthogonal strips at the same time, a contact location is detected.

4-13 Sensor signals during the diagonal slip experiments. (a) The processed signals (FI1, FI2… FI8) in the I direction. (b) The processed signals (FJ1, FJ2… FJ8) in the J direction.

4-14 Slip detection. (a) A three-dimensional time-position surface indicating the motion over the surface of the sensor with respect to time. (b) The two-dimensional motion profile during the diagonal motion experiment.
4-15. The velocity profile in both the I and J directions. The sign of the velocity amplitude shows the direction of motion. The negative velocity profile in both the I and J directions indicate a movement toward the origin of the I-J coordinate system. 

4-16. The results of the unidirectional motion experiments; (a) motion was detected purely along the \( I_6 \) element in the positive \( J \) direction. (b) The related piecewise linear velocity profile from (a) is positive. (c) motion was detected purely along the \( J_3 \) element in the negative \( I \) direction. (d) The related piecewise linear velocity profile from (c) is negative, as expected.

5-1. Schematic of the suggested tactile sensor. (a) exploded view of the top and bottom sensing parts with piezoresistive elements and intermediate insulating layer. (b) combined sensor structure

5-2. Sensor type I (a) combined sensor model, (b) exploded view of the compliant part (blue) and rigid part (grey)

5-3. Sensor type II (a) combined sensor model, (b) exploded view of the top and bottom parts with sensing elements and the intermediate insulating part. (c) top, (d) bottom parts with sensing elements in (b)

5-4. Sensor type III (a) combined sensor model. (b) exploded view of the model

5-5. Fabricated type I sensor. (a) 3D printed multi-material structure before the cleaning process. (b) the fabricated part with the pin connectors after cleaning. (c) injection of the sensing material, (d) final sensor with the injected sensing elements

5-6. Multi-layer multi-material 3D printed tactile sensor. (a) 3D printed parts (b) top and bottom parts with the printed sensing elements in the open channels (c) assembled sensor. the single connectors are used as the common ground in wiring while the other two 8-pin connectors were used as the sensor inputs

5-7. Integrated manufacturing system including DP and PSL. (a) PSL process to build the insulating layers, (b) DP process to print sensing elements

5-8. Fabricated sensor using integrated PSL and DP processes. (a) an example (partial sphere) of a 3D structure built in the PSL system. (b) the sensing elements were printed using the DP process on the insulating layers built in the PSL system. (c) the final sensor had two sensing layers. (d) a deformed sensor. All the sensing elements were connected to a common ground

5-9. Experimental results with the type I sensor. (a) three applied forces at three different locations. Results of (b) the force A, (c) the force B, and (d) the force C

5-10. Experimental results with the type II sensor. (a) four applied forces in four different locations. Results of (b) the force A, (c) the force B, (d) the force C, and (e) the force D.
5-11. Experimental results with the type III sensor. (a) - (b) applied forces using a probe, Results of (c) the force A, and (d) the force B ................................................................. 131

6-1. (a) Schematic illustration of cross-linked IL-incorporated polymer sandwiched between two conductive CNT-polymer electrodes and covered with two compliant polymeric layers. (b) The chemical structure of the 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF4) used as the IL. (c) The SEM image of 0.01 wt% of functionalized MWNT into the photopolymer ................................................................. 135

6-2. Dispersion of MWNT into the DMF with the aid of Triton X100 and DMF and ultrasonication. (a) MWNT, (b) solution of 1g CNT + in 200ml DMF + 4g Triton X-100 . (c) 1g CNT + in 200ml DMF after Sonication ................................................................. 138

6-3. Conductive nanocomposite ink. (a) A highly viscoelastic conductive ink. (b) Fully curable in room temperature. (c) A transparent film with 0.001 wt% CNT dispersed into a flexible resin ............................................................................................................................ 138

6-4. Left: Schematic of a hybrid manufacturing process. This process includes molding (a,c,k), light curing (b,f), screen printing (c,g) and thermal curing (d,h). Right: fabricated sensor ......................................................................................................................................................... 139

6-5. Input and output voltages from the sensor ................................................................................................................................. 141

6-6. The calculated electrical resistivity of the IL-polymer under the different electrical field conditions. The electrical resistivity of the IL-polymer changes as the electrical field changes ................................................................................................. 142

6-7. Electrical conductivity vs. output voltage ................................................................................................................................. 143

6-8. The performance of the sensor under the presence of an external force. (a) the recorded voltage at the half Wheatstone bridge. (b) the measured force using the weighting scale. ........................................................................................................................................................................ 145

6-9. Sensor calibration ........................................................................................................................................................................ 146

6-10. Sensitivity of sensor with respect to the used impedance ........................................................................................................ 146

6-11. The performance of the sensor under a periodic force ........................................................................................................ 147
LIST OF TABLES

Table                  Page
1-1. Conductivities and electrochemical windows of several ionic liquids [85].............. 23
1-2. Side by side comparison of typical properties of 1D conductive nanofillers [99]. .... 26
1-3. A review on the conductivity of the filler based nanocomposites [99]. For the description of Abbreviations please refer to the Table 1-4....................................................... 29
1-4. Description of Abbreviations used in Table 1-3....................................................... 31
1-5. Effect of various solvents with different values of Hansen parameters on the dispersion of nanotubes. Reprinted from [173]. Copyright © 2005 Elsevier Inc. ............................. 48
2-1. Experiment parameters to develop and customize the direct write system. Several experiments were done to understand the effect of the fluid flow rate (Fluid flow rate ∝ Applied Voltage) and translation speed. (St: Translation speed, V: Applied volt, Gd: Gap distance, Td: Tip diameter)............................................................................................... 59
2-2. Inclined printing conditions. ...................................................................................... 69
2-3. The Newtonian resin used in DPC process ............................................................... 73
2-4. The composition of inks used to fabricate the objects shown in Figure 2-18 together with the printing parameters. ............................................................................................ 75
CHAPTER I

BACKGROUND AND LITERATURE REVIEW

1.1 Advancing 3D printing process

Although the use of 3D printing technology is already prevalent in a wide range of applications ranging from simple prototypes (Figure 1-1) to direct part production (Figure 1-2), there are still many areas that could benefit from this technology [1,2].

Figure 1-1. Application of 3D printing technology in simple prototypes [3].

In recent years, researchers have investigated hybrid 3D printing processes and materials to create advanced products [4-7]. In particular, electronic/electrical components have been deposited and embedded within 3D structures by interrupting the 3D printing process [8-10].
Although it is expected that these hybrid manufacturing processes are promising in producing smart structures, there is a lack of flexibility in combining a commercial process. For example, it may not be possible to pause and resume the 3D printing process.

Figure 1-3. A hybrid process including Stereolithography and Direct Printing processes was used to fabricate a magnetic flux sensor. The structure was built using the stereolithography process. While the direct print process was used to deposit the conductive traces. Through the process interruption, the electrical components were inserted into the structure. [4].
In addition, there are limitations in the use of a customized functional material in these machines since they have been developed with specific types of materials designed for predetermined physical and rheological properties. Thus, fabrication of multi-material functional and smart structures is problematic because of the process and material limitations. Advances in materials science are opening a new area in conjunction with the existing 3D printing technology [1]. Examples include printable conductive inks [12], batteries [13] (Figure 1-4), piezoresistive materials [14-16], tissue engineering materials [17-21] and cell-seeded biomaterials [22,23].

Figure 1-4. Schematic of a 3D printed battery using Direct Print technology [13].
Among 3D printing processes, Direct Print (Also known as Direct Write) process has the most potential for the fabrication of functional 3D structures (Figure 1-4). This method is the most capable technique in utilizing the low to the high viscous functional material. In this process by means of computer-controlled translation stages, one [12,13,15,16,19,24] or multiple [18,20,23,25] pattern generator devices (e.g. a dispenser or jetting head) (Figure 1-5) are positioned to print various passive or active material.

![Figure 1-5. Direct Printing with (a) one dispenser [16], (b) multiple dispenses [23].](image)

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The printing process can print in either two and three-dimensional structures or even free-standing (i.e. self-standing) structures (Figure 1-6) [6,26-28]. The printing processes can be either on a flat [15,16,24,29] or conformal surfaces [30-33] (Figure 1-6). Development of the functional inks has given possible ways to use this technique to make functional structures. Examples of these functional structures are circuitries (Figure
1-7a,b), [12] batteries (Figure 1-4) [13], sensors (Figure 1-7d) [15,16,34], and tissue structures (Figure 1-7c) [17-21].

Figure 1-6. Different successful approaches used by direct print technology. (a) Planner printing [29]. Copyright © 2010, Royal Society of Chemistry (b) conformal printing [31]. Copyright © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim (c) free standing printing [26]. Copyright © 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

Figure 1-7. Application of direct printing technology. (a)-(b) printing circuitry [35]. (c) bio printing [18]. (d) sensor printing [15,16,34].
These inks need to have a particular rheological property that facilitates their extrusion through a nozzle with an inner diameter ranged from several microns to hundreds of microns. An optimized rheology helps the shape retention of extruded filament that further facilitates the creation of periodic or 3D structures (Figure 1-8). Viscoelastic inks have shown a great potential in the fabrication of 3D periodic structures using the DP process due to their rheological properties.

Figure 1-8. An ideal 3D printed structure where the shape of deposited filament is retained by the progress of the process [36].

In comparison to a fluid system, the flow property of the viscoelastic ink changes as it is subjected to a stress [37]. The viscosity of viscoelastic ink decreases in the presence of the shear stresses that helps the flowability through the fine deposition nozzles [38,39] (Figure 1-9a). However, upon exiting the nozzle, the ink relaxes and its viscosity increases. A strong viscoelastic ink extruded from a nozzle makes a filament to function like a solid
filament that can hold the weight of upon layers. This particular property assists the shape retention of deposited filaments. A strong ink has a larger storage modulus (G’) than its loss modulus (G”) (Figure 1-9b, Figure 1-10a). Like the elastic material, a strong viscoelastic ink can deform under the stress and quickly return to its original shape once the stress is removed [37]. Although a very strong viscoelastic ink is preferable, its deposition through the nozzle must come into the consideration (Figure 1-10b).

Figure 1-9. Rheological property of several viscoelastic inks developed by the dispersion of graphene and silica into the polymer matrix. (a) The apparent viscosity of a viscoelastic ink decreases in the presence of shear stresses. (b) Viscoelastic inks have a storage modulus (G’) greater than loss modulus (G”). A strong ink exhibit larger values for both the G’ and G” [36].
Figure 1-10. Rheological behavior of a fugitive ink used in direct print technology. (a) Ink has a viscoelastic behavior where its shear storage ($G'$) is greater than its loss moduli ($G''$) [39]. (b) An optimized rheological property of an ink by considering its deposition through the nozzle. A very strong ink with large $G'$ cannot be deposited through the nozzle [38].

Figure 1-11. A direct printed periodic structure using the fugitive ink [38] Copyright © 2005 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
Researchers have developed several types of inks to meet the mentioned requirements. Examples include organic fugitive inks (Figure 1-11) [39], concentrated polyelectrolyte complexes (Figure 1-12a) [40], colloidal suspensions (Figure 1-12b) [42] hydrogels (Figure 1-12c) [41] and thermoset polymers (Figure 1-12d) [28]. There are several solidification mechanisms to maintain the geometry of extruded filaments. These mechanism include viscoelastic recoil, [38] coagulation in reservoir, [40] suppression of repulsive forces, [42] UV polymerization [15,24,27,28], or solidification through solvent evaporation. [26,43] Some of these methods offer a high spatial resolution. However, they
exhibited limited control on the 3D printed features that affect printing an exact 3D structure (Figure 1-11). An improved dimensional accuracy can be achieved by controlling the ink rheology combined with the curing mechanism. One of the successful techniques where researcher controlled the ink rheology and the curing process was solvent casting printing method [43].

![Figure 1-13. Schematic of proposed Direct Print Photopolymerization system](image)

One of the goals of this thesis was to develop a solvent free Direct Print Photopolymerization (DPP) fabrication method able to print high-resolution functional structures. This fabrication technique can fabricate high-resolution (±50µm) 3D structures at room temperature in a layer by layer or free-form fashion. Despite its ability to control the dimensional accuracy, the use of polymers and their nanocomposites fortify this process to develop the future of functional 3D structures. Although DPP is a stand-alone process,
development of a hybrid process by combining other existing methods (e.g. 3D printing) is another area of interest to create advanced functional devices. This study explored a hybrid manufacturing method included the DPP and molding technique to build a multi-layer compliant tactile sensor for robotic applications [14-16, 24, 34, 44]. The DPP process was successfully integrated into the stereolithography process to print and embed conductive inks into a part previously fabricated via stereolithography [4]. We successfully presented the integration of the DPP and Projection based Stereolithography (PSL) to fabricate 3D structures with conductive traces [6].

1.2 Sense of touch through flexible tactile sensors

Hybrid 3D printing with direct-print (DP) shows great manufacturing flexibility over traditional manufacturing processes to fabricate more complex and advanced structures [1]. Multi-layer tactile sensors have been considered as one of the applications of hybrid 3D printing [34]. These sensors deliver adequate tactile information from the interactions with the environment to a robot [45, 46] (Figure 1-14).
In parallel with the development of dexterous robotic hands, these tactile sensors play a critical role in improving the accuracy and control of robotic manipulators such as dexterous artificial limbs and prosthetic hands [48-51]. A tactile sensor increases the accuracy of handling objects by providing tactile feedback to the controller. Subsequently it is useful to prevent any unintended damage to grasped objects. It is also helpful to have integrated tactile sensors on the surface of the robotic manipulators. This surface could have a large area and might require a distributed, conformal and flexible tactile sensor [51-55] (Figure 1-14). There are several basic requirements such as conformability, compliance, dynamic range and sensitivity, installation space, surface area, and weight, which should be satisfied during the design process [47].
1.2.1 Developing flexible tactile sensors

There have been notable advances in the design and development of tactile sensors [16,52,56]. These sensors work based on resistance [57,58], capacitance [52], optics and electromagnetics [59-61] (Figure 1-15), piezoelectricity [62], or acoustics [52]. These designs and approaches have shown great potential in providing precise and repeatable force measurement. However, their complexity, flexibility, conformability, cost of fabrication, wiring topology, signal processing, packaging and assembly still remain a major limitation for their usage in general-purpose applications [47,53,54].

Figure 1-15 A highly flexible optical fiber tactile sensor. [61]. Copyright © 2008, IEEE.

There have been many efforts to increase the flexibility of sensors toward integrated, conformal and large area fabrication of tactile sensors (Figure 1-15). Conductive liquid embedded channels within the sensor array have been reported to increase both the flexibility and the accuracy of micromanipulators [53]. In this method,
molding, embossing and lithography techniques were used to fabricate soft microfluidic devices (Figure 1-16).

Figure 1-16. Schematic of a soft tactile sensor with orthogonal microchannels. [53]. Copyright © 2005, IEEE

Using elastomers in the design of tactile sensors increases not only the flexibility and conformability of sensors but the mechanical durability and compliance of tactile sensors. These factors are favorable factors in slip detection [16,63] (Figure 1-17).
Another approach toward increasing the flexibility of sensors is using flexible and stretchable sensing materials. Recent research showed that incorporation of carbon nanotubes (CNTs) into a flexible and stretchable polymer matrix provides a new means of the development of large area, soft, elastic, and skin-like sensors [16,64,65]. These functional CNT/nanocomposite sensing materials take the advantage of both high sensitivities of CNTs and high flexibility of their polymer matrix that are important factors in designing flexible sensors. Embedding this sensing material into the elastomer through a direct-write technology [66] has shown potential in designing large area, distributed and stretchable sensors [16].

1.2.2 Designing a fully polymeric flexible tactile sensor

Skin-like flexible sensing structures are required to remain functional, avoid permanent deformation, and preserve the natural mechanics of the host system when it is stretched and released [63]. As the number of sensing elements increases, reducing the complexity of the wiring topology during the design of such a tactile sensor becomes a
challenge [47]. To overcome the difficulties mentioned previously, a multi-layer resistance based tactile sensor is proposed which consists of two layers of conductive elements arranged in an orthogonal configuration deposited on both sides of a piezoresistive and conductive polymer and covered with compliant layers (Figure 1-18).

![Figure 1-18. A fully polymeric resistance based tactile sensor](image)

The principle of the sensor is based on the changes in the electrical resistance of the sensing layer that is embedded between two conductive electrodes in an elastic body (Figure 1-18). As a result of this orthogonal configuration, taxels are formed at each cross section (Figure 1-19) that will be used for contact localization, shape detection, and pressure measurement.
The main components of this sensor are flexible electrodes and piezoresistive-conductive layer. The principle of their development will be discussed in the following.

1.3  A novel pressure sensitive polymer for the 3D printing of tactile sensors using ionic liquid based photopolymer

After their first report by Noda & Watanabe [67], researchers used Ionic Liquids (ILs) in different applications [68,69]. The term ionic liquids (ILs) refers to a liquid salt consisting ions and ions pairs with low vapor pressures. ILs are known for their high ionic conductivity that is typically on the order of 10-3 S/cm or above [70,71]. The ILs have been widely used as organic solvents [69,72,73], polymerization media [73-75], polymer additives (plastisizer, proogenic agent, etc.) [68]. ILs were also used as a dispersion agent to disperse Carbon Nanotubes (CNTs) (Figure 1-20 and Figure 1-21) [76-78].
Figure 1-20. Schematic procedures for synthesizing functionalized MWCNTs using ionic liquid [78]. Copyright © 2012 Elsevier Ltd.

Figure 1-21. SEM fracture images of composites without BMIMBF4 dispersion. Individual nanotubes are randomly distributed on the fractured surface showing no interfacial compatibility between the matrix and the nanotubes. (d) Composites with BMIMBF4 as the dispersion–curing agent. MWCNTs are dispersed well within the matrix showing excellent adhesion [77]. Copyright © 2013 Royal Society of Chemistry.

Figure 1-22. Application of Ion gel gated polymer in thin film transistor (Right). The structure of ionic liquid and triblock copolymer ion gel components (Right). Reprinted with permission from [71]. Copyright © 2007, American Chemical Society.
ILs have been also used to develop polymer electrolytes (Figure 1-22) and (Figure 1-23) [79]. The various ionically conductive polymeric electrolytes have been developed for a different range of applications ranging from rechargeable batteries, transistors (Figure 1-22) to smart windows [68].
1.3.1 Developing a conductive ionic liquid polymer

The ion conductive polymers are developed by incorporation of ionic liquid into a prepolymer and subsequent polymerization of the product (Figure 1-24) [68,80-82]. In this system, the conductivity drives from the migration of doped ions between the coordinate sites generated by the local motion of polymer chain segments under enough activation energy. Several factors are important in design and development of conductive electrodes based on the ILs. These factors include electron-donating atoms to form the coordinate bond, low bond rotation barriers, and high segmental motion of the polymer chain [83]. A higher ionic conductivity derives from a high ion mobility, a high ion density, and a low polymer Tg [81,83]. There are critical requirements for the selection of a proper IL for a successful IL-polymer. High ionic conductivity is the critical and main deciding factor while selecting the IL liquid. The IL content has a considerable effect on the final ionic conductivity. A higher ionic conductivity can be obtained by introducing more IL into the polymers. However, a more IL deteriorates mechanical strength and dimensional stability, especially at elevated temperatures. Thus, reducing the IL content while maintaining good conductivity is important for polymer electrolyte applications. Moreover, the morphology of the polymer also affects its ionic conductivity. A highly continuous and interconnected ion transport domain will have high ionic conductivity and vice versa. A block copolymer or a nanofiller introduced into the IL-based polymer electrolytes can effectively tune the morphology of polymer electrolytes to meet this requirement [80]. Another critical factor in selecting an IL is a good mechanical and dimensional stability.
IL-based polymer electrolytes usually show high ionic conductivities at elevated temperatures or with high IL contents. However, at high temperatures these membranes
lose their mechanical properties. The development of dimensionally stable IL-based polymer electrolytes with high ionic conductivities is currently an active research area.

1.3.2 Properties of several ionic liquids for the electrochemical applications

As it was described, over the past decade, Ionic Liquids have attracted much interest for their use as non-aqueous electrolytes in electrochemical applications. In this context, their conductivity, as well as their electrochemical stability, are the most important physical properties [84].

Typical conductivity values are in the range from 1.0 mS/cm to 10.0 mS/cm. Recently, ILs with conductivities above 20 mS/cm based on the imidazolium-cation were also developed. Examples include 1-ethyl-3-methylimidazolium thiocyanate and 1-ethyl-3-methylimidazolium dicyanamide (Sigma-Aldrich, Milwaukee, WI). The electrochemical window of Ionic Liquids, which is a measure of their electrochemical stability against oxidation (Cation (+) + e(-) → neutral species) and reduction processes (Anion (-) → neutral species +e(-)) is another very important property of the Ionic Liquids. Figure 1-25 and Figure 1-26 compare the Cation and Anion stability of several ionic liquids [85].

![Chemical structures of different ILs]

Figure 1-25. Cation stability [85].
Figure 1-26. Anion stability [85].

Table 1-1. Conductivities and electrochemical windows of several ionic liquids [85].

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>Electrochemical Window</th>
<th>Conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>High Conductivity</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-Ethyl-3-methylimidazolium dicyanamide</td>
<td>2.9 V</td>
<td>27 mS/cm</td>
</tr>
<tr>
<td>1-Ethyl-3-methylimidazolium thiocyanate</td>
<td>2.3 V</td>
<td>21 mS/cm</td>
</tr>
<tr>
<td><strong>Electrochemical Stability</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Triethylsulphonium bis(trifluoromethylsulfonyl)imide</td>
<td>5.5 V</td>
<td>8.2 mS/cm</td>
</tr>
<tr>
<td>N-Methyl-N-trioctylammonium bis(trifluoro-methylsulfonyl)imide</td>
<td>5.7 V</td>
<td>2.2 mS/cm</td>
</tr>
<tr>
<td>N-Butyl-N-methylpyrrolidinium bis(trifluoro-methylsulfonyl)imide</td>
<td>6.6 V</td>
<td>2.1 mS/cm</td>
</tr>
<tr>
<td><strong>Combined Properties</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-Ethyl-3-methylimidazolium tetrafluoroborate</td>
<td>4.3 V</td>
<td>12 mS/cm</td>
</tr>
<tr>
<td>1-Ethyl-3-methylimidazolium trifluoromethylsulfonate</td>
<td>4.3 V</td>
<td>8.6 mS/cm</td>
</tr>
</tbody>
</table>

According to the Table 1-1, 1-ethyl-3-methylimidazolium thiocyanate and dicyanamide showed the highest conductivities and exhibited the lowest electro-chemical stabilities. Nevertheless, these materials are good candidates for the use in any application where a high conductivity combined with thermal stability and non-volatility is necessary.
The electrochemically most stable ILs have comparable small conductivities. Examples are N-butyl-N-methylpyrrolidinium bis(trifluoromethyl-sulfonyl)imide, triethyl sulphonium bis(trifluoromethyl-sulfonyl)imide, and N-methyl-N-trioctylammonium bis(trifluoromethylsulfonyl)imide [85]. These ILs are good candidates for the applications like batteries [86], fuel cells [87], metal deposition [88], and electrochemical synthesis of nano-particles [89]. For the applications such as sensors and super capacitors [90] where conductivity and electrochemical stability are needed, imidazolium-based Ionic Liquids with stable anions (e.g., tetrafluoroborate or trifluoromethylsulfonate) are preferable candidates [85].

In this study, with the application of an IL with the combined properties (conductivity and stability) (1-Ethyl-3-methylimidazolium tetrafluoroborate [85]), we presented a unique group of printable flexible ion conductive polymers with field and strain sensitive properties. We successfully used them to print a pressures sensor.

1.4 Introducing conductivity into the nonconductive polymers

There have been increasing demands and interests in stretchable electronics especially in the context of stretchable sensors with the development of flexible or stretchable conductive materials. Advances in polymer nanocomposites with carbon nanotubes (CNTs) have offered novel material to build inexpensive conductive, as well as sensing material.

CNTs have superior physical and mechanical properties. They have high aspect ratio of ~500 to 1000, high elastic modulus of ~0.64 TPa, stiffness of ~1,000 GPa, tensile
strength of ~100 GPa, low electrical impedance of ~0.5 µΩ, and excellent gauge factor (sensitivity) of ~600 to 1000 [91,92]. Due to these remarkable properties, CNT-based nanocomposite has been regarded as one of the potential means to develop a stretchable electrode [93] and piezoresistive strain sensor [94]. These notable properties of conductive nanocomposites make them suitable for an electrode material where the flexibility and compliance play an important role.

Upon dispersion of CNTs in the solution, conductive networks are formed once the amount of dispersed CNTs exceeds a critical fraction. This critical concentration of the conductive additive is named the percolation threshold [95]. That is to say, once an amount of conducting particles in a solution reaches a limit, the composite becomes conductive due to the creation of enough conducting paths (Figure 1-27). The percolation threshold mainly depends on the types of the polymer and conductive particle [94,96]. There are several discussions on highly stretchable sensors/electronics such as silver/CNT conductive rubber adhesive [97], and stretchable rubberlike conductors [98]. One of the goals of this work was to develop highly stretchable conductive nanocomposite able to cover large tensile strains up to 30%. Following describe a comprehensive literature review in developing conductive nanocomposite through dispersion of CNTs into the polymers.
Table 1-2. Side by side comparison of typical properties of 1D conductive nanofillers [99].

<table>
<thead>
<tr>
<th>Property</th>
<th>SWCNT [100]</th>
<th>MWCNT [100]</th>
<th>AgNW [101]</th>
<th>CuNW [102]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (nm)</td>
<td>0.6-1.8</td>
<td>5-50</td>
<td>100-200</td>
<td>25-200</td>
</tr>
<tr>
<td>Aspect ratio</td>
<td>100-10,000</td>
<td>100-10,000</td>
<td>50-200</td>
<td>50-200</td>
</tr>
<tr>
<td>Density (g cm⁻³)</td>
<td>~1.3</td>
<td>~1.75</td>
<td>10.49</td>
<td>8.94</td>
</tr>
<tr>
<td>Thermal conductivity (W mK⁻¹)</td>
<td>3000-6000</td>
<td>3000-6000</td>
<td>429</td>
<td>401</td>
</tr>
<tr>
<td>Electrical conductivity (S m⁻¹)</td>
<td>105-106</td>
<td>105-106</td>
<td>6.30 × 10⁷</td>
<td>5.96 × 10⁷</td>
</tr>
<tr>
<td>Tensile strength (GPa)</td>
<td>50-500</td>
<td>10-60</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Tensile modulus (GPa)</td>
<td>1500</td>
<td>1000</td>
<td>83</td>
<td>110-128</td>
</tr>
</tbody>
</table>

1.4.1 Conductive nanocomposites developed by dispersion conductive nanoparticles into a polymer matrix

Numerous conductive composites were developed by adding electrically conductive nanofillers such as Multi-Walled Carbon Nanotubes (MWCNTs)[102-104], Single-Walled Carbon Nanotubes (SWCNTs) [105-107], graphene [108-110], and metallic nanowires [111-113] into polymer matrices. The mechanism of electron conductance within these networks is a combination of: (1) intrinsic conductance of the nanotubes; (2) direct contact conductance; and (3) electron tunneling between the conducting nanotubes.
that are in close proximity to one another [114] (Figure 1-27). Tunneling conduction occurs when the distance between the filler particles are close enough, roughly less than 10 nm [114]. At the percolation threshold, a fully 3D conductive network has not been formed. Above the percolation threshold, the filler forms a continuous network inside the polymer matrix, and the further increase in the filler loading usually has no significant effect on the composite electrical conductivity (Figure 1-28) [100].

Figure 1-27. Electron conductance mechanism in the elastomeric piezoresistive nanocomposite [114]: (a) Carbon nanotubes inside the polymer matrix form conductive networks. (b) When deformed by an object, the polymer matrix projects the deformation to the conductive networks. (c) The resistivity of these networks can be modeled by the intrinsic conductance of nanotubes (RCNTs), direct contact conductance of nanotubes (RContact) and electron tunneling conductance between the conducting nanotubes in close proximity (RTunneling).
The electrical property of a composite depends on many factors including conductivity of filler, its aspect ratio, and quality of dispersion in addition to the polymer matrix crystallinity, surface tension, and interaction between the CNTs and polymer matrix. Table 1-2 compares different physical and electrical properties of most widely used fillers. MWCNTs feature the lower price and similar properties to SWCNTs. Thus, MWCNTs, especially industrial grade MWNT, are the most favorable nanoparticle in developing conductive nanocomposites. Table 1-3 reviews and compares several parameters including filler type, polymer matrix, filler concentration (C), dispersion method, threshold, on the maximum observed conductivity ($\sigma_{\text{max}}$).
Table 1-3. A review on the conductivity of the filler based nanocomposites [99]. For the description of Abbreviations please refer to the Table 1-4

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Filler</th>
<th>Solution</th>
<th>Dispersion</th>
<th>Aspect Ratio</th>
<th>$\sigma_{\text{max}}$ (S/m)</th>
<th>C (wt%)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>Ag/MWCNT</td>
<td>MB/CM</td>
<td>-</td>
<td>-</td>
<td>2.00E-02</td>
<td>2.00</td>
<td>[116]</td>
</tr>
<tr>
<td>PS</td>
<td>AgNW</td>
<td>Toluene</td>
<td>SP/MS/CM</td>
<td>31</td>
<td>1.00E-01</td>
<td>4.80</td>
<td>[117]</td>
</tr>
<tr>
<td>PP</td>
<td>CB(Akzo Nobel)</td>
<td>-</td>
<td>MM-TSE</td>
<td>-</td>
<td>1.00E+02</td>
<td>15.00</td>
<td>[118]</td>
</tr>
<tr>
<td>PS</td>
<td>CuNW</td>
<td>CH2Cl2/CH3OH</td>
<td>SP/SC/CM</td>
<td>-</td>
<td>1.00E+04</td>
<td>19.80</td>
<td>[113]</td>
</tr>
<tr>
<td>PS</td>
<td>CuNW</td>
<td>CH2Cl2</td>
<td>SP/US/CM</td>
<td>71</td>
<td>1.00E-03</td>
<td>21.00</td>
<td>[119]</td>
</tr>
<tr>
<td>PS</td>
<td>CuNW</td>
<td>-</td>
<td>MM-TSE</td>
<td>51</td>
<td>1.00E-06</td>
<td>15.00</td>
<td>[120]</td>
</tr>
<tr>
<td>HDPE</td>
<td>MWCNT</td>
<td>-</td>
<td>MM-TSE</td>
<td>1000</td>
<td>1.00E+00</td>
<td>7.00</td>
<td>[121]</td>
</tr>
<tr>
<td>LDPE</td>
<td>MWCNT</td>
<td>-</td>
<td>MM-TSE</td>
<td>1000</td>
<td>1.00E-01</td>
<td>7.00</td>
<td>[121]</td>
</tr>
<tr>
<td>PCL/P</td>
<td>MWCNT</td>
<td>MM-R/CM</td>
<td>1000</td>
<td>1.00E-02</td>
<td>4.00</td>
<td>[122]</td>
<td></td>
</tr>
<tr>
<td>PEEK</td>
<td>MWCNT</td>
<td>MM-TSE</td>
<td>150</td>
<td>1.00E+02</td>
<td>17.00</td>
<td>[123]</td>
<td></td>
</tr>
<tr>
<td>LA</td>
<td>MWCNT</td>
<td>DMF</td>
<td>SP/MS</td>
<td></td>
<td>1.00E-01</td>
<td>20.00</td>
<td>[124]</td>
</tr>
<tr>
<td>Table</td>
<td>MWCNT</td>
<td>Dioxane</td>
<td>SP/MS/US</td>
<td>100</td>
<td>3.00E-04</td>
<td>5.00</td>
<td>[125]</td>
</tr>
<tr>
<td>PLA</td>
<td>MWCNT</td>
<td>-</td>
<td>MM</td>
<td>1000</td>
<td>7.90E+01</td>
<td>5.00</td>
<td>[126]</td>
</tr>
<tr>
<td>PMMA</td>
<td>MWCNT</td>
<td>CHCl3</td>
<td>SP/US/CS</td>
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<td>2.70E+02</td>
<td>14.1</td>
<td>[127]</td>
</tr>
<tr>
<td>PP</td>
<td>MWCNT</td>
<td>-</td>
<td>MM-R</td>
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<td>1.00E+00</td>
<td>5.00</td>
<td>[128]</td>
</tr>
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<td>MWCNT</td>
<td>-</td>
<td>MM-TSE</td>
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<td>250</td>
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<td>[129]</td>
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<td>MWCNT</td>
<td>Toluene</td>
<td>SP/US/CS</td>
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<td>9.00E+01</td>
<td>15.60</td>
<td>[127]</td>
</tr>
<tr>
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<td>MWCNT</td>
<td>-</td>
<td>MM-TSE/C M</td>
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<td>1.00E-07</td>
<td>5.00</td>
<td>[130]</td>
</tr>
<tr>
<td>PU</td>
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<td>THF</td>
<td>SP/MS/CS</td>
<td></td>
<td>2.00E+03</td>
<td>15.00</td>
<td>[131]</td>
</tr>
<tr>
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<td>CHCl3</td>
<td>SP/MS/CS</td>
<td>500</td>
<td>3.30E+01</td>
<td>10.00</td>
<td>[132]</td>
</tr>
<tr>
<td>PHBV</td>
<td>MWCNT</td>
<td>CHCl3</td>
<td>SP/MS/CS</td>
<td>500</td>
<td>1.50E+01</td>
<td>10.00</td>
<td>[132]</td>
</tr>
<tr>
<td>PP</td>
<td>MWCNT</td>
<td>-</td>
<td>MM-TSE</td>
<td>1000</td>
<td>1.00E-01</td>
<td>5.00</td>
<td>[128]</td>
</tr>
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</table>
Table 1-3. A review on the conductivity of the filler based nanocomposites [99]. For the description of Abbreviations please refer to the Table 1-4 (Cont.)

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Filler</th>
<th>Solution</th>
<th>Dispersion</th>
<th>Aspect ratio</th>
<th>$\sigma_{max}$ (S/ m)</th>
<th>C (wt%)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>MWCNT (Kentucky U)</td>
<td>DMF/THF</td>
<td>SP/US/MS/C M</td>
<td>100</td>
<td>1.00E+00</td>
<td>0.07</td>
<td>[133]</td>
</tr>
<tr>
<td>PAN</td>
<td>MWCNT(Iljin Nanotech)</td>
<td>DMF</td>
<td>SP/SC/MS</td>
<td>-</td>
<td>1.24E+00</td>
<td>15.00</td>
<td>[134]</td>
</tr>
<tr>
<td>PU</td>
<td>MWCNT, Nanocyl</td>
<td>-</td>
<td>MM-TSE/C M</td>
<td>150</td>
<td>1.00E+00</td>
<td>1.00</td>
<td>[135]</td>
</tr>
<tr>
<td>PA12</td>
<td>MWCNT, Nanocyl</td>
<td>-</td>
<td>MM-TSE</td>
<td>100</td>
<td>1.40E+01</td>
<td>5.00</td>
<td>[136]</td>
</tr>
<tr>
<td>PLA</td>
<td>MWCNT, Nanocyl</td>
<td>MM-TSE</td>
<td></td>
<td>150</td>
<td>1.00E+01</td>
<td>2.00</td>
<td>[119]</td>
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<tr>
<td>HDPE</td>
<td>Nano Ag</td>
<td>-</td>
<td>MM-TSE</td>
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<td>3.00E-01</td>
<td>75.70</td>
<td>[137]</td>
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<tr>
<td>MXD6</td>
<td>Nano Ag</td>
<td>-</td>
<td>MM-TSE</td>
<td></td>
<td>2.00E-01</td>
<td>68.20</td>
<td>[137]</td>
</tr>
<tr>
<td>PBT</td>
<td>Nano Ag</td>
<td>-</td>
<td>MM-TSE</td>
<td></td>
<td>1.00E-01</td>
<td>69.30</td>
<td>[137]</td>
</tr>
<tr>
<td>PS</td>
<td>Ni particle, Bi/Sn alloy</td>
<td>-</td>
<td>MM-SSE</td>
<td>-</td>
<td>1.00E+04</td>
<td>89.30</td>
<td>[138]</td>
</tr>
<tr>
<td>P(VDF-TrFE)</td>
<td>NiNW</td>
<td>Acetone</td>
<td>SP/SC/MS/C M</td>
<td>250</td>
<td>1.00E+02</td>
<td>28.60</td>
<td>[139]</td>
</tr>
<tr>
<td>PP</td>
<td>SG(Asbury)</td>
<td>-</td>
<td>MM-TSE</td>
<td>1.7</td>
<td>1.10E+03</td>
<td>80.00</td>
<td>[129]</td>
</tr>
<tr>
<td>PS</td>
<td>Sn-Pb alloy</td>
<td>-</td>
<td>BM/CM</td>
<td>-</td>
<td>1.00E+00</td>
<td>81.60</td>
<td>[140]</td>
</tr>
<tr>
<td>PEEK</td>
<td>SWCNT</td>
<td>MM-TSE</td>
<td></td>
<td>-</td>
<td>1.00E-02</td>
<td>1.00</td>
<td>[107]</td>
</tr>
<tr>
<td>PMMA</td>
<td>SWCNT</td>
<td>CHCl3</td>
<td>SP</td>
<td>-</td>
<td>1.00E+04</td>
<td>10.00</td>
<td>[141]</td>
</tr>
</tbody>
</table>
Table 1-4. Description of Abbreviations used in Table 1-3.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Full name</th>
<th>Dispersion Method</th>
<th>Full name</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE:</td>
<td>High-density polyethylene</td>
<td>MM-TSE</td>
<td>Melt mixing with twin screw extruder</td>
</tr>
<tr>
<td>MXD6</td>
<td>Poly(m-xylene adipamide)</td>
<td>SP</td>
<td>solution processing</td>
</tr>
<tr>
<td>PA12</td>
<td>Polyamide 12</td>
<td>SC</td>
<td>sonication</td>
</tr>
<tr>
<td>PAN</td>
<td>Polyacrylonitrile</td>
<td>MS</td>
<td>mechanical stirring</td>
</tr>
<tr>
<td>PBT</td>
<td>Polybutylene terephthalate</td>
<td>CS</td>
<td>Casting</td>
</tr>
<tr>
<td>PCL</td>
<td>Polycaprolactones</td>
<td>US</td>
<td>ultrasonication,</td>
</tr>
<tr>
<td>PDMS</td>
<td>Polydimethylsiloxane,</td>
<td>MM-R</td>
<td>melt mixing in the rheometer</td>
</tr>
<tr>
<td>PEEK</td>
<td>Poly(ether ether ketone)</td>
<td>MB</td>
<td>mixed in Brabender</td>
</tr>
<tr>
<td>PHBV</td>
<td>Polyhydroxybutyrate</td>
<td>CM</td>
<td>compression molding</td>
</tr>
<tr>
<td>PMMA</td>
<td>Polymethyl methacrylate</td>
<td>BM</td>
<td>mixing in a ball mill</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene</td>
<td>MM-SSE</td>
<td>melt mixing with a single screw extruder</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P(VDF-TrFE)</td>
<td>Poly(vinylidene difluoride)-trifluoroethylene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PU</td>
<td>Polyurethane</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Reducing the percolation threshold and making a conductive composite economically feasible, is one of the major factors in developing a nanocomposite. Nanocomposite developed with the high aspect ratio particles showed a lower percolation threshold. Building a conductive network within an insulating matrix at low concentration does not necessarily require a well-distributed filler, but a well-dispersed filler (Figure 1-29 and Figure 1-30) [100,142].

Figure 1-29. A well-dispersed MWNT whining the polymer matrix results in a higher conductivity. CNT load: 1 wt%, Dispersion method: Three Roll Milling. Shear intensity of three roll milling increases from left to right. Reprinted with permission from [142]. Copyright © 2009 Elsevier Ltd.
Figure 1-30. The dependence of conductivity on the distribution and dispersion of CNTs. Different type of MWNTs (NLIG: Length 0.2 µm, Diameter: 3.4 nm, NL15L: Length 0.3 µm, Diameter: 3 nm, C100: Length 0.1 µm, Diameter: 5 nm, C150P: Length 0.08 µm, Diameter: 4.5 nm) were dispersed into the epoxy resin using three roll milling machine under different shear intensity. A higher shear intensity results in a better dispersion but lower conductivity due to the lower connection between adjacent CNTs. Reprinted with permission from [142]. Copyright © 2009 Elsevier Ltd.

In the filler based conductive nanocomposites, the percolation threshold is affected by the type of polymer matrix, its surface tension, polarity, and crystallinity. Higher polymer surface tension results in a lower filler-polymer interfacial tension. Thus, the polymer matrix can easily wet the filler particles and thereby distribute them well [100]. A well distributed of fillers increases the percolation threshold. Similarly, a higher polymer polarity also leads to better interactions with the nanofillers. A better interaction also helps to a better distribution of the fillers and a higher percolation threshold. It was found that the weak interaction results in a higher conductivity [115].

In comparison to the amorphous polymer nanocomposite [133,143,144], semi-crystalline polymer systems have shown a better conductivity with a lower percolation
thresholds [145-147]. In this systems, filler particles are ejected from the crystalline region during crystallization and concentrate in the amorphous region. This phenomenon is called the double-percolation threshold. It was reported that Semi-crystalline polystyrene (PS) exhibited a four times large conductivity threshold compared to their amorphous counterparts [147].

Analyses showed that the performance of the nanocomposites depends on many factors, such as: types of CNTs (SWNTs or MWNTs), their morphology, their structure (diameter, length and chirality), the processing method, the choice of matrix, the CNT dispersion within matrix, the interfacial interaction between CNTs and matrix [148]. Currently, there are several problems in developing CNT nanocomposites and using all the potentials of CNTs. These problems can be listed as; Structure control of CNTs, Dispersion of CNTs within the polymer matrix, Interfacial Interaction between CNTs and polymer matrix, Contacts between individual CNTs [148].

1.5 Challenges in front of the dispersion of CNTs into the polymers

Since their discovery, the dispersion of Carbon Nanotubes (CNTs) into the prepolymer matrices has become a fundamental challenge to producing nanocomposites with enhanced and reproducible properties.[149-151]. The effective utilization of CNTs and the full exploitation of their potential in development of nanocomposites depend on several key factors such as dispersion quality [148,151-153], Morphology [154,155], Interfacial interaction, and also arrangement of CNTs in the polymer matrix CNTs [148,152,156,157]. Dispersion quality of CNTs can change not only the mechanical or
electrical properties of the nanocomposite, but also it can change the rheological property of nanocomposite [158]. Han, et al., [151] showed that the poorly dispersed CNTs nanocomposites have a lower viscosity than the better dispersed CNTs nanocomposites.

Figure 1-31. Dispersion of MWNT in polypropylene. (a) 5 wt% of non-treated MWNTs were dispersed into the polypropylene. The MWNTs were functionalized using Triton X-100 as a surfactant in an ethanol solution. Agglomerations of MWNTs are obvious in the dispersion. (b) Individual MWNTs are obvious in a well-dispersed solution. Printed with permission from [159]. Copyright © 2011, SAGE Publications

High aspect ratio, large surface area and strong van der Waals interaction make them prone to entanglement and bundling [148-150,157]. Aggregates (Figure 1-31a), beside the poor solubility of CNTS [150], are found to be a barrier to most carbon nanotube applications. Entangled aggregates, which are difficult to disperse uniformly into prepolymer matrixes without damaging the nanotubes [157], prevent efficient transferring the superior properties of CNTs to the nanocomposite and cause only modest improvements in mechanical, physical properties of nanocomposites [150,151,158]. The aggregates not only may not provide integrated networks to efficiently carry mechanical
loads or transport properties [157], but also they can act as stress concentration points that reduce the mechanical properties of nanocomposites [149].

There are significant numbers of literature reported on the techniques developed for the dispersion of CNTs into the polymer matrix. Many studies have been directed towards producing CNT/polymer composites using the mechanical methods including ultrasonication and mechanical shear mixing processes (stirring, extrusion, ball milling, calendaring) [152], or in-situ polymerization [156]. Chemical (covalent) and physical (non-covalent) functionalization have been developed to modify surface energy and improve the wetting and chemical compatibility of CNTs to achieve good dispersion in prepolymer matrixes [93,150,157].

1.5.1 Ultrasonication an effective dispersion method

Among different mixing system, ultrasonication plays a critical role in dispersion and unbundling of CNTs (Figure 1-32). It is the simplest and most convenient way, universally used as a main or as a part of nanocomposites preparation processes to assist the dispersion and stabilization of CNTs in solvents or prepolymer matrixes [93,149,150]. This process produces high frequency sound waves and ultrasonic energy using a bath type as a mild sonication or a tip (horn) type sonication as a high power to induce cavitation (process of bubble formation, growth and collapse [93,149].
In general cavitation can be initiated by applying a tension or deposition of energy into the liquid. Tension appears in fluid flow or occurs during the pressure cycle of the sound waves. Heat, light, and elementary particles into the liquid can also be as a source of cavitation [160]. The strong shear force that can exfoliate bundles and break up CNT agglomerates during sonication comes from the implosion of cavitation bubbles.
The implosion of cavitation bubbles causes intensive shock waves that subsequently results in the liquid flow with high velocity in the surrounding fluid [162]. Imposing these shear forces forms small gaps to the CNT tails to facilitate an individual CNTs to be separated from the bundles. The gaps further promote more surfactant (in surfactant base system) to be immobilized onto CNT surfaces and exfoliate more individual CNTs from the bundles as the process continues (Figure 1-40) [150].
The efficiency of the cavitation process is closely related to many solvent parameters, including vapor pressure, viscosity, surface tension, as well as the sonication frequency, intensity and time in sound base cavitation (Figure 1-33) [93,161,162]. Gas bubbles, as a result of local cavitation, are generated in the immediate vicinity of the sonicator surface. However, cohesive pressure (the resistance of the liquid to form the cavities due to expansion), limits the growth and transportation of bubbles into the bulk liquid. As the viscosity increases (due to the dispersion of CNTs [149,150,157]), the attractive forces between the molecules increases which limits the onset of cavitation [162].

1.5.2 Ultrasonication with the aid of a long-term shear mixer

The rapid attenuation of sound energy makes the ultrasonication as a short-distance effects treatment and limits its application for very low viscous matrix materials and small volume batches [150]. Consequently, dispersion in the liquids with higher viscosities, especially CNT/prepolymer nanocomposites, due to their viscosity variations by dispersion degree, is a complex problem [150,153]. In the CNT-based nanocomposite, morphology change (Figure 1-34), defects (Figure 1-35), rupture (Figure 1-36), and fragmentation (Figure 1-37) can be induced as a result of the localization of the high-energy sound field around the tip of the sonicator [149,150,153]. Any of these defects eventually deteriorates the physical and mechanical properties of the final nanocomposite.
Figure 1-34. Disorders are introduced into the CNTs as a result of sonication. Reprinted with permission from [155]. Copyright © 1996 Published by Elsevier Ltd.

Figure 1-35. Induced defects in the CNTs under the sonication process. (a) bend with buckling, (b) fracture of graphene layers, (c) stripping of the outer layer. (d) The outer
layer of graphene sheet stripped off. Reprinted with permission from [155]. Copyright © 1996 Published by Elsevier Ltd.

Figure 1-36. Effect of sonication time on the length of nanofillers. Reprinted with permission from [163]. Copyright © 2009 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim
Several ways are used to overcome this problem such as dilution of the suspension with a lower viscosity liquid (solvent) [164], and pre dispersion of the particles in another liquid before mixing in the main matrix as a solution mixing. In this method after dispersion in a solvent, the solvent is substituted with the polymer through complete evaporation of the solvent. A typical problem with these approaches is completely removing the excess solvent and preventing the reagglomeration of CNTs during this removal [153].

A multiple source of shear forces is another way for a homogeneous dispersion of CNTs [165]. M. N. Bougot, et al. proposed a combined method of ultrasonication bath and a horn sonicator to have a homogenous dispersion (Figure 1-38). However, localization of energy around the sonicator is still a problem.
Using a mechanical stirrer as a shear mixing process to assist the dispersion of CNTs during ultrasonication has been shown a good result in dispersion [150,153,166]. Shear mixing as a common technique to disperse particles in liquid systems can be used to disperse nanotubes. The efficiency of this method is related to the size and shape of the propeller and the mixing speed [149]. Sandler et al. [167] showed that it is possible to disperse CNTs into the polymer matrix using an intense stirring process. Xu and Wang [150] used mechanical stirrer as a long-distance effect and ultrasonication alternatively to improve the short-distance effect of ultrasonication. Mechanical stirrer generates fluid flow which transports the CNTs far from the ultrasonic source and makes the cluster to experience more ultrasonication treatment as they move into the effective range with strong ultrasonication. One drawback of alternatively using mechanical stirring and ultrasonication is the possibility of reagglomeration or retwisting the CNT cluster into the large particles due to the mechanical stirrer.
Figure 1-39. Sonicator with the magnetic stirrer for the dispersion of CNTs: (a) magnetic stirrer, (b) material container, (c) sonicator horn, and (d) sonicator controller.

In the current work, the method of conjunction of shear mixing (mechanical stirrer) and ultrasonication is presented (Figure 1-39). Two sources of a mixing process is integrated to each other, the tip sonication as a high energy shear mixing and short distance effect mixer is united to the mechanical shear mixer as a long distance effect mixer to disperse CNTs and prevent the localization of high-energy sound around the tip to homogeneously treat the entire sample in different viscosity ranges. The integration of two systems prevents the retwisting of CNTs due to the mechanical shear mixer.

As it mentioned the quality of dispersion along other parameters such as an aspect ratio, the orientation of the nanotubes and interaction of nanotubes and polymer matrix can change the mechanical, electrical and rheological properties of CNT-nanocomposites. Therefore, besides the study of morphological behavior, the study of these properties is an interesting way to evaluate the degree of dispersion. Although several test methods such as mechanical property tests.
1.6  Noncovalent functionalization of CNTs in the presence of solvent

The full utilization of CNTs in a CNT/polymer nanocomposite depends on the dispersion of CNTs in the matrix and interfacial interactions between the CNT and the polymer. Due to the aromatic nature of the bond, the carbon atoms on CNT walls are chemically stable. As a result, the CNTs are inert. They can mainly interact with the surrounding matrix through van der Waals interactions. Significant efforts have been directed towards modifying the surface properties of CNTs to increase their interaction. These methods are divided into chemical functionalization and physical methods based on the interactions between the active molecules and carbon atoms on the CNTs. Chemical functionalization is based on the covalent linkage of functional entities onto carbon scaffold of CNTs. In this method, the hybridization changes from sp2 to sp3 functionalization that results in the simultaneous loss of p-conjugation system on graphene layer. This method has several drawbacks. Firstly, during the functionalization, especially during the ultrasonication process, a large number of defects are inevitably created on the CNT sidewalls, and CNTs are fragmented into smaller pieces. These damaging effects result in severe degradation in mechanical properties of CNTs. In addition the π electron system in nanotubes is disrupted. The disruption of π electrons is detrimental to transport properties of CNTs. Because defect sites scatter electrons and phonons. The disruption of π electrons also deteriorates the electrical and thermal conductions of CNTs. Therefore, many efforts have been put forward to developing methods that are convenient to use, of low cost and less damage to CNT structure. Among the efforts to increase processability and utilization of CNTs, chemical and especially noncovalent functionalization represents
a keystone, as it is a nondestructive method meaning it does not alter the intrinsic properties of CNTs. Using surfactants in dispersion of CNTs is considered as one of the method of physical or noncovalent functionalization [93].

The mechanism of nanotube exfoliation from bundles with the aid of a surfactant and ultrasonication is called unzippering mechanism [168]. According to this mechanism proposed by Strano et al. [169] ultrasonication provides high local sheer. This high energy dangles ends in the nanotube bundles (Figure 1-40b) which become adsorption sites for surfactants. The local adsorption prevents reaggregation of the loosened tubes from (Figure 1-40c). Continuing the process, the surfactant continuously progresses along the nanotube length resulting in the isolation of the individual tube (Figure 1-40d).

Figure 1-40. Dispersion of nanotubes into the solution in the presence of surfactant and ultrasonication [168].
1.6.1 Selection of a proper solvent for the zippering mechanism

The proper selection of solvent and surfactant is the key factor in exfoliation of CNTs using solution mixing. It was found that the tubes were dispersed very well in the solvents with dispersive component (δ2d) between certain boundaries (17–18 MPa₁/₂). It was observed that CNTs were precipitated in the solvents with high polar (δ2p) and hydrogen-bonding (δ2h) components. It was also found that the dispersion state had no specific dependency on the total solubility parameter (δ2t) [170]. Table 1-5 provides a comprehensive comparison for different solvents and their effects on the dispersion states.

The solvents reported for generating CNT dispersions are amides. N,N-dimethylformamide (DMF) and Nmethylpyrrolidone (NMP) have shown the most power for the dispersion of CNTs. These solvents have high values for β (electron pair donicity), negligible values for α (the hydrogen bond donation parameter of Taft and Kamlet), and high values for π (solvochromic parameter)[171]. The former solvent (NMP) was proved to be more powerful in the dispersion of MWNTs. However, its high boiling points (202°C) [172] is its disadvantage for solution mixing.
Table 1-5. Effect of various solvents with different values of Hansen parameters on the dispersion of nanotubes. Reprinted from [173]. Copyright © 2005 Elsevier Inc.

<table>
<thead>
<tr>
<th>Organic solvents</th>
<th>δd</th>
<th>δp</th>
<th>δh</th>
<th>δt</th>
<th>Molecular weight (g/mol)</th>
<th>Dispersion state</th>
</tr>
</thead>
<tbody>
<tr>
<td>N,N-Dimethylformamide</td>
<td>17.4</td>
<td>13.7</td>
<td>11.3</td>
<td>24.8</td>
<td>73.10</td>
<td>Dispersed</td>
</tr>
<tr>
<td>Chloroform</td>
<td>17.8</td>
<td>3.1</td>
<td>5.7</td>
<td>19.0</td>
<td>119.38</td>
<td>Dispersed</td>
</tr>
<tr>
<td>1-Methyl-2-pyrrolidone</td>
<td>18.0</td>
<td>12.3</td>
<td>7.2</td>
<td>22.9</td>
<td>99.13</td>
<td>Dispersed</td>
</tr>
<tr>
<td>2-Propyl alcohol</td>
<td>15.8</td>
<td>6.1</td>
<td>16.4</td>
<td>23.5</td>
<td>60.10</td>
<td>Swollen</td>
</tr>
<tr>
<td>1-Pentyl alcohol</td>
<td>16.0</td>
<td>4.5</td>
<td>13.9</td>
<td>21.7</td>
<td>88.15</td>
<td>Swollen</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>16.8</td>
<td>5.7</td>
<td>8.0</td>
<td>19.4</td>
<td>72.11</td>
<td>Swollen</td>
</tr>
<tr>
<td>Toluene</td>
<td>18.0</td>
<td>1.4</td>
<td>2.0</td>
<td>18.2</td>
<td>92.14</td>
<td>Swollen</td>
</tr>
<tr>
<td>o-Methoxyphenol</td>
<td>18.0</td>
<td>8.2</td>
<td>13.3</td>
<td>23.8</td>
<td>124.14</td>
<td>Swollen</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>18.2</td>
<td>6.3</td>
<td>6.1</td>
<td>20.3</td>
<td>84.93</td>
<td>Swollen</td>
</tr>
<tr>
<td>Benzene</td>
<td>18.4</td>
<td>0.0</td>
<td>2.0</td>
<td>18.6</td>
<td>78.11</td>
<td>Swollen</td>
</tr>
<tr>
<td>Dimethyl sulfoxide</td>
<td>18.4</td>
<td>16.4</td>
<td>10.2</td>
<td>26.7</td>
<td>78.13</td>
<td>Swollen</td>
</tr>
<tr>
<td>Styrene</td>
<td>18.6</td>
<td>1.0</td>
<td>4.1</td>
<td>19.0</td>
<td>104.15</td>
<td>Swollen</td>
</tr>
<tr>
<td>Methyl methacrylate</td>
<td>13.7</td>
<td>9.8</td>
<td>6.1</td>
<td>17.9</td>
<td>100.12</td>
<td>Sedimented</td>
</tr>
<tr>
<td>Methanol</td>
<td>15.1</td>
<td>12.3</td>
<td>22.3</td>
<td>29.6</td>
<td>32.04</td>
<td>Sedimented</td>
</tr>
<tr>
<td>Hexane</td>
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<td>0.0</td>
<td>0.0</td>
<td>15.3</td>
<td>86.18</td>
<td>Sedimented</td>
</tr>
<tr>
<td>Acetone</td>
<td>15.5</td>
<td>10.4</td>
<td>7.0</td>
<td>20.0</td>
<td>58.08</td>
<td>Sedimented</td>
</tr>
<tr>
<td>Water</td>
<td>15.6</td>
<td>16.0</td>
<td>42.3</td>
<td>47.8</td>
<td>18.02</td>
<td>Sedimented</td>
</tr>
<tr>
<td>Ethanol</td>
<td>15.8</td>
<td>8.8</td>
<td>19.4</td>
<td>26.5</td>
<td>46.07</td>
<td>Sedimented</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>16.4</td>
<td>17.4</td>
<td>6.8</td>
<td>24.8</td>
<td>53.06</td>
<td>Sedimented</td>
</tr>
</tbody>
</table>

1.6.2 Selection of a proper surfactant for zippering mechanism

Surfactants are extensively used for noncovalent functionalization and dispersion of CNTs in the polymers and nanocomposites. Surfactant by reducing the surface tension of the CNTs promote a stable dispersion in different media. The structure of a surfactant consists of two features; the hydrophilic region or the polar head group; and the hydrophobic region or the tail group that usually consists of one or few hydrocarbon chains. The hydrophobic end of a surfactant will attach to CNTs, while the hydrophilic end helps pull the CNTs into solvents such as water [170] or interact with the epoxy through hydrogen bonding (Figure 1-41). There are three classes of surfactants: anionic (negative
charge in water), cationic (positive charge in water), and nonionic (neutrally charged in water) [170].

Figure 1-41. Schematic of (a) single surfactant molecule (Triton X-100) with the hydrophilic region and hydrophobic region. (b) Attachment of the surfactant to the CNT through its hydrophobic end. Reprinted with permission from [174]. Copyright © 2008 Elsevier

1.6.2.1 Advantage of noncovalent functionalization

- Surfactants are adsorbed to the surface of CNTs through several mechanisms such as π-π stacking, Van der Waals interaction, or Physical interaction. As a result, in contrast to the covalent functionalization, they don't change the morphology of the CNTs, or hybridization from Sp2 to Sp3. thus, they non-covalently functionalize the CNTs [168,170,175].

- Surfactants attached to the surface of MWNTs increase the steric hindrance of CNTs and act as a chemical bridging agent of Coulomb interactions. The steric hindrance increases the distance between the CNTs and decreases the attractive force that made CNTs agglomerate (Figure 1-42) [175,176].
• The chemical bridging of the surfactant between the polymer matrix and CNTs through hydrogen bonding increases the compatibility of CNTs with the polymer matrix. They reduce the surface energy of CNTs and decrease the Van der Waals force between CNTs.

• They can help the dispersion through exert unzipping force to disperse CNT (Figure 1-40).

• Surfactants decrease the conductivity of CNT to CNT through covering the CNTs and blocking the electrons (Figure 1-43, Figure 1-44).
To date, a wide variety of surfactants have been investigated for the dispersion of CNTs, such as sodium dodecyl benzenesulfonate (SDBS)[177], dodecyltrimethylammonium bromide (DTAB) [178], hexadecyltrimethylammonium bromide (CTAB) [179], octyl phenol ethoxylate (Triton X-100) [159,175,176] and sodium
dodecyl sulfate (SDS)[180-182]. A comparative study of dispersion of MWNTs using different types of surfactants was reported in [175]. It was found that Triton X-100 is a powerful surfactant in the dispersion of MWNTs with the following order [175].

$$SDS < Tween\ 20 < Tween\ 80 < Triton\ X-100$$

Figure 1-45. SEM images of dispersed MWNTs into the Polypropylene. The MWNTs were functionalized using Triton X-100 in the presence of ethanol. (a) 1 wt% of functionalized CNT dispersed into the Polypropylene. (b) 5 wt% of functionalized CNT dispersed into the Polypropylene. (c) 1 wt% of non-treated CNT dispersed into the Polypropylene. (b) 5 wt% of non-treated CNT dispersed into the Polypropylene Printed with permission from [159]. Copyright © 2011, SAGE Publications.

The poor dispersion power of SDS might be as a result of its poor temperature stability [175]. No well-isolated MWNTs were observed in the solution using Tween 20, Triton X-100, and Tween 80. An optimized ratio surfactant to the CNTS was found to be
to be 1:466.66, 1:520, 1:400, and 1:350 for Tween 20, SDS, Tween 80, and Triton X-100, respectively [175].

In this thesis, through a solution mixing, a highly stretchable conductive CNT-based nanocomposite was developed. To functionalize the MWNT, DMF (powerful solvent) and Triton X-100, a powerful surfactant was used. A globally dispersion method was also utilized for a homogenous dispersion. Focusing on developing highly flexible conductive electrodes, 5 wt% of CNTs was dispersed to reach the maximum conductivity of nanocomposite.

1.7 Thesis organization

This thesis was organized to cover the fundamental knowledge of developing material and machine to fabricate flexible, stretchable tactile sensors. Chapter three presents a Direct-Print, Direct-Cure Photopolymerization process together with a comprehensive study of material characterization together with presenting several fabricated macro-micro structures with this method. In that chapter, we also present a conformal printing algorithm. In chapter four, the developing process for fabrication of conductive stretchable nanocomposite is presented. In chapter five several manufacturing methods were employed to build stretchable tactile sensors. In chapter six, the principle of an ionic liquid-based conductive polymer for the developing pressure sensitive polymers is presented. Finally, conclusions and recommendations are stated in Chapter six.
CHAPTER II

DIRECT PRINT PHOTOPOLYMERIZATION (DPP) PROCESS

2.1 Introduction

DPP technology is a maskless, non-lithographic process able to create complex 2D/3D structures [66]. Integration of micro-dispensing mechanisms with computer-controlled translation stages is a way to create non-planar objects in the field of microfabrication processes [28]. There are different types of dispensing mechanisms such as time-pressure mechanism [183], rotary screw mechanism [184], and positive-displacement mechanism [185]. However, the rotary screw type is known as one of the most suitable devices to dispense fluid materials with a wide range of viscosity [183]. It is believed that the shape, size, accuracy and consistency of a deposited pattern are affected by four groups of parameters: dispensing mechanism specification (screw geometry, tip geometry and size, etc.), fluid properties (Newtonian or non-Newtonian, viscosity, etc.), surface properties (surface tension, hydrophobic or hydrophilic, etc.), and working parameters (applied air pressure, translation speed of a stage, gap distance between a tip and substrate, dispensing speed (flow rate). However, there is a paucity of the literature to specify the effects of these parameters on the physical deposition features.
2.2 Direct Print Photopolymerization (DPC) machine

DPC process consists of micro extrusion of a structured and viscoelastic photopolymer combined with its photopolymerization right after leaving the micronozzle. In comparison to a fluid system, the flow property of the viscoelastic ink changes as it is subjected to a stress [37]. If the viscoelastic ink passes through the dispenser mechanism, enters to and exits from the micronozzle, it undergoes different stress states that change its flow behavior. The viscosity of viscoelastic ink decreases in the presence of the shear stresses that helps the flowability through the fine deposition nozzles [38,39]. However, upon exiting the nozzle, the ink relaxes and its viscosity increases. This particular property assists the shape retention of deposited filaments. Combining the viscoelastic property with the rapid solidification of the filaments through photopolymerization is the heart of DPP process. This integration potentially enables the creation of different multifunctional 3D structures with the wide range of mechanical, physical, and electrical property. Figure 2-1a shows the schematic of the DPC machine where the material is deposited using a micro dispenser and solidify in the presence of the UV light. We developed the DPP system by integration of a screw-driven micro-dispensing head (PCD3, GPD Global, Grand Junction, CO) installed on a high precision XYZ translation stage with a 500 nm resolution (Aerotech, Pittsburg, PA). As we mentioned earlier, the screw-driven dispensers are one of the most promising systems to control the filament deposition, and to achieve a high flow rate while dispensing a fluid with a wide range of viscosity. [24,184] To automate the system, an open source 3D printing software (SLIC3r) was used to generate the tool paths.
The Aerotech programming language was used to control the motion, the dispenser, and the lamp.

Figure 2-1. Schematic of the DPC process. (a) Schematic of a multi-dispenser DPP machine. (b) Light intensity profile of a beam light around the tip. (c) Light distribution around the nozzle.

A four-leg optical fiber connected to a high-power UV lamp (OmniCure S2000, Lumen Dynamics Group Inc., Ontario, Canada) was installed around the dispensing head in a position to have a minimum light intensity close to the nozzle. This prevents the curing the material inside the nozzle. Figure 2-1b shows the distribution of light near the nozzle. It was measured using a large-area beam profiler (BeamGage, Ophir Optronics Solutions Ltd., North Andover, MA, US). The maximum measured light intensity was 8 mW.
This light gradually increases to partially cure the material in the close vicinity of the nozzle. Then, the printed filaments are fully cured once they are fully subjected to the maximum light intensity. This gradient curing was achieved by knowing the numerical aperture of the light guide. According to the numerical aperture equation (NA = 0.37 for high power fiber light guide, OmniCure S2000, Lumen Dynamics Group Inc., Ontario, Canada), the divergence angle is calculated by following equation:

$$\theta_1 = \sin^{-1}(NA)$$  \hspace{1cm} (1)

Then, $\theta_2$ (the orientation of light guide) is calculated according to the design criteria (L1, L2), Nozzle diameter (D), and an experimental gap (t) to prevent nozzle clogging (Figure 2-2).

$$L_3 = L_2 - t - D/2$$  \hspace{1cm} (2)

100μm <D<500 μm → D=500 μm, t~100μm,

$$\theta_2 = \tan^{-1}\left(\frac{L_3}{L_1}\right) - \theta_1$$  \hspace{1cm} (3)
Figure 2-2. Placing the light guide near the nozzle to minimize the light intensity near the nozzle.

2.2.1 Adjusting the printing parameters in planner printing

The success of the DP process depends on controlling process parameters including the material flow rate, the translation speed, and the gap height. Variations in any of these parameters during the process significantly affect the geometry of printed filaments [16,24,184,186,187]. It is believed that the profile shape, accuracy and consistency of the deposited material are affected by several parameters.

The mentioned parameters should be tuned carefully to have a consistent geometry for the deposited filaments. As a rule of thumb, any filament deformation mainly caused by lagging or leading phenomena right after the deposited material should be minimized [187] (Figure 2-3).
Figure 2-3. Adjusting dispensing parameters in direct printing. (a) Leading in the deposited material. (b) Lagging in the deposited material

Due to the lack of literature about the relationship between the parameters and desired features of the dispensed material, experimental data was regarded as the best estimation to help choosing the above parameters. Table 2-1 shows the lists of experiments to test the effects of parameters above.

Table 2-1. Experiment parameters to develop and customize the direct write system. Several experiments were done to understand the effect of the fluid flow rate (Fluid flow rate $\propto$ Applied Voltage) and translation speed. (St: Translation speed, V: Applied volt, Gd: Gap distance, Td: Tip diameter)

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Fixed Parameters</th>
<th>Variable parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No. of Exp.</td>
<td>Td</td>
</tr>
<tr>
<td></td>
<td>(µm)</td>
<td>(µm)</td>
</tr>
<tr>
<td>1</td>
<td>4</td>
<td>437</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>437</td>
</tr>
</tbody>
</table>
To accomplish the suggested experiments, the developed DPC system was used to dispense the MWCNT/polymer composite over a polyurethane substrate. Figure 2-4 shows the rheological behavior of 4 wt% CNT dispersed into the photopolymer.

![Graph showing rheology of 4% CNT nanocomposite](image.png)

Figure 2-4, Rheology of 4% CNT nanocomposite. The viscosity of nanocomposite without any shear force is about $\sim 7 \times 10^6$ cps

Although this nanocomposite behaves as a viscoelastic fluid that will not spread after deposition while dispensing the material, the created wires were directly cured by UV light. Then, three widths in the same wire line were randomly selected and measured using an optical microscope (Stereo discovery V12, Carl Zeiss Micro Imaging, LLC, Thornwood, NY). Experiments were repeated 4 times for each parameter to get an average. Before each test, the distance between the dispensing tip and substrate was manually calibrated to maintain precisely the same gap distances in all experiments. The calibration was
performed using two different feeler gauges (300 µm and 350 µm) with the Go-No gauge manner.

2.2.2 Experimental Results: Manufacturing Parameters

As it was discussed before, the dispensing parameters directly affect the size and resolution of the dispensed material. There are several important parameter sets to maintain continuous and smooth flow of the material delivered from the dispensing tip to the substrate surface. Figure 2-5 (a) shows the effect of the fluid flow rate on the created patterns with a fixed translation speed. The line width decreases as the flow rate increases (high to low rate from left to right in the figure). Figure 2-5 (b) shows that the smaller flow rates could not create consistent and continuous line widths. Figure 2-6 and Figure 2-7 represent the results of the experiments described in Table 2-1. These results include the effects of translation speed and fluid flow rate with the other fixed parameters (see Table 2-1) on the line width of the dispensed material. In the first experiment, there is a power relationship between the fluid flow rate and the width of created wires (Figure 2-6). The second experiment result shows a logarithmic relationship between the translation speed and the line width (Figure 2-7). For both experiments, relatively larger line widths were produced compared to the tip diameter (437 µm). These data are important because they show that high flow rates and slow translation speeds result in inconsistent line widths of conductive elements.
Figure 2-5. Effects of dispensing parameters on the line widths. (a) line width variation according to the fluid flow rate, (b) inconsistent and non-continuous line widths due to the too low fluid flow rate.

Figure 2-6. Line width variation with respect to the fluid flow rates at fixed translation speed. (Tip diameter: 437µm; translation speed: 20 mm/s; gap height: 300–350 µm).
Figure 2-7. Line width variation with respect to the translation speed at a fixed fluid flow rate. (Tip diameter: 437µm; fluid flow rate: 1V; gap distance: 300~350 µm).

A smaller line width than the tip size was achieved by a higher translating speed or a lower the fluid flow rate. However, an excessively fast translation speed and slow fluid flow rate resulted in the discontinuous or inconsistent line widths as shown in Figure 2-5(b). We also investigated the use of smaller gap distances, but continuous dispensing was not possible since the material became clogged at the tip. In addition to the clogging, it was seen that the dispensed material was widely spread and then narrowed on the substrate due to the pressure rise and drop.

Due to the dependency of the deposition accuracy on the material and the machine parameters, line width variations were observed in Figure 2-6 and Figure 2-7, typically on the order of 0.3 mm. Several factors caused these line width inconsistencies. Variation of the gap distance caused inconsistent line widths. Since the polyurethane material used as the substrate is flexible with a relatively broad surface area (~10cm × 10cm), small variations in gap distance were unavoidable. It is expected that the use of a highly accurate
and uniform substrate, and also a real-time distance measurement device installed in the dispensing head would be a method to reduce this variation. Material agglomeration generated during the dispersion process is another source of line width variation. The agglomerated material sometimes partially occluded the tip and resulted in a pressure change in the tip. This pressure change caused inconsistent linewidths. The material agglomeration can be improved by using a better material dispersion process and chemicals such as surfactants and dispersants. Finally, vibrations during the manufacturing process could be a reason.

2.2.3 Conformal printing algorithm for adjusting gap height

In the general DPP process while printing patterns on a flat surface, the gap height is simply maintained along the vertical direction by setting a predetermined distance between the nozzle and the substrate or the surface of the last layer. This distance can be determined by dispensing experiments. Contrarily, maintaining a consistent gap distance for the conformal printing on a freeform surface or inclined flat surface is a challenge. In these situations, the angle between the local normal vector of the motion profile and the axis of the dispensing nozzle changes with locations.
Figure 2-8. Leading and lagging phenomena in the inclined printing. (a) leading in the downward printing, (b) lagging in the upward printing. The angle of the inclined surface is 35 degrees, printing speed is 10 mm/s, and nozzle has an outside diameter of 635 µm with an inside diameter of 535 µm.

Figure 2-8 shows an example of leading and lagging phenomena when a filament is formed on an inclined surface, where leading and lagging mean the position of the immediately dispensed material compared to the dispensing nozzle. In Figure 2-8a the immediately dispensed material is in front of the nozzle (leading), whereas in Figure 2-8b it is behind of the nozzle (lagging). These leading and lagging phenomena are the result of any change in the effective gap height, make changes in the width of printed filaments and subsequently affect the uniformity of printing.

Adjustment with a constant gap height along the vertical direction during the conformal (or inclined) DP process causes leading and lagging due to variations in the actual (effective) gap height (He) between the printing surface and the corner of the nozzle (first row in Figure 2-9). Where, the effective gap distances are dominated by the right corner of the nozzle and the material leaves lastly since the nozzle moves in the left
direction. Thus, to create a uniform effective gap height which must be the same as the desired gap height (Hd), the desired freeform profile must be traversed at each point with respect to the local normal vector of the surface profile (Figure 2-9 (second row)). However, since the effective gap height (He) is not equal to the predetermined (desired) gap height (Hd), there would be still leading due to conglomeration of the dispensed material at the nozzle during the downward motion or lagging due to the nozzle position during the upward motion as shown in Figure 2-9 (second row). To overcome this problem, the nozzle is translated again with the horizontal component of the motion. By applying these two vector translations, leading and lagging are significantly decreased due to the new location of the nozzle (Figure 2-9 (third row)).
Figure 2-9. Conformal printing algorithm - an optimized tool location to adjust the gap height in the downward printing (left column) and upload printing (right column) on the inclined surface. The Final gap heights (third row) were set by having the two translation vectors along the normal direction (second row) of the surface and the horizontal direction (third row).
The algorithm mentioned above has been qualitatively proved by printing patterns on inclined surfaces with the angle of 35 degrees (Figure 2-10). It is obvious that there is a significant improvement in the download printing whereas the difference is not apparently shown for the upload printing. There is less conglomeration of the dispensed material in front of the dispensing nozzles (Figure 2-10 (a)), while after applying the algorithm there is no more conglomeration of the dispensed material (Figure 2-10(c)). Consequently, it results in creating uniform patterns for both upward and downward printing (Figure 2-10 (f)).

Figure 2-10. Effect of applying conformal printing algorithm in creating a uniform gap height. (a) Downward, (b) upward, and (c) a 2D view of printing filaments before applying the conformal algorithm. (d) Downward, (e) upward, and (f) a 2D view of printing filaments after applying the conformal algorithm. (Nozzle outside diameter: 635 µm, inside diameter: 535 µm, gap height: 350 µm, and scale bar, if it has not been mentioned, is 500 µm).
To show the quantitative effectiveness of the proposed tool path generation, several experiments were designed. Each experiment set included the upward and downward printing on an inclined surface with different angles before and after applying the conformal printing algorithm. Table 2-2 shows the entire printing conditions.

After printing all the sets of experiments, the widths of printed filaments were measured at eight different locations with the 2 mm interval using an optical microscope (Stereo discovery V12, Carl Zeiss Micro Imaging, LLC, Thornwood, NY). The measured widths before and after applying the algorithm are shown in Figure 2-11. Before applying the algorithm, there is a pronounced difference between the upward and downward printing. This difference is even greater for the surfaces with the higher inclined angle (Figure 2-11 (a)), indicating there is a relationship between the inclined angle and the printing quality. However, after applying the proposed conformal algorithm, a uniform printing even on the surfaces with the higher inclined angle was achieved (Figure 2-11(b)).

Table 2-2. Inclined printing conditions.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Printing speed</td>
<td>10 mm/s</td>
</tr>
<tr>
<td>Nozzle inside diameter</td>
<td>535 µm</td>
</tr>
<tr>
<td>Nozzle outside diameter</td>
<td>636 µm</td>
</tr>
<tr>
<td>Desired gap height</td>
<td>350 µm</td>
</tr>
<tr>
<td>Angles of the surface</td>
<td>5° ~ 45° by 5° increment</td>
</tr>
</tbody>
</table>
2.2.3.1 The effect of conformal printing algorithm on the printing quality

The printing quality of the DP process on an inclined surface is shown in Figure 2-10. As shown in Figure 2-10a and Figure 2-10b due to variations in the effective gap height, once the gap is set based on the vertical translation with the desired distance between the nozzle and surface, there is a difference in the width of printed filaments in the upward and downward printing (Figure 2-10c). However, through applying the proposed conformal printing algorithm, the variation of the effective gap height was
minimized. Thus, a uniform printing on the inclined surfaces were achieved (Figure 2-10f). The effect of the inclined angle on the printing quality is also shown in Figure 2-11. Printing on the surfaces with a higher inclined angle, without applying the proposed conformal algorithm, resulted in a non-uniform pattern in width. As shown in Figure 2-11a, by increasing the inclined angle, the difference in widths between the upward and downward printing increased. However, by applying the conformal printing algorithm, this difference was minimized and resulted in a uniform printing regardless of inclined angles.

2.3 Viscoelastic photopolymers used in the DPC process

The success of DPP process relies on the proper selection of and tuning the ink rheology to ensure its flowability through the nozzle without clogging, while the extruded filament is stiff enough to retain its geometry with minimum deformation. Viscoelastic inks that exhibiting both elastic and viscous properties under an external pressure fulfill the requirements mentioned previously. These non-Newtonian liquids possess a shear thinning and/or thixotropic property under the presence of a strain. Where a strong shear thinning characteristic allows better flowability under the existence of shear stresses inside the nozzle. Based on the nozzle geometry, deposition speed, and ink property, the ink experiences shear rates up to 400 s\(^{-1}\) during the deposition process. [32,33] Thus, the viscoelastic property of the ink needs to be tailored to have sufficient elasticity to support the shape retention until the fabricated structure becomes strong enough by continuous photopolymerization.
2.3.1 Introducing viscoelastic property using Fumed Silica (Sio2)

A viscoelastic (or thixotropic) property can be introduced into a liquid by the dispersion of fumed silica particles. Upon uniform dispersion, Hydrogen bonds between the surface hydroxyl groups that link these aggregates together. Thus, a three-dimensional network of silica is formed, and the liquid becomes trapped in the resulting network (Figure 2-12). These hydrogen bonds are weak and thus can easily be broken in the presence of shear forces. Nevertheless, the 3D network of the material is rapidly rebuilt once the shear force is removed. Fumed silica provides this characteristic to a liquid materials system [31].

Figure 2-13 shows the experimental results of the rheological property of the test sample (TS0) (SR 150, Sartomer, USA, LLC, Exton, PA) which exhibits a Newtonian behavior with 700 cps viscosity at 25 °C. The storage modulus (G’) of this monomer is much lower than the loss modulus (G’’) in all possible shear stress ranges, meaning that it is a liquid.

Figure 2-12. Schematic representation of the formation of hydrogen bonding between the surface hydroxyl groups to form a gel [34].
Thus, upon extrusion from the nozzle, the filament shape cannot be retained. Subsequently, a 3D structure cannot be printed with this material due to high flowability.

![Image](image.png)

**Figure 2-13.** Rheological behavior of the test sample (TS0) as received with a loss modulus ($G''$) higher than its storage modulus ($G'$).

### 2.3.1.1 Material development

Several commercially available Newtonian photocurable resins were selected to be used in the DPP process. Table 2-3 shows a list of resins that were used in this experiment.

<table>
<thead>
<tr>
<th>Resin</th>
<th>Company</th>
<th>Viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>FullCure® 930 TangoPlus</td>
<td>Objet Geometries, MA., USA</td>
<td>NA</td>
</tr>
<tr>
<td>Ethoxylated Bisphenol a Dimethacrylate (SR 150)</td>
<td>Sartomer, USA, LLC, Exton, PA</td>
<td></td>
</tr>
<tr>
<td>1,6-Hexanediol Diacrylate (HDDA)</td>
<td>Sigma-Aldrich, Milwaukee, WI</td>
<td>9 cps @25 °C</td>
</tr>
</tbody>
</table>
To study the effect of fumed silica and its concentration, commercially available fumed silica powder (Cabot Corporation, Billerica, MA) with different concentration was added to the resins. To improve the thixotropic property BYK E-411 (BYK Additive Inc, Louisville, KY), as a spacer and stabilizer, was also added to the resin. 2,2-Dimethoxy-2-phenylacetophenone (DMPA) (Sigma-Aldrich, Milwaukee, WI) was used as a photoinitiator.

2.3.1.2 Material preparation and characterization

The photocurable resin used for characterization was prepared by dissolving 2 wt% of DMPA in the SR150 using a magnetic stirrer for 30 min. Then, two separate batch of samples with 5 and 10 wt% of the fumed silica were prepared by adding the fumed silica to the photopolymers. They were mixed using a high-speed mixer (DAC 150.1 FVZ-K, FlackTek Inc. Landrum, SC) for 30 min. After preparation of each batch, 0.5 and 1 wt% of BYK e-411 were added to each batch separately and mixed using the high-speed mixer for 30 min. A reference sample was also prepared without adding the fumed silica or stabilizer. The viscoelastic property of the prepared photopolymers was measured using a cone/plate Rheometer (AR-G2, TA Instruments) with a 2° cone at 25°C.
Table 2-4. The composition of inks used to fabricate the objects shown in Figure 2-18 together with the printing parameters.

<table>
<thead>
<tr>
<th>Ink composition</th>
<th>Printing Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ink 1</td>
<td></td>
</tr>
<tr>
<td>Resin 1</td>
<td>HDDA</td>
</tr>
<tr>
<td>Resin 2</td>
<td>Tango</td>
</tr>
<tr>
<td>Resin 3</td>
<td>SR 150</td>
</tr>
<tr>
<td>Fumed Silica</td>
<td>100%</td>
</tr>
<tr>
<td>Stabilizer</td>
<td>10 wt%</td>
</tr>
<tr>
<td>Printing Speed</td>
<td>13.5 mm/s</td>
</tr>
<tr>
<td>Applied Voltage</td>
<td>150 mV</td>
</tr>
<tr>
<td>Applied Pressure</td>
<td>40 Psi</td>
</tr>
<tr>
<td>Nozzle size</td>
<td>152 µm</td>
</tr>
<tr>
<td>Layer thickness</td>
<td>80 µm</td>
</tr>
<tr>
<td>Ink 2</td>
<td></td>
</tr>
<tr>
<td>Resin 1</td>
<td>-</td>
</tr>
<tr>
<td>Resin 2</td>
<td>-</td>
</tr>
<tr>
<td>Resin 3</td>
<td>100%</td>
</tr>
<tr>
<td>Fumed Silica</td>
<td>16 wt%</td>
</tr>
<tr>
<td>Stabilizer</td>
<td>0.5 wt%</td>
</tr>
<tr>
<td>Printing Speed</td>
<td>13.5 mm/s</td>
</tr>
<tr>
<td>Applied Voltage</td>
<td>200 mV</td>
</tr>
<tr>
<td>Applied Pressure</td>
<td>40 Psi</td>
</tr>
<tr>
<td>Nozzle size</td>
<td>233 µm</td>
</tr>
<tr>
<td>Layer thickness</td>
<td>150 µm</td>
</tr>
<tr>
<td>Ink 3</td>
<td></td>
</tr>
<tr>
<td>Resin 1</td>
<td>50%</td>
</tr>
<tr>
<td>Resin 2</td>
<td>50%</td>
</tr>
<tr>
<td>Resin 3</td>
<td>-</td>
</tr>
<tr>
<td>Fumed Silica</td>
<td>10 wt%</td>
</tr>
<tr>
<td>Stabilizer</td>
<td>1 wt%</td>
</tr>
<tr>
<td>Printing Speed</td>
<td>5 mm/s</td>
</tr>
<tr>
<td>Applied Voltage</td>
<td>300 mV</td>
</tr>
<tr>
<td>Applied Pressure</td>
<td>25 µm</td>
</tr>
<tr>
<td>Nozzle size</td>
<td>233 µm</td>
</tr>
<tr>
<td>Layer thickness</td>
<td>190 µm</td>
</tr>
</tbody>
</table>

Figure 2-15 shows and compares the effect of adding 5 wt% (TS1) and 10 wt% (TS2) of fumed silica into the TS0. Dispersion of fumed silica into the monomer introduces a 3D dimensional network that alters the rheological behavior of its host liquid. After the dispersion of fumed silica into the monomer, it showed a viscoelastic behavior with a higher storage modulus ($G'$) than its loss modulus ($G''$). Adding more fumed silica particles introduces more networks and subsequently, the final ink exhibits more solid behavior that can withstand higher shear stresses until those networks break and liquid flows. In the solution with 5 wt% fumed silica, for the shear stresses greater than 10 Pa, $G''$ becomes greater than $G'$ in which ink flows easily. This behavior is needed to allow the ink to be extruded through the nozzle where a shear force is applied to the ink. Since the stress applied to the fluid while flowing through the nozzle is much higher than this value, the ink should be strong enough to be able to retain its geometry after deposition (Figure 2-14).
Figure 2-14. An example of a viscoelastic ink. (SR150 with 10 wt% fumed silica)

Figure 2-16 shows the effect of adding 1 wt% of stabilizer (BYK E-411) in altering the viscoelastic property of solutions with of 5wt% (TS3) and 10 wt% (TS4) of fumed silica. The stabilizer results in the formation of a very strong structure where it can withstand the larger shear forces. As it is shown in Figure 2-16 for the shear strains less than 500 Pa, the G’ is much higher than the G”, which results in a high elastic behavior. The stabilizer helps create a stronger 3D dimensional network. It also helps reach a specific level of the rheological property with a less amount of dispersed fumed silica particles. Figure 2-17 compares the effect of the stabilizer on the viscosity behavior of the ink with 10 wt% of fumed silica under both applying and removing the shear strain. The stabilizer helps not only create a stronger network but enable fast reconstruction of broken networks.
Figure 2-15. The effect of fumed silica on the rheological behavior of the photocurable resin.

Figure 2-16. The effect of stabilizer on the rheological behavior of the photocurable resin.
As shown in Figure 2-17, the viscosity of the ink with 1wt% stabilizers reaches its original value after removing the applied shear with negligible time delay. The fast recovery helps the retention of the filament geometry right after deposition until it solidifies. This also increases the stability of the filaments and reduces their flow over lower printed layer. These properties lead to print a true 3D structure from a liquid ink with high resolution.

Figure 2-17. The effect of stabilizer on viscosity behavior of a viscoelastic photocurable resin.

Several 3D structures were fabricated by the DPP process to show its capability in printing true high-resolution 3D structures (Figure 2-18a-f). This flexible and scalable method is a unique technique that can fabricate macro/microstructures using polymers and their nanocomposite. Figure 2-18a shows a thin-wall micro blade fabricated using this process with ink1 (Table 2-4). This 4 mm height thin-wall microstructure was fabricated by
stacking only one path of filaments in each layer using a 150 µm nozzle and 80 µm layer thickness (Figure 2-18b). As it is shown in Figure 2-18b the layers and filaments are not clear that indicates the used ink was not strong enough to hold the filament geometry. Thus, a stronger ink was developed to fabricate object shown in Figure 2-18c, d. Figure 2-18c shows a 20-layer object fabricated using a nozzle with an inner diameter of 233 µm and a layer thickness of 150 µm. The layers are distinguishable and have 150 ±15 µm height. After optimizing the required ink properties, several other objects including a tiny hand (Figure 2-18e) and a 3D structure that several connectors were needed to be inserted into it, were fabricated (Figure 2-18f). In addition to the ink rheology, the dimensional accuracy of DPP process also depends on printing parameters including layer thickness, translation speed, and flow rate. These parameters should adjusted carefully to reach a desired resolution.[4]

Figure 2-18. 3D printed structures using the DPC process. (a,b) a thin-wall micro blade fabricated with ink1 (Table 2-4). (c,d) an object fabricated with the ink2 (Table 2-4). (e) a 3D printed hand with ink3 (Table 2-4). (f) a 3D printed part with embedded connectors fabricated with ink2 (Table 2-4). The scale bars in (c,d) are 500 µm.
2.4 Conclusion

In summary, a DPC technique including material and controlling algorithm was developed which offers a highly flexible and powerful route for 3D printing of functional polymeric 3D structures. This process is a solvent free process to print high-resolution functional 3D structures at room temperature in a layer by layer or free form fashion with viscoelastic photopolymers and their nanocomposites. The use of polymers and ultimately their nanocomposites fortify this process to fabricate 3D structures featuring mechanical, physical and electrical functionalities. The capability of this process and the presented characterization can be extended through the use of other functional inks (e.g. electrical conductive piezoresistive inks [15,24], recycle particle-based inks and bio-based inks). Due to the potential of this process in fabrication of 3D structures on pre-fabricated freeform surfaces [33], together with continues progress in ink development, it is envisioned that the process can be successfully used in fabrication of freeform and conformal electronic components.
CHAPTER III

STRETCHABLE ELECTRODES AND SENSORS USING CARBON NANOTUBES-POLYMER MATRIX

3.1 Introduction

This chapter presents a method to develop a highly stretchable conductive nanocomposite using Single-Walled Carbon Nanotubes (SWCNTs) and monofunctional acrylate monomers (cyclic trimethylolpropane formal acrylate and acrylate ester). This nanocomposite can be either used for detecting large strain, 3D deformation, and a free-form shape or used as stretchable electrodes in the stretchable electronics. The suggested sensors have been fabricated using DPP process. The result of stretchability test and impedance experiments showed that the sensor had a large strain range up to 90% with a linear resistance change and gauge factor ~2.7. Based on the results, it is expected that the application area for the suggested nanocomposite can be extended to the wearable electronics, tactile sensors, 3D structural electronics, etc.

Significant advancements in the use of CNTs in structural and functional nanocomposite have been achieved [92]. These particles have unique physical and mechanical properties. They have exceptionally high aspect ratio (~500 to 1000), high Young’s modulus (~0.64 TPa), high stiffness (above 1,000 GPa), high tensile strength
(~100 GPa), very low density and the ability to withstand large strain rates (up to 6-10%) [92,190]. In addition to their outstanding physical and mechanical properties, they show exceptional electrical properties. Depending on their radius or chirality, CNTs can be metallic or semiconducting. Metallic CNTs have exceptionally low electrical impedance (~0.5 µΩ), and piezoresistivity (gauge factor ~600 to 1000 on a small scale) [191]. Due to these extraordinary properties (physical, mechanical and electrical), CNTs are one of the ideal candidate materials to develop a flexible conductive polymer nanocomposite. Reinforcement of polymers through dispersion of CNTs in a polymer matrix is one potential way to ameliorate the mechanical properties [192], and also to embed a highly conductive electrical element within the polymers [192-194]. CNTs-polymer composite strain sensors showed a high strain sensitivity (~3.5 times of that of traditional strain sensors) and also showed the capability to withstand high strain rates (~20%) [64]. They exhibit a linear symmetric strain response [65]. These notable properties of conductive nanocomposites make them suitable for a tactile sensor material where the flexibility and compliance play an important role. Due to their exceptional structure, CNTs are also considered as the acceptor material [83,195]. Thus, they can participate in the electron donation process.

This chapter presents the fabrication and characterization of a highly stretchable nanocomposite embedded into a compliant structure. The following sections will discuss materials, fabrication process, measurements, and results in more detail.
3.2 Preparation of a SWCNT/Prepolymer solution

To prepare a stretchable prepolymer matrix, two photocrosslinkable monomers were blended using a magnetic stirrer (VWR, Radnor, PA, USA) for 5 min at room temperature: cyclic trimethylolpropane formal acrylate as a highly stretchable and tough monomer with 15 cps viscosity and acrylate ester as a diluent with 5 cps viscosity. Both monomers were provided from Sartomer LLC (Exton, PA, USA). 2 wt% of 2,2-dimethoxy-2-phenylacetophenone (DMPA) as a photoinitiator from Sigma-Aldrich (Milwaukee, WI, USA) was dissolved in the monomer solution using the magnetic stirrer for 30 min. To introduce conductivity, commercial SWCNTs from NanoLab (Waltham, MA, USA) with the concentration of 1 wt% were dispersed into the prepared prepolymer solution, where they have the purity of more than 95%, average diameter of 1.5 nm, and average length of 1-5 µm. Uniform dispersion of SWCNTs in a solution plays an important role in creating continuous and consistent wire patterns during the DPP process. The solution was blended using a sonicator (Q700, Qsonica, Newtown, CT, USA) with a power of 700 W, frequency of 20 kHz, and amplitude of 50% for 5 min in pulse mode (1 min on, 10s off). Ultrasonication needs to be monitored carefully since it could cause defects to the CNTs and subsequently deteriorate physical and electrical properties of nanocomposites [154,155,196]. During the sonication, ultrasound propagation in the solution results in the growth of cavities. The implosion of these cavities leads to violent and localized release of energy that can separate and disperse individual CNTs from bundles and agglomerates, where cavitation and wave propagation are directly related to the viscosity of the liquid. Non-uniform energy release distribution during sonication leads to weak and non-
homogeneous dispersion especially in medium to high viscosity liquid. To overcome this problem and to prevent the localization of the high-energy ultrasound field around the tip of the sonicator, a combination of sonicator and magnetic stirrer was used to globally disperse the CNTs in the polymer matrix as shown in Figure 1-39. Subsequently, the prepared material was degassed under the vacuum for 5 hours. The mechanically compliant part of the sensor was fabricated using polyurethane casting rubber material (Poly PT Flex 50, Polytek, Easton, PA) as a substrate (bottom), and cover (top). A polyurethane rubber material (SkinFlex III, BJB Enterprises, Tustin, CA, USA) with 930% elongation was molded to provide a substrate and cover.

3.3 Fabrication and characterization of the flexible conductive wires

To build a stretchable sensor, the prepared SWCNT/prepolymer solution was dispensed on the polyurethane rubber substrate using the developed DW system. Working parameters were selected for the sensor fabrication such as 437 µm for the nozzle size, 1 Volt for the dispensing motor speed and 10 mm/s for the speed of the XYZ stage. All created lines were post-cured by UV light (OmniCure S2000, Lumen Dynamics Group Inc., Ontario, Canada). Once the conductive wires were fully cured, they were covered by the polyurethane rubber, which was the same material for the substrate. Figure 3-1 shows the entire processes to build the stretchable sensor. Finally, the resistance of the fabricated wire in the sensor was continuously measured using a multimeter tester (MM1000, KLEIN tools, Lincolnshire, IL, USA) while stretching it until the wire was broken. Due to the variation of resistance, each measurement was conducted in 10 minutes once the sensor was elongated with a specified distance. Figure 3-2 shows the schematic of the setup for
the resistance measurement, where a stage was used to elongate the sensor. Both ends of
the sensor were secured with a clamp, and one end secured on the stage was pulled with
the speed of 0.5 mm/s. The initial resistance and distance were recorded, and resistance
was measured at each 10% elongation.

Figure 3-1 Schematic of the entire process to fabricate the stretchable sensors.
Figure 3-2 Schematic of the resistance measurement.

3.4 Results and discussion

Figure 3-3a and Figure 3-3b show the fabricated SWCNT/polymer wires on the rubber substrate and folded sensor. The folded sensor indicates that the wire inside the polyurethane material is highly flexible and robust without breakage. Although the suggested system and material were successfully used to create stretchable sensors, there should be further considerations on a higher resolution and better accuracy in the line width. Higher resolution can be accomplished by the better dispersion of SWCNTs, which affects continuous and consistent dispensing of a material. The agglomerated SWCNTs in the prepolymer solution create a non-continuous and locally larger or smaller wire pattern. Another consideration would be the gap distance between the tip and substrate, which may vary along the surface due to the imperfection of flatness of the working table.
3.4.1 Resistance measurement

Incorporation of SWCNTs into a stretchable polymer matrix with a polyurethane substrate offers an opportunity to achieve highly stretchable conductive wires. Figure 3-4 shows the resistance test while stretching the sensor. The measured initial resistance (R0) was 1.19MΩ, and the distance (L0) between two wire interconnections in the wire was 34 mm. The measured resistance change is relatively proportional to the applied strain as shown in Figure 3-5. The fabricated wire and rubber material as well were not broken up to 90% elongation, as shown in Fig. 6. After 90% elongation, the wire started to be broken. Moreover, after 140% elongation, the wire was fully broken, and there was no resistance to be detected. The experimental result shows a wide range of the linear relationship between the resistance change and strain. The sensitivity of this material upon strain can be calculated by the following Equation.
Where, $\Delta R$ is the resistance change, $R_0$ is the initial resistance, $S$ is the gauge factor and $\varepsilon$ is the strain. The fabricated sensor has the sensitivity of $\sim 2.7$, which is comparable with that of metals. For example, the gauge factor of the commercial metallic strain gauges is about 2-6. Due to the entanglement of SWCNTs in the polymer matrix, a highly stretchable conductive material was achieved. Experimental results showed that the dispersion of SWCNTs in the photocurable monomers offers not only electrical conductivity but the remarkable elongation rate. The combination of DPP technology and conductive materials is a potential means to create complex 3D electronic objects. It is expected that the suggested materials and DW technology will provide many application areas requiring significant deformation.
Figure 3-4, Photos of the specimen for the resistance measurement while tensioning.

Figure 3-5 Resistance changes according to the applied strain.
3.5 Conclusion

A stretchable sensor can be used for many application areas such as a robotic tactile sensor, pressure mapping sensor, and automotive car seat. In this work, a fabrication method and material were introduced to develop a stretchable sensor. A highly stretchable conductive nanocomposite was developed through dispersion of SWCNTs in tough and flexible photocurable monomers. Wire patterns were printed on a polyurethane rubber substrate using the DPP process and nanocomposite. Then, the printed wire patterns were embedded by covering the top using the same polyurethane rubber material. The successfully fabricated sensor was elongated for stretchability and resistance tests. The results showed the ability of the fabricated wires to sustain strain as large as 90% with the sensitivity ~2.7. Finally, it is concluded that the developed system and material are promising to build stretchable sensors, and many applications are expected.
CHAPTER IV

A MULTI-LAYER COMPLIANT TACTILE SENSOR FOR DETECTION OF THE POSITION, DIRECTION, AND SPEED OF SLIDING CONTACT

4.1 Introduction

In this chapter, a multi-layer resistance based compliant tactile sensor was fabricated using direct-print (DP) and soft molding processes. The sensor consists of two layers of embedded stretchable sensing nanocomposite sandwiched by three layers of a polyurethane rubber material. The sensing elements were created by the DP process using a photopolymer filled with multi-wall carbon nanotubes (MWNTs), which exhibit the property of piezoresistivity. The printed sensing elements were fully cured using ultraviolet (UV) light. The sensing elements within each layer of the sensor structure change in electrical resistance when external forces are applied. The fabricated sensor was able to detect the position of contact forces with a 3 mm spatial resolution, as well as their two-dimensional translation directions and speeds. Based on the results, it is concluded that the fabricated sensors are promising for the robotic applications. The developed process and material can be a reliable and robust way to build highly stretchable tactile sensors.
4.2 Tactile sensors

Along with the development of dexterous artificial robotic hands [49,51,197], the success of precise object grasping can be improved through tactile feedback during manipulation [48]. Tactile sensors mimicking the function of mechanoreceptors in human skin that provide appropriate tactile feedback play a critical role in improving the control of robotic manipulators [16,198]. Of particular relevance to this work, human fingertips contain Meissner’s corpuscles for motion detection and Pacinian corpuscles for detection of temporal changes in skin deformation. These rapidly adapting mechanoreceptors are highly sensitive to dynamic skin deformation and provide tactile feedback to facilitate grip control and grasp stability. They are known to be responsible for both detection and discrimination of low-frequency vibrations and slip between the skin and an object held in the hand [199-201]. Providing necessary tactile feedback improves precise control of robotic manipulators, especially in dexterous artificial hands and prosthetic hands [48-51].

There have been notable advances in the design and development of flexible, integrated, conformal and large-area tactile sensors [16,45,46,53,202,203]. Although these sensors have shown great potential in providing precise and repeatable information, there remain many limitations for their usage in general-purpose applications. These drawbacks include complexity, flexibility, conformability, cost, wiring, signal processing, packaging, and assembly [53,54,203]. Recent reports have shown the possibility to overcome these challenges. For example, the hybrid printing process with stretchable, piezoresistive polymer/nanocomposites was utilized to produce a low-cost, conformal, stretchable tactile sensor [15,16,24].
4.3 Sensor design and its mechanism

In the present design, both sensor body and sensing elements have been fabricated using an elastomer not only to improve the flexibility and conformability but also to enhance the mechanical durability and compliance of the sensor. The elastic behavior of the sensing elements and sensor body is also required to avoid permanent deformation and preserve the natural mechanics when the sensor is deformed and released [204]. As shown in Figure 4-1, the dispersion of nanotubes in a polymer matrix forms conductive networks inside the polymeric matrix. The mechanism of electron conductance within these networks is known as a combination of: (1) intrinsic conductance of the nanotubes; (2) direct contact conductance; and (3) electron tunneling between the conducting nanotubes that are in close proximity to one another [114]. Based on this mechanism, any deformation of the conductive matrix changes the number of nanotubes in contact or changes the tunneling distance, which results in a change in the resistivity of the conductive network.
Figure 4-1. Electron conductance mechanism in the elastomeric piezoresistive nanocomposite [114]: (a) Carbon nanotubes inside the polymer matrix form conductive networks. (b) When deformed by an object, the polymer matrix projects the deformation to the conductive networks. (c) The resistivity of these networks can be modeled by the intrinsic conductance of nanotubes (RCNTs), direct contact conductance of nanotubes (RContact) and electron tunneling conductance between the conducting nanotubes in close proximity (RTunneling).

4.3.1 Sensor structure

The proposed compliant tactile sensor is a multi-layer resistance based structure consisting of $8 \times 8$ straight strips of sensing elements arranged in an orthogonal configuration embedded into a polyurethane structure (Figure 4-2). The number of sensing elements can be increased or decreased based on design criteria. The proposed arrangement reduces the complexity of wiring topology and signal processing since only 16 sensing elements ($8$ strips in each layer) are used to create 64 taxels. Any of these taxels can be used to detect a two-dimensional location of a force applied to the surface of the sensor.
Extrapolating from this, the motion and speed of forces can be detected as they move along the surface of the sensor.

Figure 4-2. Multi-layer compliant tactile sensor structure. Two layers of orthogonal sensing elements are separately embedded into an elastomeric body in the two orthogonal directions. The juxtaposition of sensing elements in I and J directions forms taxels that can be used to detect the two-dimensional location of a force applied to the surface of the sensor.

4.4 Materials and fabrication

A commercially available photocurable rubber-like resin (FullCure® 930 TangoPlus, Objet Geometries Inc, MA., USA) was used as the composite matrix. Commercially available industrial grade multi-wall carbon nanotubes (MWNTs) with purity greater than 85%, diameter of 10 to 30 nm, and length of 5 to 20 μm (NanoLab, Waltham, MA, USA) were dispersed into the matrix to introduce piezoresistivity to the sensing elements. The compliant sensor body was fabricated using a highly stretchable
(930% elongation) polyurethane casting rubber (SkinFlex III, BJB Enterprises, Tustin, CA, USA).

4.4.1 Preparation of a piezoresistive nanocomposite

The piezoresistive nanocomposite is a solution of 0.5 wt% of noncovalent functionalized MWNTs dispersed into the FullCure® 930 TangoPlus. To prepare a uniform, well dispersed and stable solution, the weighted amount of MWNTs were noncovalently functionalized through their dispersion into a solution of 0.1 mM of zinc protoporphyrin IX (ZnPP, Sigma-Aldrich, Milwaukee, WI, USA) [23] in dimethylformamide (DMF, Sigma-Aldrich, Milwaukee, WI, USA). DMF is a well-known, powerful solvent for processing CNT-based nanocomposites [24-25]. The solution was blended using a sonicator (Q700, Qsonica, Newtown, CT, USA) with a power of 700 W, frequency of 20 kHz, and amplitude of 50% for 5 min in pulse mode (1 min on, 10s off). Ultrasonication needs to be monitored carefully since it could cause defects to the CNTs and subsequently deteriorate physical and electrical properties of nanocomposites [26-28]. Limiting the amplitude to 50% decreases the chance of the cavitation phenomenon [29] while using the pulse mode in the presence of an external magnetic stirrer according to the method described in the authors’ previous work [6] prevents the localization of ultrasound energy around the tip of the sonicator due to viscosity increment. This method results in creating well distributed CNTs with minimal defects during the dispersion process.

After the functionalization process, the prepared solution of DMF/MWNTs was blended with TangoPlus resin using the same process for five more minutes. Then, the prepared MWNT/prepolymer was placed on a hot plate magnetic stirrer (VWR 10 × 10
ALU Hotplate 120V, VWR, IL) at 100 °C for 48h to evaporate the solvent completely. After the dispersion and evaporation, the solution was filtered using a 150 μm filter (Sterlitech Kent, WA, USA) and degassed for 24h under a vacuum pump (ME 4 NT, Vacuubrand, Germany) to remove any trapped gas bubbles.

4.4.2 Fabrication of multi-layer compliant tactile sensors

A hybrid manufacturing process comprised of the DP (Figure 4-4) and soft molding processes was used to fabricate the sensor. Since the proposed sensor consists of two layers of sensing elements embedded into the sensor structure (Figure 4-3), a layer by layer fabrication process was employed.

Figure 4-3. Schematic of the developed sensor. The sensor was built layer by layer to embed the sensing patterns into the elastomeric structure. The sensing patterns are printed using a DP process on the soft-molded compliant layer.
As shown in Figure 4-5a, after building the bottom (first) insulating skin layer using the polyurethane rubber material through the soft molding process, the sensing material is printed on it using the developed DP system (Figure 4-5b). Once all the sensing elements are created; UV light is illuminated to cure them (Figure 4-5c). Then, the cured elements are covered again with the polyurethane rubber so that the sensing elements are sandwiched between two layers of the rubber material (Figure 4-5d). The upper layer at this point serves as the intermediate insulating layer upon which the next bank of orthogonally oriented sensing elements is printed. The printing process (Figure 4-5e), curing process (Figure 4-5f) and covering process (Figure 4-5g) are repeated for the next layer of sensing elements to fabricate the entire sensor (Figure 4-5h). These entire processes can be repeated to have more sensing layers depending on the sensor design.
Figure 4-5. Hybrid manufacturing process to build multi-layer compliant tactile sensor. Manufacturing process follows the steps (a) to (h). Steps (a), (d), and (g) are used to build the base (bottom), intermediate, cover (top) insulating layers, respectively. In step (b), the first layer of the sensing patterns is printed onto the base molded layer. In step (e) the orthogonal sensor pattern is printed onto the layer that has been built in step (d). First and second layers of sensing material are cured in steps (c) and (f) with UV light before being covered, respectively. After all steps (a) to (g), the final sensor (h) is ready.

The generated sensor includes eight straight sensing elements in the two layers which have a common end on one side as shown in the Figure 4-3 and Figure 4-5. The line width and spacing of these strips were experimentally chosen to be 1 mm and 3 mm, respectively [16]. Building parameters including the translation speed, gap distance, and dispensing feed rate were also chosen based on the work presented in [16]. These parameters were set to be 15 mm/s, 300 µm, and 1 V, respectively. Briefly, these factors can significantly change the geometry of the deposited lines and subsequently influence the performance of the sensor. These parameters are coupled together and are related to the properties of the deposited material and substrate. Increasing the dispensing feed rate
increases the line width and increasing the translation speed, or gap distance eventually creates inconsistent line width features. Figure 4-6 shows the fabricated compliant tactile sensor, which is comparably flexible in the sensing elements, as well as the bottom, intermediate, and top insulating layers.

![Fabricated compliant multi-layer tactile sensor](image)

**Figure 4-6.** Fabricated compliant multi-layer tactile sensor. The sensor is comparably stretchable in both body structure and sensing elements. There are two orthogonal layers of 16 sensing elements that make a 64-taxel tactile sensor.

4.5 Evaluation of compliant tactile sensor

The goal of this paper is to fabricate the multi-layer compliant tactile sensor and detect the position and motion of any applied force over the surface of the sensor. As shown in Figure 4-1 and based on the conductance mechanism [194], any external force applied to the sensor deforms and changes the length of the CNT conductive network. When deformed by an object, the sensor body conforms to its surface, maintains the same local contour, and thus projects the deformation to the sensing elements. Subsequently, surface deformation changes the impedance of each conductive sensor strip. In order to detect the changes in sensor impedance that are indicative of applied forces, resistors of comparable
impedance were placed in series with each sensing strip in a half Wheatstone bridge formation (Figure 4-7). In total, 16 half bridges were built for the 16 sensing elements within the sensor although a multiplexer is envisioned to simplify signal processing. The impedance of each conductive strip in the sensor is on the order of 1MΩ. The voltage from each half-bridge was measured with a DAQ card (PCI-6229, National Instrument Co., Austin, TX) interfaced with MATLAB/Simulink (The MathWorks, Natick, MA, USA) with the real-time Windows target kernel. The sample rate was 1 kHz.

Figure 4-7 Wiring diagram: (a) all the sensing elements are wired in a half Wheatstone bridge circuit supplied with a DC voltage. (b) Schematic of a single sensing element in a half Wheatstone bridge measures the change in electrical impedance resistivity as a result of an external force.
4.5.1 Sensor calibration

Prior to using the sensor, it was necessary to calibrate all the output signals with respect to a reference force applied to each taxel. This process was done using a developed motorized force stand with an XYZ stage and a digital force gauge with 0.1 N resolution (GTX plus 250, Dillon, Fairmont, Minnesota, USA) interfaced with LabView (National Instrument Co, Austin, TX, USA). The test stand was equipped with a cylindrical probe with a 2 mm diameter. The test stand was programmed to move vertically over each taxel to apply repetitive and consistent forces. The average of every signal from each sensing element was used to normalize the data of the motion detection experiments.

4.5.2 Signal processing

This chapter focused on two different sensory goals: first, detect the 2D location of a force applied to the sensor surface; second, detect the direction and translation speed of a moving force in contact with the sensor. To that end, all the signals in both the I direction (SI1, SI2,…, SIm) and J direction (SJ1, SJ2,…, SJK) were first low pass filtered and differentiated. The low-pass filter is used to attenuate high-frequency noise while the derivative makes the resulting signals quickly responsive and impervious to drift [44]. According to the algorithm shown in Figure 4-8, after acquiring the derivatives of the signals they are again filtered to reduce noise that could be amplified by the derivative. A threshold classifier was used to detect the location of applied forces on the surface of the sensor. However, to improve the classification success rates, the signal outputs from each low pass filter were raised to a power of P to accentuate voltage spikes from applied forces and also to decrease the likelihood of mechanical cross talk between adjacent sensor strips.
Each signal was then passed through a relay. When the input to each specific sensing element’s relay (FIm or FJk) rises above a predetermined threshold (TIm or TJk), the output of the relay is triggered to have an amplitude of 1. Once the input signal drops below the threshold, the output of the relay returns to its initial value of 0. This threshold value can define the tactile sensitivity [205]. When two relays are triggered at the same time but in different layers, a 2D contact location is detected.

Referencing the positions in both directions is used to map the two-dimensional motion of the applied force in the I-J coordinate system with respect to time. This 3D time-position relationship is later used to measure the speed of motion in both the I and J directions. If the two detected unidirectional positions happen in consecutive sensing elements, the algorithm detects a movement over the surface of the sensor between those strips.

The speed of motion between two consecutively triggered relays in each direction is calculated based on the distance (d, Figure 4-2) between each two adjacent elements (Im –Im-1) or (Jk –Jk-1) and the amount of time that transpires between when the relays are triggered. After calculating the velocity in each direction, they are low-pass filtered to smoothen out the speed calculation (Figure 4-8).

4.5.3 Contact point detection experiment

Several experiments were performed to check the ability of the sensor to detect the position of objects in contact with the sensor. As shown in Figure 4-9, the developed test stand was programmed to press a probe at three predefined locations on the surface of the
sensor. Position C was chosen in a way that the probe was pressed between two consecutive sensing elements (J2 and J3) along strip I3.

4.5.4 Motion detection experiments

The ability to detect the two-dimensional motion of forces applied to the surface of the sensor was also demonstrated using several tests. First, a rubber probe was pressed and manually slid on the sensor surface in the negative I and J directions as shown in Figure 4-10a. In the other two experiments, the rubber probe was slid purely in the positive J direction along strip I6 (Figure 4-10b) and in the negative I direction along strip J3 (Figure 4-10c), respectively. Corresponding velocities of motions were also calculated as described in section 4.2.
m=1:8, k=1:8
t_s = sampling time
s=0:∞

Figure 4-8 Signal processing algorithm. The signal from each element is first passed through a filter to attenuate high-frequency noise. Then to accentuate the signal, its derivative is passed through a nonlinear gain with power P. The signals are then compared with the threshold values to detect the location a force is applied. As a force is applied, the position of the force is determined, and the 3D position/time profile is recorded. The velocity profile in both I and J directions is calculated.
translated along the surface of the sensor, the direction and speed of motion is calculated by referencing the time and distance between detected contacts in adjacent strips in each direction.

Figure 4-9 Contact force detection experiment: the test probe was automatically placed on the predefined positions at A (I7, J7), B (I5, J5), and C, a position between the J2 and J3 strips along the I3 sensing element.

Figure 4-10 Evaluation of the sensor to detect the motion of applied force. (a) A rubber probe was manually slid from the start point (I8, J8) to the end point (I2, J1). (b) A rubber probe was slid purely in the J direction from the start point (I6, J1) to the end point B (I6,
A rubber cylinder was slid purely in the I direction from the start point (I8, J3) to the end point (I1, J3).

4.6 Results of Contact point detection experiment

Through scanning the output signals of the 16 sensing elements in both layers, each of the 64 taxels can be monitored independently to detect the contact location of a force. As shown in Figure 4-9, there are three distinct contact forces applied at three different positions and times. Figure 4-11 shows the corresponding sensor signals in the I and J directions before and after the nonlinear gain: fIm, fJk and FIm, FJk, respectively. The location of contact point A (Figure 4-9) can be clearly discerned because the signals in strips I7 (Figure 4-11a) and J7 (Figure 4-11b) both increased at the same time of t=12.8s. The signals after the nonlinear gain FI7 and FJ7 are noticeably sharper than the fI7 and fJ7 signals to facilitate the detection of translation speed, as will be subsequently discussed. The same is of true contact locations B and C which occur at t=18s and t=23.4s, respectively. In Figure 4-12, the output of each taxel is plotted to indicate the location of each force in bar-graph form during each of the three mentioned times of contact with the sensor. Contact location A can be cleanly detected because the relays for I7 and J7 both were triggered at the same time (Figure 4-12a). The same is true for the positions B and C (Figure 4-12b and Figure 4-12c, respectively).
Figure 4-11 Sensor signals in the contact point detection experiments. (a) Output signals from sensing elements that lay in the I direction. (b) Output signals from sensing elements that lay in the J direction.

Figure 4-12 Contact point detection. (a), (b), and (c) show contact point detection of points A, B, and C as depicted in Figure 9, respectively. When the relays are triggered in orthogonal strips at the same time, a contact location is detected.

4.7 Results of motion detection experiments

As is clear from Figure 4-13, the starting location of the diagonal motion can be easily detected since FI8 (Figure 4-13a) and FJ8 (Figure 4-13b) are both triggered at the
same time of $t=5\text{s}$. As the rubber probe was slid diagonally along the sensor surface towards the origin of the I-J coordinate system, the adjacent sensing elements in each layer were sequentially triggered. Interpolating between the contact points and times in both sensing layers creates a surface that relates the time and location in each respective direction. The intersection of these two surfaces creates a 3D position-time relationship (Figure 4-14a). The 2D spatial motion of the force along the surface of the sensor can be seen from the top view of this surface (Figure 4-14b), and resembles the expected path motion as shown in Figure 4-10a.

By calculating the time when each relay is triggered in both the I and J directions, the amplitude and direction of speed are calculated based on the algorithm in Figure 4-8. The calculated velocity profile in both the I and J directions are negative, indicating the movement is toward the origin of the I-J coordinate system as shown in Figure 4-15. Due to the physical dimensions of the sensor (Figure 4-2), the speed of motion is updated after every 3mm of displacement of the applied force in the I and J directions.

4.8 Unidirectional slip results

The results of the unidirectional slip experiments with both the vertical sliding motion in the J direction over the I6 element (Figure 4-10) and the horizontal sliding motion along the I direction over the J3 element (Figure 4-10c) are shown in the Figure 4-16a and Figure 4-16c, respectively. The velocity profiles for both experiments are shown in Figure 4-16b and Figure 4-16d.
Figure 4-13 Sensor signals during the diagonal slip experiments. (a) The processed signals (FI1, FI2… FI8) in the I direction. (b) The processed signals (FJ1, FJ2… FJ8) in the J direction.

Figure 4-14 Slip detection. (a) A three-dimensional time-position surface indicating the motion over the surface of the sensor with respect to time. (b) The two-dimensional motion profile during the diagonal motion experiment.
Figure 4-15. The velocity profile in both the I and J directions. The sign of the velocity amplitude shows the direction of motion. The negative velocity profile in both the I and J directions indicate a movement toward the origin of the I-J coordinate system.

Figure 4-16. The results of the unidirectional motion experiments; (a) motion was detected purely along the I6 element in the positive J direction. (b) The related piecewise linear velocity profile from (a) is positive. (c) motion was detected purely along the J3
element in the negative I direction. (d) The related piecewise linear velocity profile from (c) is negative, as expected.

4.9 Discussion

The goal of this chapter was to design, fabricate and empirically characterize a skin-like compliant tactile sensor to detect the position and motion of the applied forces over the sensor surface using the developed nanocomposite and DPP process. A novel hybrid manufacturing method including the DP and layer by layer soft molding processes was used to embed the developed piezo-resistive sensing material within an elastic structure. The combination of the DP manufacturing process with the soft molding process used in this work showed a significant potential in the fabrication of multi-layer compliant tactile sensors. However, this combined process is limited in manufacturing complex, conformal and thin sensor structures since the molding process involves a manual material feed into a prepared mold. It is expected that developing a hybrid 3D Printing process including the DPC process with multiple nozzles, which can layer-by-layer deposit not only sensor material, but structure and resistor materials will create very complex 3D sensors including sensing, insulating and resisting components within a single system.

The results showed that the developed algorithm and characterization method combined with the developed sensing material and manufacturing techniques, led to an effective solution for the localization of the contact points and detection of the direction and speed of motion of the applied force over the sensor surface. However, since the spatial resolution of the fabricated sensor is 3 mm in each direction, there is a possibility that the sensor cannot distinguish between continuous motion and a series of sequential,
intermittent contacts. This risk can be mitigated by increasing the resolution of spatial
detection by adding more sensing elements in both the I and J directions.

To draw a parallel between the developed artificial skin-like tactile sensor and
human skin, the outer layer of the polyurethane body is analogous to the epidermis while
the sensing elements are functionally comparable to mechanoreceptors in some ways.
When an object is translated while in contact with the sensor, the designed signal
processing algorithm (Figure 4-8) produces ensembles of temporally sequenced pulses that
resemble action potentials. While people can discern the relative timing of afferent signals
from the fingertips to rapidly ascertain the direction that forces are applied, the algorithm
for the tactile sensor can interpret the timing of pulses from adjacent sensing strips to
estimate the direction and speed in which forces are moving.

Although there are similarities between the human skin and the developed tactile
sensor, there is still room for improvement because human skin is superior in a number of
ways. For example, humans have the ability to detect forces with a resolution as fine as 1
mm on the fingertips [205] while the developed tactile sensor currently has a spatial
resolution of 3 mm. Human fingertips also offer a tremendous amount of mechanoreceptors
per unit area. However, if a single sensing strip in the sensor is damaged, a 3 mm wide
tactile blind spot results that are as long as the sensing element itself. The reason for this
design methodology is to simplify the number of interconnects and external wiring required
to integrate eventually the tactile sensor into an electromechanical system since only 16
sensing elements in two layers were used to create 64 taxels in this paper. As a general
rule, the number of taxels is equal to the number of sensing elements squared. The number
of taxel and sensing elements will be an exponentially important factor to develop and implement practical large area skin-like sensors for robotic applications.

For such an endeavor, the number of interconnects should be minimized to reduce the likelihood of mechanical failure. This has been facilitated by the design of the proposed sensor because one side of each layer of sensing elements shares a common ground that was directly printed using the hybrid manufacturing process (Figure 4-3 and Figure 4-5). Thus, only 18 interconnects would be required to link the 16 sensing strips to the half Wheatstone bridges, and in general, the necessary number of interconnects would be equal to the number of sensing elements plus two (one for the common ground in each layer).

4.10 Conclusion

This chapter discussed a multi-layer compliant tactile sensor developed using the DP and soft molding processes with a piezoresistive photopolymer filled with MWNTs. The sensor was comprised of two sensing layers sandwiched by the polyurethane insulating rubber. The developed sensor has successfully detected the location of contact forces with a 3 mm resolution. The direction and speed of the motion of an object in contact with the sensor were also demonstrated. The algorithms developed in this chapter showed the potential of the sensor to detect the motion of forces applied to the surface of the sensor for artificial systems. While there is already an excellent tactile sensor available for robotic fingertips [198], development of a commercially available large area skin-like sensor is still lacking for robotic manipulators. In the Chapter six, a novel piezoresistive polymer
will be presented where through using the flexible conductive nanocomposite in the hybrid DPP process, a highly flexible and fully polymeric tactile unit is fabricated.
CHAPTER V

COMBINED 3D PRINTING TECHNOLOGIES AND MATERIALS FOR
FABRICATION OF TACTILE SENSORS

5.1 Introduction

The use of 3D printing technology is already prevalent in a wide range of applications ranging from simple prototypes to direct the part production. However, there are still many areas that could benefit from this technology [1,2]. In recent years, researchers have investigated hybrid 3D printing processes and materials to create advanced products [4-7]. In particular, electronic/electrical components have been deposited and embedded within 3D structures by interrupting the 3D printing process [9,10]. In addition, advances in materials science are opening a new area in conjunction with the existing 3D printing technology [1]. Examples include printable conductive inks [29], batteries [13], piezoresistive materials [14-16,24,33,34,44], tissue engineering materials and cell-seeded biomaterials [22]. These materials have been used with the Direct-Print (DP) technology, which is considered as the most flexible process to utilize low to highly viscous functional materials. Although DP is a stand-alone process, development of a hybrid process by combining other existing processes (e.g. 3D printing) is another area of interest in the creation of advanced functional devices. Also, the DP
process was successfully integrated with a stereolithography process to print and embed conductive inks into and onto the surface of a 3d printed part [4].

We successfully developed a DP process integrated with projection stereolithography (PSL) to fabricate 3D structures with conductive traces [6]. As it was discussed in the previous chapter, the combination of the DP and soft molding processes was investigated to produce a multi-layer compliant tactile sensor for robotic applications. As an extension of previous investigations on the hybrid manufacturing process, the feasibility of both commercial multi-material 3D printing technology and developed hybrid DP-PSL technology was investigated in this chapter. This proposed process acted as substitutions for the layer by layer soft molding processes work that were used to fabricate compliant tactile sensors. The following describes the design, fabrication method, material synthesis, and characterization of a multi-layer tactile sensor in more detail.
The proposed compliant tactile sensor consists of two sensing layers with straight piezoresistive elements arranged in an orthogonal configuration, embedded into an elastomeric sensor body structure (Figure 5-1). Based on design criteria, the number of sensing elements can be increased or decreased. One of the advantages of the proposed configuration is the capability to reduce the complexity of wiring topology and signal processing since only \( m + n \) sensing elements (\( m \) and \( n \) elements in the first and second layers, respectively) are used to create \( m \times n \) taxel array. Any of these taxels is then used to detect a two-dimensional location of a force applied to the surface of the sensor [34]. Both the sensor body structure and the two sensing layers were fabricated using elastomeric materials. Elasticity improves the flexibility and the conformability of the sensor. In addition, elastomer material enhances the mechanical durability and compliance of the

Figure 5-1. Schematic of the suggested tactile sensor. (a) exploded view of the top and bottom sensing parts with piezoresistive elements and intermediate insulating layer. (b) combined sensor structure
tactile sensors that are preferable factors in the detection of sliding contact [49] as well as the prevention of permanent deformation and preservation of the natural mechanics when the sensor is deformed and released. The working principle of the sensor was presented in the chapters three and four. The following sections describe three different hybrid manufacturing approaches to develop the suggested tactile sensor.

5.2.1 Sensor type I fabricated by the multi-material 3D printing and injection processes

A commercial 3D printing system is capable of producing multi-material structures, with innate properties such as rigidity and flexibility that are required in the suggested sensors. A 3D model (Figure 5-2) was designed with a compliant part and a rigid part in a single body. The compliant part consists of two sensing layers with eight circular hollow channels. Each channel is 600 µm in diameter and 27.5 mm in length. The channels are evenly spaced with the interval of 2.54 mm in both sensing layers that are 500 µm apart.
Figure 5-2. Sensor type I (a) combined sensor model, (b) exploded view of the compliant part (blue) and rigid part (grey).

The size of the sensor is 45 mm × 45 mm × 4 mm. These channels are filled with the sensing material. Once the sensing material is injected and cured, a connector is inserted into the slots, which are wired with signal processing devices. The dimensions of the channels and slots were determined to use the standard 8-pin connector (XG8V-0831 Single-row Header Plugs, OMRON electronic components LLC, Schaumburg, IL). These prebuilt channels secure the sensing materials with a constant cross-sectional area, which provides a more consistent performance for each sensing element. The suggested method is advantageous in reducing the number of manufacturing steps. In addition, these embedded channels decrease the possibility of causing a short circuit.

5.2.2 Sensor type II fabricated by the multi-material 3D printing and DP processes

3D printing of the sensor structure with embedded channels may have a drawback from the injection process when the channels are freeform and long. To overcome this issue, a second method (Figure 5-3) was suggested. Two sensing structures were designed
with eight rectangular open channels with the width of 1.5 mm, depth of 0.5 mm, length of 27.5 mm, and spacing of 2.54 mm between adjacent channels (Figure 5-3c and Figure 5-3d), where the sensing material is directly printed and cured. The entire dimensions of the part are 45 mm × 45 mm × 4 mm. These sensing structures also have the same connector slots at the ends so that the sensing elements are easily wired to the external devices.

![Figure 5-3. Sensor type II (a) combined sensor model, (b) exploded view of the top and bottom parts with sensing elements and the intermediate insulating part. (c) top, (d) bottom parts with sensing elements in (b)](image)

One intermediate insulating structure was also designed (the middle structure in Figure 5-3b). These structures were all 3D printed with rigid and compliant materials so that the compliant part was framed by the rigid part. Once the DP process was accomplished, three structures are bonded together, and the two sensing structures were orthogonally placed (Figure 5-3b).
5.2.3 Sensor type III fabricated by the PSL and DP processes

The suggested sensor models presented in the previous sections involve a commercial 3D printing process. Although it was expected that these models and manufacturing processes are promising in producing tactile sensors, there is a lack of flexibility in combining a commercial process and developed DP process. For example, when DP is necessary during the 3D printing process, it may not be possible to pause and resume the 3D printing process. In addition, there are limitations in the use a customized functional material in these machines since they have been developed with particular types of photocurable materials designed for predetermined physical and rheological properties. As a result, to have more versatile and customized capabilities, a combination of PSL and DP is suggested. With this combined process, a multi-material sensor model (Figure 5-4) was proposed.

![Figure 5-4. Sensor type III (a) combined sensor model. (b) exploded view of the model.](image)

This process involved the photocrosslinking a sensor’s body material and the DPP of the sensing material within a single system. The suggested model consisted of multiple layers including the sensor structure and the sensing elements where the dimensions of the
entire sensor are 22 mm × 22 mm × 5 mm. Each sensing element is ~1 mm in width, 20 mm in length and 1.5 mm in spacing. The distance between two sensing layers was selected to be 1 mm.

5.3 Materials and methods

A piezoresistive, photocurable and stretchable polymer/nanocomposite was developed for sensing elements. A commercially available resin (TangoPlus FullCure®, 930, Objet Geometries Inc, MA., USA) was used to meet the printability of both the sensing elements and the elastic body. This resin is a highly stretchable rubber-like photopolymer (170-220 % elongation) with low shore hardness (26-28 Shore A). These properties are favorable to fabricate a skin-like compliant tactile sensor. Piezoresistivity was introduced into this polymer matrix by the dispersion of commercially available industrial grade MWNTs (NanoLab, Waltham, MA, USA). Since TangoPlus is an ultraviolet (UV) curable resin, several materials were used so that the prepared material could be compatible with visible light PSL, which will be discussed in the following section. These materials include 0.1 wt% of 5,7-diiodo-3-butoxy-6-fluorone (H-Nu 470, Spectra, Inc., Millury, OH, US) as a visible photoinitiator, 5 wt% of amine acrylates (AA, Spectra, Inc., Millury, OH, US) as an co-initiator and 0.15 wt% of iodonium salt 4-(octyloxy) phenyl iodonium hexafluoroantimonate (OPPI, Spectra, Inc., Millury, OH, US) as an accelerator. The prepared material was stirred for 30 min. Then, it was stored in a dark room to prevent the photocrosslinking by ambient light.
5.3.1 Preparation of a photocurable CNT/Prepolymer

The prepolymer/nanocomposite was prepared with the dispersion of 0.5 wt% of MWNTs in dimethylformamide (DMF, Sigma-Aldrich, Milwaukee, WI) using a sonicator (Q700, Qsonica, Newtown, CT) with the power of 700 W, frequency of 20 kHz, and amplitude of 50% for 1 min in pulse mode (20s on, 10s off). Sodium dodecyl sulfate (SDS, Sigma-Aldrich, Milwaukee, WI) as a surfactant was used to noncovalently functionalize the MWNTs. Weight ratios of SDS to MWNTs were selected to be 1.5:1.[181] The TangoPlus resin was then blended with the prepared solution using the same sonication process for two minutes. Then, all the organic solvent was completely removed by using a hot plate magnetic stirrer (VWR 10 × 10 ALU Hotplate 120V, VWR, IL) at 80 °C for 48h. Then, the MWNT/prepolymer solution was filtered using a 150 μm filter (Sterlitech, Kent, WA) and degassed for 24h under a vacuum pump (ME 4 NT, Vacuubrand, Germany).

5.4 Fabrication of multi-layer tactile sensors

The following describe the different manufacturing approaches used to fabricate the tactile sensor.

5.4.1 Sensor type I: hybrid manufacturing process including the multi-material 3D printing and injection processes

A commercial multi-material 3D printer (Connex 500, Stratasys Ltd) was used to build the type I sensor (Figure 5-5a). A colorless photopolymer (VeroClear, Stratasys Ltd) was selected to print the rigid base, and a rubber-like photopolymer (FullCure® 930
TangoPlus, Stratasys Ltd) was used to print the compliant structure. The fabricated structure was then carefully cleaned and washed using a 2% Sodium Hydroxide water solution to remove the support material. The developed piezoresistive prepolymer/nanocomposite as a sensing material was injected into the channels using a dispensing pump (PCD3, GPD Global, Grand Junction, CO) (Figure 5-5c). After all channels were filled, an 8-pin connector (XG8V-0831, OMRON electronic components LLC, Schaumburg, IL) at one slot, and 1-pin connector (XG8V-0131, OMRON electronic components LLC) at the other slot were mounted for connecting the sensing elements to the signal processing device, that was discussed in the section 4.5.2. Then, the sensor was placed under the UV light (OmniCure S2000, Lumen Dynamics Group Inc., Ontario, Canada) so that the prepolymer/nanocomposite can be fully photopolymerized. Figure 5-5d shows the final sensor using the suggested method.
5.4.2 Sensor type II: hybrid manufacturing process including multi-material 3D printing and DPC process.

Similar to the type I sensor, the designed three parts were fabricated using the same Connex 500 3D printer. TangoPlus and VeroClear resins were used again to build the compliant and rigid parts, respectively (Figure 5-6a). Using the developed DP system, the sensing elements were printed on the open channels (Figure 5-6b). After the DPC of the sensing material had been done, the same 8-pin and 1-pin connectors were mounted as were used for the type I sensor. Finally, the three parts were assembled and bonded together (Figure 5-6c).
5.4.3 Sensor type III: hybrid manufacturing process including the PSL and DPC processes

The suggested model for the type III sensor was fabricated using the developed DP system and the PSL system [6] (Figure 5-7). The PSL process was used to build the compliant structure (Figure 5-7a), and the DP process was used to print the sensing elements (Figure 5-7b). The PSL system included a commercial digital light processing (DLP) projector (Joybee Gp2, BenQ America Corp., CA, US) retrofitted with a UV plano-concave lens (Edmund Optics Inc., Barrington, NJ, US) with the diameter of 12 mm and an effective focal length of -30 mm. The new lens configuration provides an adjustable focus length ranging from 50 mm to 100 mm, with a relatively high intensity required to cure the visible photopolymer (TangoPlus with H-Nu 470 visible photoinitiator). The working principle of this PSL is the same as the PSL process that employs a patterned light
to cure the entire layer of the resin (i.e. no hatching process in the line-scan stereolithography) [206].

Figure 5-7. Integrated manufacturing system including DP and PSL. (a) PSL process to build the insulating layers, (b) DP process to print sensing elements.
Figure 5-8. Fabricated sensor using integrated PSL and DP processes. (a) an example (partial sphere) of a 3D structure built in the PSL system. (b) the sensing elements were printed using the DP process on the insulating layers built in the PSL system. (c) the final sensor had two sensing layers. (d) a deformed sensor. All the sensing elements were connected to a common ground.

Figure 5-8a shows an example of the fabricated 3D structure with a partial sphere. Each layer was formed by projecting a light pattern representing a cross section of the part. To build the compliant structure, each light pattern was irradiated on the resin surface for 7 s, which was empirically set to fully cure the layer. Once a layer was formed, a platform attached to the z stage in the PSL’s system was descended deeply, dwelled for 5 s, and ascended to leave a given layer thickness (50 µm) so that a new layer could be prepared. Then, additional 10 s was allowed so that the resin could settle by gravity. Once the predetermined thickness (2 mm) was achieved, the DP system was positioned to print the
sensing elements (Figure 5-8b). The created sensing elements were cured and connected with a bare wire, which was connected to the external device. The above steps were continued to build the entire sensor (Figure 5-8 c and Figure 5-8d).

5.5 Contact point detection experiment

Several experiments were performed to check the capability of the sensors to detect the locations of forces in contact with the sensors. A probe manually placed in predefined positions (Figure 5-9a, Figure 5-10a, Figure 5-11a, and Figure 5-11b. The contacts were clearly detected and shown in Figure 5-9 b – d, Figure 5-10 b – e and Figure 5-11c and Figure 5-11d. These dimensionless bar maps were plotted by comparing the filtered and normalized output signals with a predefined threshold as it was discussed in section 4.5.2.

Figure 5-9. Experimental results with the type I sensor. (a) three applied forces at three different locations. Results of (b) the force A, (c) the force B, and (d) the force C.
Figure 5-10. Experimental results with the type II sensor. (a) four applied forces in four different locations. Results of (b) the force A, (c) the force B, (d) the force C, and (e) the force D.

Figure 5-11. Experimental results with the type III sensor. (a) - (b) applied forces using a probe, Results of (c) the force A, and (d) the force B
5.6 Discussion

Three sensor types were designed and fabricated with the same sensing material, whereas the sensor body and sensing elements were differently built. All sensors were tested and compared. Based on the experimental results, while using a commercial 3D printing machine, the approach used to fabricate the sensor type I resulted in simpler, more reliable and functional sensor than the approach used to fabricate sensor type II. However, this approach has several drawbacks if the channels are long and conformal. In comparison, it is believed that an integrated DP and PSL system significantly reduces the deficiency of the approach utilized in fabrication of the sensor type I. Since commercial 3D printers layer by layer build a structure, printing of the sensing elements over conformal and arbitrary surfaces is still a major challenge and needs more efforts in system development including printing algorithm and process planning. The developed sensing materials together with the signal processing algorithm could detect the location of the applied forces. However, detection of the force amplitude is a challenge for these materials due to their force adaption behavior. This behavior is somewhat similar to human fingertips, which contain Meissner’s corpuscles and Pacinian corpuscles which detect the motion and temporal changes in skin deformation [199-201]. Chapter six present the development of an artificial skin-like sensor using the nanocomposite sensing material.

5.7 Conclusion

3D printing technology is becoming more ubiquitous every day; however, fabrication of multi-material functional and smart structures is problematic because of the
process and material limitations. In this chapter, several manufacturing processes including the DPP, the PSL, and multi-material 3D printing technology as well as a developed 3D printable stretchable sensing material were evaluated to fabricate a tactile sensor. The suggested integrated manufacturing processes to fabricate the tactile sensor consists of a micro-dispensing head, translation stages, a light curing module, the PSL, and an automatic control system. This process enabled the building of the entire sensor body in a layer by layer fashion, printing the sensing elements, and building the additional layers, where the deposited sensing elements were able to directly cured. The developed 3D printable stretchable sensing material was a photocurable and stretchable liquid resin filled with multi-walled carbon nanotubes (MWNTs). In parallel with this suggested manufacturing system, a commercial machine was also used to build the sensor body, and a dispensing system was used to create sensing elements. The results of the sensor characterizations showed that suggested processes and materials are promising as required for the development of stretchable tactile sensors.
CHAPTER VI

FLEXIBLE POLYMERIC PRESSURE SENSOR

6.1 Introduction

The ion conductive polymers are developed by incorporation of ionic liquid into a prepolymer and subsequent polymerization of the product [68,81,82]. In this system, the conductivity drives from the migration of doped ions between the coordinate sites generated by the local motion of polymer chain segments under enough activation energy. Several factors are important in design and development of conductive electrodes based on the ILs. These factors include electron-donating atoms to form the coordinate bond, low bond rotation barriers, and high segmental motion of the polymer chain [83]. A higher ionic conductivity derives from a high ion mobility, a high ion density, and a low polymer Tg [81,83]. In the proposed sensor system, the required activation energy to transport ions is generated by an external electric field through sandwiching the ILs-polymer between two electrodes connected to a power supply (Figure 6-1). The selected material for the electrodes for the purpose of strain detecting sensor must possess enough stretchability to cover the flexibility of the ILs-Polymer. Their change in conductivity under the deformation should be negligible in comparison with the change in the ILs-Polymer resistivity. In addition, they should participate in the charge transfer phenomena. Carbon
Nanotubes (CNTs) based conductive nanocomposites are the best candidate for this purpose. Due to their exceptional structure, CNTs are considered as the acceptor material [83,195]. Thus, they can participate in the electron donation process. Recently, Authors developed a highly stretchable conductive nanocomposite by the dispersion of CNTs into a photocurable stretchable monomer to achieve up to 80% elongation [16,24]. The conductivity of this nanocomposite can be tuned to a required level needed to prevent any conflict between the change in their resistivity and the change in resistivity of IL-polymer under the deformation.

Figure 6-1. (a) Schematic illustration of cross-linked IL-incorporated polymer sandwiched between two conductive CNT-polymer electrodes and covered with two compliant polymeric layers. (b) The chemical structure of the 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF4) used as the IL. (c) The SEM image of 0.01 wt% of functionalized MWNT into the photopolymer.

Ionic conductivity is simply defined by [207]:

1) \( \sigma = cZ\varepsilon \)
Where $\sigma$ is conductivity, $c$ is the concentration of mobile anions or cations. $Z_e$ is their charge. $\mu$ is their mobility [207]. During the ionic conductivity, ions are accelerated and jump from one stable site to another one while the direction of movement is not random, and it is in the direction of the electrical field. The mobility, $\mu$, is defined as the velocity when the magnitude of the electrical field is unity.

$$2) \quad \mu = \frac{vZ_e a^2}{k_BT} \exp \left[\frac{-E_a}{k_BT}\right]$$

Where $v$ is the vibration frequency of the solid, $a$ is the distance between two adjacent site where ions jump between them. $E_a$ is activation energy of diffusion, $k_B$ is Boltzmann constant, and $T$ is them temperature. The following equation then gives the conductivity equation (Equation 1) by substituting the mobility into the conductivity equation:

$$3) \quad \sigma = \frac{cvZ^2e^2a^2}{k_BT} \exp \left[\frac{-E_a}{k_BT}\right]$$

As a result, any variation in the electrical field or the temperature results in changing the conductivity of the IL-polymer. The electrical field establishes between two parallel plates connected to a power supply (Figure 6-1). Since the field lines are parallel to each other, there is a uniform electrical field. The following equation calculates the magnitude of the established electrical field [208]:

$$4) \quad E=V/d$$

Where $V$ represents the voltage supplied by the battery, and $d$ stands for the distance between the plates. According to the field intensity formula (Equation 4), the smaller the distance between the plates, the stronger the electric field becomes if the potential
difference is held constant. This principle and behavior propose a pressure sensor based on a sandwiched IL-polymer between two CNT-polymer nanocomposite electrodes (Figure 6-1 a).

6.2 Material and method

The base and covering compliant layers were built using a commercially available photocurable resin (FullCure® 930 TangoPlus, Objet Geometries, MA., USA) as it was received. The conductive stretchable electrode was a solution of 5 wt% of noncovalent functionalized MWNTs dispersed into the FullCure® 930 TangoPlus. MWNTs were dispersed first into a solution of Triton X100 (Sigma-Aldrich, Milwaukee, WI, USA) in dimethylformamide (DMF, Sigma-Aldrich, Milwaukee, WI, USA) [168]. The ratio of CNT to Triton X100 was 1:350 [175]. The solution was blended using a globally dispersion method [16,34]. In this method, a sonicator (Q700, Qsonica, Newtown, CT, USA) with 700 W power, 20 kHz frequency, and amplitude of 50% was used for 20 min in pulse mode (1 min on, 10s off) in presence of an external magnetic stirrer. After the functionalization process (Figure 6-2), the prepared solution of DMF/MWNTs was blended with the TangoPlus resin using the same process for five more minutes. Then, the prepared MWNT/prepolymer was placed on a hot plate magnetic stirrer (VWR 10 × 10 ALU Hotplate 120V, VWR, IL) at 100 °C for 48h to completely evaporate the solvent. After the dispersion and evaporation, the solution was again mixed using a high-speed mixer (DAC 150.1 FVZ-K, FlackTek Inc. Landrum, SC ) at 2500 rpm for 1 hr. Finally, 4 wt% of the thermal initiator (TRIGONOX 125C75, Akzo Nobel Functional Chemicals,
LLC, IL) was added to the solution and mixed using the same high-speed mixer for 5 min. This solution is thermally curable as shown in Figure 6-3.

Figure 6-2. Dispersion of MWNT into the DMF with the aid of Triton X100 and DMF and ultrasonication. (a) MWNT, (b) solution of 1g CNT + in 200ml DMF + 4g Triton X-100. (c) 1g CNT + in 200ml DMF after Sonication.

Figure 6-3. Conductive nanocomposite ink. (a) A highly viscoelastic conductive ink. (b) Fully curable in room temperature. (c) A transparent film with 0.001 wt% CNT dispersed into a flexible resin.

To prepare the IL-polymer, a highly flexible photocurable monofunctional monomer (SR 278, Sartomer America, PA) as diluent was mixed with Tangoplus with the
ratio of 1:4 using a magnetic stirrer for 30 min. Then, 1 wt% of 1-ethyl-3-
methylimidazolium tetrafluoroborate (EMIBF₄, Sigma-Aldrich, Milwaukee, WI, USA) 
was mixed with the solution using the high-speed mixer at 2500 rpm for 5 min.

6.3 Sensor fabrication

Figure 6-4. Left: Schematic of a hybrid manufacturing process. This process includes 
molding (a,c,k), light curing (b,f), screen printing (c,g) and thermal curing (d,h). Right: 
fabricated sensor

A hybrid manufacturing and layer by layer process, including the molding and the 
screen printing was used to fabricate the sensor. As shown in Figure 6-4a, the base 
compliant layer was made through a molding process. A 1mm base layer was created by 
pouring the Tangoplus into the mold (Figure 6-4a) and curing under UV light (Figure 6-4b). 
Then, using a mask the first electrode with 1 mm width, 30 mm length, and 200µm 
thickness was printed on it (Figure 6-4c). The printed electrode cured using the heat at 
100ºC (Figure 6-4d). In the next step, the cured electrode was covered with a 1 mm layer 
of the IL-polymers so that the electrode was sandwiched between two layers of the rubber 
material (Figure 6-4e). The IL-polymer layer at this point serves as the pressure sensitive
layer upon which the next bank of the orthogonally oriented electrode was printed. The light curing (Figure 6-4f), printing (Figure 6-4g), thermal curing (Figure 6-4h) and covering process (Figure 6-4k) were repeated to fabricate the entire sensor (Figure 6-4Right). The fabricated taxel has 1×1 mm² area with an approximate 1mm IL-polymer layer between the two electrodes.

6.4 Sensor evaluation

The goal of this work was to fabricate a highly flexible tactile sensor capable of measuring the applied forces over its surface. Based on the principle of an IL-polymer sandwiched between two electrodes, the resistivity of IL-polymer is a function of the amplitude of the electrical field and the distance between the two electrodes. As a result, when deformed by an object, the sensor body conforms to its surface, maintains the same local contour, and thus projects the deformation to the electrodes and IL-polymer. Subsequently, this deformation changes the distance between the electrodes. Accordingly, it changes the impedance of the IL-polymer.

6.4.1 Field effect property

In order to evaluate the field effect property of fabricated sensor, it was connected to a power generator device (HP 33120A, Hewlett-Packard Company). The output voltage from Half Wheatstone Bridge was measured using an oscilloscope (Tektronix TBS1064, Tektronix, Inc, OR). This experiment was repeated using different external resistors (1.2MΩ, 2.2MΩ, 4.7MΩ, 8.2MΩ, 20MΩ, 30MΩ, and 90MΩ) used in a half Wheatstone Bridge. The electrical resistivity of the IL-polymer was estimated by [208]:

140
5) \( R_s = \frac{V_{in}}{V_{out}} R_e - R_e \)

Where \( R_s \) is the resistivity of the sensor, and \( R_e \) is the resistivity of an external resistor. Figure 6-5a shows a sinusoid input voltage supplied to the sensor. Figure 6-5b shows the output voltage measured at the half Wheatstone bridge. Based on the input and output voltages for each test, the resistivity of the sensor was measured according to the equation 5. Figure 6-6 shows the calculated resistivity.

![Input Voltage Graph](image1.png)

**Figure 6-5.** Input and output voltages from the sensor.
Figure 6-6. The calculated electrical resistivity of the IL-polymer under the different electrical field conditions. The electrical resistivity of the IL-polymer changes as the electrical field changes.

Figure 6-7 shows the electrical resistivity of the sensor and output voltage recorded at the half Wheatstone Bridge.
The proposed IL-polymer showed a field effect property means its electrical conductivity changes in the presence of an electrical field. Any change in the input voltage results in a change in the generated electrical field between two electrodes which subsequently changes the electrical conductivity of the IL-polymer.

6.4.2 Pressure test.

According to the equation 4, the electrical field can be also changed as the distance between the two electrodes changes. A customized motorized force test stand (Z stage, Aerotech, Pittsburg, PA, USA) was programmed to apply a repeatable and step-stairs like force profile with a 2 mm flat probe in range of 0 to 140 gram with 0.1 mm step to the surface of the sensor. Simultaneously, the applied force was measured using a Weighting
scale (XS60025, Mettler Toledo Inc Columbus, OH) (Figure 6-8b). Figure 6-8a shows the concurrently measured voltage at the half Wheatstone Bridge with a 30MΩ external resistor. The resistivity of the IL-polymer changes as the distance between the two electrodes changes with a polynomial relation (Figure 6-9). The polynomial relation is believed to be a result of the pressure propagation into the top covering layer of the sensor. This behavior indicates that any change in its thickness or its mechanical property changes the performance and sensitivity of the sensor. The above experiment was also repeated for different external resistors (2.2MΩ, 4.7MΩ, 8.2MΩ, 20MΩ, 30MΩ, and 90MΩ) used in the half Wheatstone bridge in order to change the electrical field. Figure 6-9 shows the relation between the output voltages and the amplitude of applied force in order to calibrate the sensor. All the output voltages recorded in Figure 6-9 were compared with each other and the results are shown in Figure 6-10 which represents the relative output voltages for each resistor with respect to the minimum external resistor (2.2 MΩ). The sensor showed a higher sensitivity while a higher external resistor was used. This higher resistivity is also believed to be a result of wider variation in the IL-polymer electrical conductivity.
Figure 6-8. The performance of the sensor under the presence of an external force. (a) the recorded voltage at the half Wheatstone bridge. (b) the measured force using the weighting scale.
Finally, a periodic sinusoid force was applied to the sensor in a 50s period with the frequency of 1.8 Hz. The recorded voltage is shown in Figure 6-11a. A close view of the
behavior of the sensor in a 10 s time frame is shown in Figure 6-11 b. The applied force is measured by having a calibration between the output voltage and input force (Figure 6-9).

![Graph showing sensor performance](image)

**Figure 6-11.** The performance of the sensor under a periodic force.

6.5 Conclusion

In conclusion, we successfully developed a highly flexible fully polymeric pressure sensitive polymer based on the incorporation of an Ionic Liquid into a flexible polymeric matrix with approximately 200 % elongation. By embedding the developed IL-polymer between two highly stretchable conductive CNT-nanocomposite with 30% elongation [24],
a multi-layer pressure tactile sensor was developed with a promising application in the robotic application.
CHAPTER VII

CONCLUSIONS AND FUTURE WORK

7.1 Conclusion

In this thesis, a solvent free Direct Print-Direct Cure photopolymerization (DPC) fabrication method was developed which offers a highly flexible and powerful route to fabricate high-resolution 3D structures at room temperature in a layer by layer or free form fashion with viscoelastic photopolymers and their nanocomposite. In parallel with the development of the system, photocurable viscoelastic inks were characterized to advance the DPC process to print functional 3D structures. The effect of Fumed Silica (Sio2) as the thixotropic particles, as well as a thixotropic enhancer on the viscoelastic property of photocurable inks, was studied. The effect of flow rate, gap height, and velocity on the accuracy of the deposited filament was explored. In addition, A conformal printing algorithm was successfully developed to control the DPC process over the free form surfaces to achieve a uniformly deposited features.

Furthermore, a conductive piezoresistive photo/thermal curable composite was developed through dispersion of noncovalently functionalized industrial grade MWNT into
the prepolymer using a solution mixing process. This nanocomposite was successfully embedded into an elastomeric structure using the DPC and molding process. The result showed the developed embed nanocomposite can withstand a high elongation up to 30% while it has conductivity with a linear change in its conductivity. A multi-layer tactile sensor capable of detecting slip, position, and direction of applied force was fabricated.

Finally, We developed a highly stretchable pressure sensitive printable photopolymer capable of detecting strains up 30% through the incorporation of the 1-ethyl-3-methylimidazolium tetrafluoroborate as an Ionic Liquid (IL) into a stretchable photopolymer. The developed IL-polymer showed the field effect property as well as piezoresistivity once it is embedded between two layers of Carbon Nanotube (CNTs) based stretchable electrodes. Thus, a multi-layer pressure sensitive tactile taxel was fabricated using a hybrid manufacturing process included molding and screen printing, where the IL-polymer was placed between the two highly stretchable electrodes. The electrodes were developed through dispersion of Carbon Nanotube (CNT) into a highly stretchable photo-thermal curing prepolymer. The fabricated sensor was evaluated with different forces ranged from 0 to 140 gram. The results showed the great potential of IL-polymer in detecting both applied pressure and high strain.

Due to the potential of DPP process in fabrication 3D structures on pre-fabricated freeform surfaces, together with continues progress in ink development, it is envisioned that developed process and material can be successfully used in fabrication of freeform and conformal electronic components. Especially, 3D printed skin like tactile sensors.
7.2 Future work

The current work proved the potential of 3D printing process especially DDP process in fabrication of smart structures. Future research should extend the process and material developed in this work to fabricate a fully 3D printed skin like tactile sensor. The following aspects are recommended for more exploration in the future work:

1) The modeling and simulation of the DPP process should be performed. This is beneficial in better understanding the process and developing the inks.

2) Due to the advantage of DPP process in printing over free form surfaces, the non-planner printing algorithm for 3D printing over the prefabricated 3D structures should be developed.

3) A multi-material and hybrid DPP process including both the extrusion and jetting system is believed to significantly enhance the capability of the DPP process.

4) The conductivity of the developed stretchable conductive electrodes should be increased. Better conductivity is believed to be achieved by dispersing other particles such as graphene and silver particles, or improving the dispersion method. Characterization of conductivity of polymer is another area of interest.

5) The effect of other ionic liquids, as well as their concentration, on the sensitivity of the pressure sensitive polymers, should be investigated.

6) The performance of other stretchable conductive nanocomposite such as silver-based stretchable electrodes should be investigated.

7) The temperature sensitivity of the IL-polymer is another area of research that should be investigated.
8) One of the applications of the developed IL-polymers is a multi-touch flexible tactile sensor. The multi-touch algorithm to detect pressure, location, speed, and direction of applied force is needed to develop.

9) One taxel can detect both normal and shear forces. A method of discrimination between these two types of forces should be developed.

10) The slip detection algorithm needs to be developed to use the compliant tactile sensor as a slip detection tactile sensor.

11) Since the pressure and temperature can be detected at the same time. An algorithm to distinguish these parameters is needed to develop.
REFERENCES


[143] Q. Zhang, F. Fang, X. Zhao, Y. Li, M. Zhu And D. Chen, "Use Of Dynamic Rheological Behavior To Estimate The Dispersion Of Carbon Nanotubes In Carbon


