The Pennsylvania State University
The Graduate School
College of Engineering

TAILORABLE MANUFACTURING OF POLYMER
NANOCOMPOSITES USING OSCILLATING MAGNETIC FIELDS

A Dissertation in
Aerospace Engineering

by

Mychal Spencer

© 2019 Mychal Spencer

Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

August 2019
The dissertation of Mychal Spencer was reviewed and approved* by the following:

Namiko Yamamoto  
Professor of Aerospace Engineering  
Dissertation Advisor  
Chair of Committee

Christine Keating  
Professor of Chemistry

George Lesieutre  
Professor of Aerospace Engineering

Raymond Schaak  
Professor of Chemistry

Amy Pritchett  
Professor of Aerospace Engineering  
Head of the Department of Aerospace Engineering

*Signatures are on file in the Graduate School
Abstract

Hierarchical integration of nanoscale additives has the potential to improve properties of traditional aerospace composites, such as fiber-reinforced composites (FRPs). While traditional aerospace composites can supply high mass-specific properties, their transport properties and interlaminar mechanical properties can be still improved. Proper integration of nanofillers with advanced properties into polymer matrices, so-called polymer nanocomposites (PNCs), can contribute to transport property (electrical and thermal) improvement for electrostatic protection and heat dissipation, in addition to mechanical property improvement and unconventional, anisotropic, multi-functional properties. However, application of PNCs is currently limited due to two challenges: unknown structure-interface-property relationships and missing scalable and precise manufacturing methods. While the advanced properties of PNCs are designed based on the nanofillers’ properties, the PNC properties are often largely affected by nanofiller structures and their interface conditions (both polymer-nanofiller and nanofiller-nanofiller). Without tailored nanofiller structuring, specifically for the property of interest, property enhancement with nanofiller implementation has been observed to be smaller than theoretical estimation, or even negative, in the past. Thus, in this work, 1D assembly of nanofillers using magnetic fields of low frequency (<1 Hz) is studied as a scalable and precise way to organize nanofillers, including the number of inter-nanofiller contacts. Oscillating magnetic fields are chosen over other active assembly approaches (such as electric, acoustic, etc.) because such assembly is non-contact, energy-efficient (approximately 100 G), fast (<1 hour), and can achieve high periodicity and precise patterning over large areas. Unlike past magnetic assembly studies using pulsed fields that rely on weak thermal diffusion, with oscillating magnetic fields, lateral and transverse assembly mechanisms can be balanced by induced magnetic field gradients. The method also enables nanofiller organizational tuning, and therefore interface and interphase property control, even in highly viscous polymer matrices.

As a model case, theoretical and experimental studies were conducted about the magnetic organization of superparamagnetic iron oxide nanoparticles (SPIONs). Using an image processing technique, assembly trends were quantified (such as size, length, width, and separation) against the assembly parameters (flux density, frequency, waveform, and volume fraction). By allowing enough time for the nanoparticles to respond to the oscillating field, nanoparticle assembly was controlled using a sinusoidal waveform at very low frequencies (<0.1 Hz, 100 G): the assembly line length, width, and separation was increased by 43%, 59%, and 139%, respectively, when compared to those prepared using static fields of the same strength. Based on the above study on SPION assembly, large-sized PNCs (20 mm × 20 mm × 10 mm) were fabricated with ferrimagnetic maghemite within an aero-grade thermoset. Two fabrication methods with different surface modification and magnetic assembly processes were evaluated: dry-processed nanoparticles (surface modification only) assembled with the magnetic field of a solenoid coil pair, and wet-processed nanoparticles (surface modification and aggregate size control) assembled with the magnetic field of a Helmholtz coil pair. Nanoparticle structures were evaluated using optical microscopy and microCT scans, which were then correlated with the field conditions (static vs. oscillating and solenoid vs. Helmholtz coil), and nanoparticle conditions (dry- vs. wet-processed). Magnetic assembly with a sinusoidal field was observed to produce thicker nanoparticle lines, which enhanced transverse assembly, forming a continuous nanoparticle network and achieving percolation. Meanwhile, thinner nanoparticle lines, with fewer inter-nanoparticle contacts, were observed when assembled with a DC field. The above PNCs were characterized for anisotropic electrical and thermal conductivities. As for the PNC samples with dry-processed nanoparticles,
transverse assembly with a sinusoidally oscillating field enhanced continuity of the assembly lines, decreasing the percolation threshold (0.15 vol% for sinusoidal field vs. 0.45 vol% for a DC field). On the other hand, due to the different mechanisms between thermal vs. electrical transport, the reduced number of inter-nanoparticle contacts formed with a DC field (thin lines) was observed to be more effective at enhancing thermal conductivity (80% enhancement with a DC field at 4.7 vol% vs. 20% enhancement with a sinusoidal field at 3.5 vol%). As for the PNC samples with wet-processed nanoparticles, while homogeneous dispersion was improved and inter-nanoparticle contacts could be controlled (DC vs. sinusoidal), discontinuity of the assembly lines led to no observed percolation (up to 4.0 vol%) and small thermal conductivity increases (15% enhancement with a 300 G DC field at 4.0 vol%). These results demonstrate that an oscillating magnetic field is useful in tailoring nanoparticle structures and interfaces/interphases in a highly viscous matrix for anisotropic property control and potentially as a solution to the scalable manufacturing of PNCs.

From the above studies about magnetic assembly and structure-property relationships, a design space and corresponding guidelines were developed for the fabrication of polymer nanocomposites. I expect this work will provide a foundation for future investigations into the scalable manufacturing of PNCs with tunable transport properties. Further work is necessary in the future to overcome the limitations of this work: additional structure-interface-property relationship studies to supply more precise structure quantification and the integration of field oscillation to tailor PNCs of other types than those investigated in this work.
# Table of Contents

List of Figures .................................................................................................................. viii

List of Tables ...................................................................................................................... xvii

Acronyms ............................................................................................................................ xix

Nomenclature ...................................................................................................................... xxi

Acknowledgements ............................................................................................................ xxiii

Chapter 1 Introduction ....................................................................................................... 1

Chapter 2 Background and Prior Work ........................................................................... 4

2.1 Structure-Interface-Property Relationship Study of PNCs ...................................... 4
  2.1.1 Effect of nanofiller structure on PNC properties .............................................. 5
  2.1.2 Effect of nanofiller-polymer and nanofiller-nanofiller interfaces on PNC properties .................. 6

2.2 Manufacturing of PNCs ............................................................................................. 9
  2.2.1 Bottom-up vs. top-down .................................................................................... 9
  2.2.2 Field-assisted assembly of micro- and nanofillers ......................................... 10

2.3 Applications of Magnetically Assembled PNCs .................................................. 12

Chapter 3 Objectives and Approach ............................................................................ 14

3.1 Objectives .................................................................................................................. 14

3.2 Approach .................................................................................................................. 15
  3.2.1 Quantitative study of nanoparticle assembly using oscillating magnetic fields ........................................ 15
  3.2.2 Fabrication and characterization of tailored one-dimensional iron oxide thermoset nanocomposites ............................................................... 17
  3.2.3 Development of a design space to direct future work in the tailorable fabrication of polymer nanocomposites using oscillating magnetic fields .... 18

Chapter 4 Theoretical Studies of the 1D Magnetic Assembly of Superparamagnetic Nanoparticles .............................................................................................................. 19

4.1 Brief Review of Magnetism ....................................................................................... 19
  4.1.1 Classical theory of electromagnetism ................................................................. 19
  4.1.2 Characterization of magnetic materials ............................................................ 22
  4.1.3 Magnetic material types .................................................................................. 26
  4.1.4 Superparamagnetic materials ........................................................................ 31

4.2 On-Axis Magnetic Field Between Solenoid Pair .................................................. 33

4.3 Forces and Energies Applied to SPIONs in Magnetic Fields .................................. 37
  4.3.1 Interaction energies ......................................................................................... 38
  4.3.2 Magnetic forces .............................................................................................. 40
4.3.3 Magnetic and thermal interactions .................................................. 42
4.3.4 Gravitational, hydrodynamic, and thermal interactions ....................... 44
4.3.5 Magnetic moment reorientation and hydrodynamic drag ....................... 45
4.4 Analysis of SPION Assembly in Static and Oscillating Magnetic Fields ...... 48
  4.4.1 SPION assembly using static magnetic field ..................................... 48
  4.4.2 SPION assembly using oscillating magnetic field .............................. 49
4.5 Simulation of SPION assembly in static magnetic fields ......................... 52

Chapter 5 Experimental Study of 1D Magnetic Assembly of Nanoparticles ....... 59
  5.1 In Situ Observation of the Magnetic Assembly of Superparamagnetic
      Nanoparticles .................................................................................. 59
    5.1.1 Magnetic assembly time ............................................................... 64
    5.1.2 Image processing of magnetic assembly behaviors ........................... 65
  5.2 Experimentally Observed Magnetic Assembly Behaviors ......................... 67
  5.3 Parametric Studies of Magnetic Assembly ......................................... 69
    5.3.1 Effects of magnetic field frequency and flux density ........................ 69
    5.3.2 Effects of magnetic field waveform .............................................. 74
    5.3.3 Effects of nanoparticle volume fraction ....................................... 76
    5.3.4 Effects of nanoparticle type ......................................................... 77
  5.4 Summary of Magnetic Nanoparticle Parametric Studies .......................... 81

Chapter 6 Fabrication of 1D Tailored Polymer Nanocomposites using Magnetic Fields .... 82
  6.1 Preparation of Maghemite Nanoparticles .......................................... 83
    6.1.1 Characterization of maghemite nanoparticles .................................. 83
    6.1.2 Silane surface modification of maghemite nanoparticles ................... 88
    6.1.2.1 Processing ............................................................................... 89
    6.1.2.2 Characterization ................................................................. 91
  6.2 Magnetic Assembly of 1D-Tailored Polymer Nanocomposites ................. 95
    6.2.1 Solenoid magnetic assembly of dry-processed maghemite nanoparticles .. 97
    6.2.2 Helmholz coil magnetic assembly of wet-processed maghemite
      nanoparticles .................................................................................. 99
  6.3 Microstructure Inspection of 1D-Tailored Polymer Nanocomposites ........ 100
    6.3.1 Local nanoparticle volume fraction measurements .......................... 102
    6.3.2 Optical microscope inspection of cross-section surfaces ...................... 105
    6.3.3 3D MicroCT inspection of nanoparticle structures ............................ 109

Chapter 7 Characterization of Anisotropic Transport Properties of 1D Tailored Polymer
      Nanocomposites ............................................................................... 118
  7.1 Bulk DC Volume Electrical Resistivity ................................................. 118
    7.1.1 Measurement method and set-up ............................................... 118
    7.1.2 Measurement conditions and error range estimation ....................... 120
    7.1.3 Electrical resistivity values and their correlation with the nanoparticle
      structures ....................................................................................... 122
  7.2 Bulk Volume Thermal Conductivity ...................................................... 129
    7.2.1 Measurement method and set-up ............................................... 129
7.2.2 Measurement conditions and error range estimation ........................................ 132
7.2.3 Thermal conductivity values and their correlation with the nanoparticle structures ......................................................................................................................................................... 133

Chapter 8 Conclusions and Recommendations ........................................................................... 139

8.1 Contributions of this Work ................................................................................................................. 140
8.2 Recommendations for Future Work ................................................................................................... 144
  8.2.1 Design space and guidelines for magnetic tailoring of polymer nanocomposites .................. 144
  8.2.2 Future Work .................................................................................................................................. 149

Appendix A Image Analysis of Nanoparticle Assembly ................................................................. 152

  A.1 Image Processing Algorithm Frontend (Matlab) ........................................................................... 152
  A.2 Image Processing Algorithm (Matlab) .............................................................................................. 154

Appendix B Confidence Interval of the Characteristic Dimensions .................................................. 170

  B.1 Histograms....................................................................................................................................... 170

Appendix C Optical Images of PNCs with Wet-Processed Nanoparticles at the Edge Location ................................................................................................................................. 173

  C.1 Optical Images................................................................................................................................. 173

Appendix D Current/Voltage Measurements of PNCs ...................................................................... 176

  D.1 GADD Script Files............................................................................................................................ 176
  D.2 Current/Voltage Plots ....................................................................................................................... 176
    D.2.1 Data scattering ............................................................................................................................. 176
    D.2.2 Non-linear trend ......................................................................................................................... 177

Appendix E Local (Surface) Mechanical Properties ......................................................................... 182

  E.1 Measurement Method and Set-up ..................................................................................................... 182
  E.2 Reduced Elastic Modulus and Hardness ............................................................................................ 185

Bibliography ............................................................................................................................................ 189
List of Figures

Figure 1.1: Polymer nanocomposites: nanofillers with (or without) a surface modifier coupled to a polymer matrix (not to scale). The nanoparticles can be on the order of 1 nm – 100 nm, while the polymer chain components are typically long and thin (e.g. a thickness of 0.4 nm and length of 204 nm) ........................................3

Figure 2.1: Effect of nanofiller assembly on the A) transport and B) fracture properties of PNCs .................................................................................................................................6

Figure 2.2: Effect of surface modification on the uniform dispersion of nanofiller ..............8

Figure 2.3: Different A) interphases and B) interfaces of PNC components ......................8

Figure 2.4: The difference in the fabrication of PNCs through the A) bottom-up and B) top-down manufacturing approaches .........................................................................................9

Figure 3.1: The objectives of this thesis work to achieve scalable manufacturing of PNCs .................................................................................................................................15

Figure 4.1: Gauss’s law for magnetism: the divergence of the magnetic field is zero – magnetic monopoles do not exist .........................................................................................20

Figure 4.2: A) A hypothetical magnetic dipole moment, and B) minimum and maximum energy states ..................................................................................................................23

Figure 4.3: A) Randomly orientated regions of uniform magnetic dipole moments, and B) alignment of the domain magnetic moments with application of an external magnetic field – the material becomes magnetized ........................................23

Figure 4.4: A) Vibrating sample magnetometer experimental setup and B) typical H-M plot of a ferromagnet produced by the VSM ...........................................................................25

Figure 4.5: Dependence of magnetic susceptibility on temperature ..................................26

Figure 4.6: A) H-M plot and B) relative magnetic permeability of common diamagnetic materials .........................................................................................................................27

Figure 4.7: A) H-M plot and B) relative magnetic permeability of common paramagnetic materials ..................................................................................................................28

Figure 4.8: Orientation of the magnetic dipole moments in ferromagnetic materials; long range order of the magnetic dipoles is observed .........................................................29

Figure 4.9: Orientation of the magnetic dipole moments in antiferromagnetic materials; long range order of the magnetic dipoles is observed .........................................................30
Figure 4.10: Orientation of the magnetic dipole moments in ferrimagnetic materials; long range order of the magnetic dipoles is observed .................................................................30

Figure 4.11: Néel (top) vs. Brownian (bottom) magnetic moment reorientation mechanisms ..................................................................................................................32

Figure 4.12: Brownian and Néel relaxation times for the 15 nm diameter SPIONs. ........33

Figure 4.13: Biot-Savart relationship for a current element ........................................34

Figure 4.14: Geometry of finite thickness solenoid .....................................................35

Figure 4.15: A pair of finite length and thickness solenoids in series .........................36

Figure 4.16: Magnetic flux density between an identical solenoid pair; A) on-axis values using Equation 4.22, and B) contour simulated using FEMM .................................37

Figure 4.17: Interaction energies for a magnetic dipole pair ......................................40

Figure 4.18: Comparison between the magnetic dipole and external field gradient forces...42

Figure 4.19: The magnetic capture radius for SPION aggregates of various size based upon VSM data of Chapter 5 .................................................................43

Figure 4.20: Calculated Brownian rotation angle of a model spherical SPION over time in oscillating magnetic fields: A) magnetic moment rotation slowed down by smaller flux density (top), by sinusoidal waveform (middle), and by higher matrix viscosity (bottom), and B) slow magnetic moment rotation (top) or incomplete rotation (middle and bottom) with increasing field oscillation frequency ........................................................................................................46

Figure 4.21: Reorientation of a permanent magnet due to oscillations in the external field ...............................................................................................................................47

Figure 4.22: Schematic of SPION assembly using a static magnetic field: A) SPION aggregate with zero magnetic remanence due to randomly orientated magnetic moments, B) reorientation of SPION magnetic moments along the external static field direction forming a high, locally induced magnetic field gradient, and C) needle-like anisotropic SPION aggregate due to lateral assembly. Not to be scaled; more particles exist within the aggregates and assemblies ........................................................................................................49

Figure 4.23: Schematics of SPION assembly behaviors as a magnetic field is applied and as the field direction is switched. Not to be scaled; more particles exist within the aggregates and assemblies .................................................................51

Figure 4.24: COMSOL simulation domain for magnetic particle interaction ..............52

Figure 4.25: Simulation setup for moving magnetic particle interactions .................53
Figure 4.26: The magnetization (top) of one iron particle in a DC magnetic field of 50 G; the vectors represent the direction of the magnetic field, the legend represents the magnetic flux density in Gauss, and the axis are in µm. The displacement (bottom) of the iron particle with respect to time.......................55

Figure 4.27: Interaction between a pair of 2D, homogenous magnetic particles at different orientations: A) slight repulsion, B) slight attraction, and C) attraction between the particles due to interactions between their induced magnetic fields..........................................................................................................................56

Figure 4.28: The attraction between two iron particles at 200 µm (top) and 170 µm (bottom) separation .................................................................................................................................57

Figure 4.29: Induced magnetic dipole interactions between 10 2D iron particles at a magnetic flux density of 100 G. The dashed arrows indicate the particle direction of motion. The legend is in Gauss, and the axis are in µm ............58

Figure 5.1: TEM images of the as-received SPIONs at different magnifications: A) 5800x and B) 79000x..........................................................................................................................60

Figure 5.2: Optical microscope images of the SPIONs dispersed in a DI water matrix at volume fractions of A) 0.04 and B) 0.08 vol% ..............................................................60

Figure 5.3: VSM of the SPIONs demonstrating the saturation magnetization and no magnetic hysteresis ......................................................................................................................61

Figure 5.4: A) Digital image and B) schematic of the magnetic assembly set-up.............62

Figure 5.5: Optical microscope images of SPION aggregate assembly in DI water due to application of an external magnetic field.................................................................64

Figure 5.6: Assembly morphology variations of 0.06% volume fraction SPIONs in DI water with time. A) and B) demonstrate morphology variations for a DC field at 15 and 30 minutes, respectively. C) and D) represent variations for an oscillating 0.1 Hz AC field at 15 minutes and 25 minutes, respectively. E) and F) represent variations for a pulsed 0.1 Hz AC field at 15 minutes and 23 minutes, respectively..............................................................65

Figure 5.7: A) Optical microscope input image of SPION assembly in DI water (0.08 vol%, ± 50 G, 1.0 Hz square waveform at 15 minutes) used for B) image processing. C) The characteristic dimensions of the SPION assemblies .........67

Figure 5.8: Optical microscope images of SPION assembly in DI water (0.04 vol%): A) needle-like assemblies upon static field application and B) zipperng ............68

Figure 5.9: Optical microscope images of SPION assembly in DI water (0.04 vol%): A) free aggregates in matrix due to magnetic field below the threshold, B) full assembly of aggregates due to an increased magnetic field, and C) reduction in assembly length due to an increased field frequency .........................68

x
Figure 5.10: A) Selected optical microscope images of SPION assemblies in DI water (0.04 vol%) using a square oscillating magnetic field with varying flux density and frequency. Corresponding characteristic dimensions of the SPION assemblies for the 50 G and 100 G flux densities: average B) separation, C) length, and D) width. A 95% bootstrap confidence interval based upon the mean parameter values is indicated in the figures........................70

Figure 5.11: Characteristic dimensions of SPION assemblies (0.04% volume fraction in DI water) using a square oscillating magnetic field (50 G) below 1 Hz. A 95% bootstrap confidence interval based upon the mean parameter values is indicated in the figure .................................................................72

Figure 5.12: Dependence of the characteristic dimensions on magnetic flux density for a SPION volume fraction of 0.04%. A 95% bootstrap confidence interval based upon the mean parameter values is indicated in the figure ....................73

Figure 5.13: Characteristic dimensions of SPION assemblies in DI water using oscillating magnetic fields of varying magnetic flux density, frequency, and waveform: A) 0.04 vol%, square waveform and B) 0.02 vol% sinusoidal waveform. A 95% bootstrap confidence interval based upon the mean parameter values is indicated in the figure .................................................................75

Figure 5.14: Characteristic dimensions of SPION assemblies in DI water using oscillating magnetic fields with square waveform of varying SPION volume fractions....77

Figure 5.15: A) TEM image and B) VSM plot of ferrimagnetic Fe$_3$O$_4$. Taken from www.us-nano.com (US7568)...............................................................................................78

Figure 5.16: Magnetic assembly comparison of A) SPIONs and B) ferrimagnetic Fe$_3$O$_4$ (both 0.04 vol% in DI water) by optical microscope images and measured characteristic dimensions ............................................................................79

Figure 5.17: ‘Breathing’ of ferrimagnetic nanoparticle (Fe$_3$O$_4$ at 0.04% volume fraction in DI water) assemblies due to a sinusoidal waveform at an external magnetic field of 50 G, frequency of 0.05 Hz, and assembly time of 10 minutes. The time between each successive image (A-E) is approximately 2 seconds. (F) Ferrimagnetic nanoparticle assembly morphology for a 50% duty cycle square waveform at the above assembly parameters – ‘breathing’ of the assemblies is not observed ..............................................................................80

Figure 6.1: TEM images of the maghemite nanoparticles at different scales: A) nanoparticles within an aggregate, B) multiple aggregate, and C) large aggregates........................................................................................................84

Figure 6.2: Optical microscope images of the maghemite nanoparticles (0.04% volume fraction in DI water): A) as-received, B) dry-processed (mortar and pestle) and C) wet-processed (ball-milled)........................................................84
Figure 6.3: DLS results of the as-received and ball-milled maghemite nanoparticles dispersed in water; each plot is the average value over three consecutive measurements...85

Figure 6.4: VSM plot of the as-received maghemite nanoparticles: (left) full-range plot, and (right) plot of a selected range near 0 kA/m...86

Figure 6.5: X-ray diffraction plot of the as-received maghemite nanoparticles, aligned with the theoretical peak values of maghemite...87

Figure 6.6: BET surface area plot for the as-received maghemite nanoparticles...88

Figure 6.7: Process to attached the silane surface modifier GPS to the surface of the maghemite aggregates: A) the chemical structure of the selected surface modifier GPS, B) hydrolysis of the surface modifier, C) hydrogen bond formation with the maghemite aggregates, and D) covalent bond formation due to a loss of water...90

Figure 6.8: ATR FTIR absorbance spectrum of the A) as-received maghemite, B) GPS surface modifier, and C) the surface modified maghemite nanoparticles (GPS-γ-Fe₂O₃) using the dry-process...93

Figure 6.9: DRIFTS absorbance spectrum of the A) as-received maghemite, and B) surface modified maghemite nanoparticles (GPS-γ-Fe₂O₃) using the dry-process...93

Figure 6.10: PNC samples prepared to investigate the effect of a surface modifier on reducing nanoparticle sedimentation: A) schematics showing the cut section location, and B) optical microscope images showing the sedimentation (lighter regions) close to the bottom surface of the PNC samples consisting of the as-received and dry- and wet-processed surface modified maghemite nanoparticles...94

Figure 6.11: The viscosity vs. temperature of EPON 862 (bisphenol-F type)...96

Figure 6.12: Chemical structures of A) bisphenol-F, B) DETDA and C) bonding of the bisphenol-F resin with DETDA and DETDA with the surface modified maghemite nanoparticles (GPS-γ-Fe₂O₃)...96

Figure 6.13: Magnetic assembly set-up using a solenoid pair: digital images of A) experimental components, B) solenoids and C) mold, and D) schematic...98

Figure 6.14: Magnetic assembly set-up using a Helmholtz coil: digital images of A) triaxial Helmholtz coil, B) LabVIEW user interface to control the generated magnetic fields and C) power supply work station, and D) schematic...100
Figure 6.15: Schematic showing sections extracted from PNCs fabricated using nanoparticles with dry- and wet-processes for characterization. The nanoparticle assemblies are orthogonal to the cross-sectional plane for the axial (A) direction, and parallel to the cross-sectional plane for transverse (T) direction ............................................................................................................. 101

Figure 6.16: Nomenclature designation for the fabricated PNCs ................................................................. 101

Figure 6.17: Estimation of the sample surface area through image processing using ImageJ Fiji ............................................................................................................................................. 104

Figure 6.18: Optical microscope images of the PNC samples with dry-processed nanoparticles (bulk volume fraction of 5%) with varying assembly conditions and sample orientations/locations. The nanoparticle assemblies are the lighter regions in the images ............................................................................................................. 106

Figure 6.19: Comparison of optical microscope images for PNC samples with dry-processed nanoparticles (bulk volume fraction of 5%, sinusoidal, axial) at center vs. edge locations. The nanoparticle assemblies are the lighter regions in the images ............................................................................................................. 107

Figure 6.20: Optical microscope images of the PNC samples with wet-processed nanoparticles (center location) with varying assembly conditions and sample orientations. The nanoparticle assemblies are the lighter regions in the images ............................................................................................................. 108

Figure 6.21: Optical microscope images of the PNC samples with wet-processed nanoparticles (center location, axial direction) with varying assembly condition (DC vs. sinusoidal) and volume fractions. The nanoparticle assemblies are the lighter regions in the images ............................................................................................................. 109

Figure 6.22: Extracted section from bulk PNC sample for microCT evaluation .............................................. 110

Figure 6.23: Axial views of microCT tomograms of PNCs with dry-processed nanoparticles at varying volume fractions and different sample locations. The rectangular region enclosed within the dashed lines (--) corresponds to the PNC sections prepared for property characterization. The nanoparticle assemblies are indicated by the lighter regions in the images ............................................................................................................. 112

Figure 6.24: Transverse views of microCT tomograms of PNCs with dry-processed nanoparticles at varying volume fractions and different sample locations. The rectangular region enclosed within the dashed lines (--) corresponds to the PNC sections prepared for property characterization. The nanoparticle assemblies are indicated by the lighter regions in the images ............................................................................................................. 113

Figure 6.25: Transverse and axial views of microCT tomograms of PNCs with wet-processed nanoparticles at varying volume fractions. The nanoparticle assemblies are indicated by the lighter regions in the images ............................................................................................................. 114
Figure 6.26: Comparison of pristine vs. segmented tomograms of a PNC sample with dry-processed nanoparticles (bulk 5%) assembled using a sinusoidal field (axial direction). The nanoparticle assemblies are indicated by the lighter regions in the images .......................................................... 115

Figure 6.27: Binary segmented microCT tomograms of PNCs with dry-processed nanoparticles at varying nanoparticle volume fractions and sample locations. The nanoparticle assemblies are indicated by the lighter regions in the images .................................................................................. 116

Figure 6.28: A three-dimensional rendering of the microCT tomograms for the PNC samples with dry-processed nanoparticles (5.0 % bulk volume fraction) assembled using DC vs. sinusoidal field .................................................. 117

Figure 7.1: A) Schematic and B) digital image of the set-up to measure DC volume resistivity of PNC samples. C) Schematic of PNC sample placement against the electrodes to measure anisotropic electrical properties .................................. 120

Figure 7.2: Steady-state current-voltage response of the unmodified matrix ............. 121

Figure 7.3: Measured electrical resistivity data, normalized by the unmodified matrix resistivity ($\rho_{\text{PNC}}/\rho_m$), for the PNC samples with dry-processed maghemite nanoparticles ........................................................................................................ 124

Figure 7.4: Estimated percolation threshold observed with the measured axial electrical resistivity data for PNC samples prepared with dry-processed maghemite particles using A) DC and B) sinusoidal fields, at the edge location. The power law correlation (--) and the parallel model (—) with varying baseline maghemite resistivity values are also plotted ........................................... 126

Figure 7.5: Tailoring of nanoparticle interfaces to control charge carrier pathways by modification of the external field waveform: A) DC and B) sinusoidal. A shorter pathway produces reduced resistance. Insert images were captured from microCT of Section 6.3 and are the approximate dimensions of the measured samples ........................................................................................................ 127

Figure 7.6: Estimated percolation threshold observed with the measured transverse electrical resistivity data for PNC samples prepared with dry-processed nanoparticles using A) DC and B) sinusoidal fields. The power law correlation (--) and the parallel model (—) with varying baseline maghemite resistivity values are also plotted .......................................................... 128

Figure 7.7: Digital images of the A) test fixture and B) experimental set-up for comparative IR microscopy. C) Schematic for the PNC sample orientation within the test fixture to measure anisotropic thermal conductivities .......... 130

Figure 7.8: Digital images of temperature map across the three-layer stack (reference-sample-reference): during A) emissivity and B) conductivity measurements .. 131
Figure 7.9: Measurement of the PNC sample thermal conductivity using comparative IR microscopy: A) temperature gradient plot and B) temperature map across the three-layer stack (reference-sample-reference) .......................................................... 132

Figure 7.10: Estimation of the PNC sample thermal conductivity through a linear regression of the four-measurement temperature heat flux and temperature gradients as output from the measurement code. Example linear regression of selected wet-processed PNC samples are shown.......................................................... 133

Figure 7.11: Measured thermal conductivity data, normalized by the unmodified matrix conductivity ($k_{PNC}/k_m$), of PNC samples with dry-processed nanoparticles assembled using a DC field. The dotted lines (---) are just guidelines. The solid line (—) is the conductivity calculated from the parallel model using three different element conductivities .......................................................... 136

Figure 7.12: Measured thermal conductivity data, normalized by the unmodified matrix conductivity ($k_{PNC}/k_m$), of PNC samples with dry-processed nanoparticles assembled using a sinusoidal field. The dotted lines (---) are just guidelines. The solid line (—) is the conductivity calculated from the parallel model using three different element conductivities .......................................................... 136

Figure 7.13: Measured thermal conductivity data, normalized by the unmodified matrix conductivity ($k_{PNC}/k_m$), of PNC samples with wet-processed nanoparticles assembled using a DC field (top) and sinusoidal field (bottom). The dotted lines (---) are just guidelines. The solid line (—) is the conductivity calculated from the element conductivity using the parallel model ................. 137

Figure 8.1: Design space for nanofiller assembly using an oscillating magnetic field. It is assumed that the nanoparticles are undergoing a Brownian magnetic moment reorientation mechanism .......................................................... 145

Figure 8.2: Flow chart for tailored PNCs using oscillating magnetic fields .................. 151

Figure B.1: A) Optical microscope image of SPION assembly after 15 minutes of field application for a volume fraction of 0.04% and a field condition of ±100 G, 0.1 Hz square waveform. Corresponding histograms for the characteristic dimensions: B) length, C) separation, and D) width ......................................................... 170

Figure B.2: A) Optical microscope image of SPION assembly after 15 minutes of field application for a volume fraction of 0.06% and a field condition of 100 G DC. Corresponding histograms for the characteristic dimensions: B) length, C) separation, and D) width ......................................................... 171

Figure B.3: A) Optical microscope image of SPION assembly after 15 minutes of field application for a volume fraction of 0.08% and a field condition of ±50 G, 1.0 Hz square waveform. Corresponding histograms for the characteristic dimensions: B) length, C) separation, and D) width ......................................................... 172
Figure C.1: Optical microscope images of the PNC samples with wet-processed nanoparticles (edge location, axial direction) with varying volume fractions at a DC field (300 G). The inspection regions (bottom, middle, and top of the sample) are indicated. The nanoparticle assemblies are the lighter regions in the images .........................................................174

Figure C.2: Optical microscope images of the PNC samples with wet-processed nanoparticles (center and edge location, axial direction) with varying volume fractions and DC field (300 G). The nanoparticle assemblies are the lighter regions in the images .........................................................175

Figure D.1: Current-voltage trends of A) two unmodified matrix samples and B) one pure (cold-sintered) maghemite sample .................................................................179

Figure D.2: Current-voltage trends for a PNC sample with randomly orientated (no magnetic field) nanofiller ........................................................................................................179

Figure D.3: Current-voltage trends for selected dry-processed PNCs. A) DC, axial, center location at 1.4 vol%, B) DC, axial, edge location at 1.3 vol%, C) sinusoidal, axial, center location at 1.3 vol%, and D) sinusoidal, axial, edge location at 0.5 vol%. Onset of the nonlinear current-voltage trends are shown in B) and D) for a DC and sinusoidal waveform, respectively. Corresponding microCT tomograms are also indicated in the figure (approximately 5 mm x 5 mm) ................................................................................180

Figure D.4: Current-voltage trends for selected wet-processed PNCs. A) DC, axial, center location at 1.5 vol%, B) DC, axial, center location at 1.9 vol%, C) DC, axial, center location at 4.0 vol%, and D) sinusoidal, axial, center location at 3.6 vol% .........................................................181

Figure E.1: Nanoindentation experimental set-up: A) digital image of the sample platform with automated indentation head and microscope, B) digital image of PNC samples embedded in the epoxy, and C) Schematic of PNC sample placement against the indentation tip to measure anisotropic mechanical properties ..................................................................................183

Figure E.2: Nanoindentation grid locations on a sample cross-section: A) schematic showing nanoindentation locations at the top, middle, and bottom, and B) SEM image of an exemplary 9x9 indentation grid .........................................................184

Figure E.3: Example load-displacement curve measured about a PNC sample with wet-processed nanoparticles (DC, axial, 1.9 vol%, center location) .........................................................184

Figure E.4: Measured reduced elastic modulus for A) dry- and B) wet-processed PNC samples. The standard deviation is indicated ................................................................................187

Figure E.5: Measured hardness for A) dry- and B) wet-processed PNC samples. The standard deviation is indicated ................................................................................188
List of Tables

Table 4.1: Curie temperatures of ferromagnetic materials ........................................ 24
Table 4.2: Summary of characteristics of magnetic materials ..................................... 27
Table 4.3: Properties of soft and hard ferromagnetic materials .................................. 29
Table 4.4: The Néel temperature for several antiferromagnetic materials .................... 30
Table 4.5: Relative magnetic permeability of several ferrimagnetic materials ............... 31
Table 4.6: Percent ratio of Brownian and gravitational motion for a model SPION aggregate after 30 minutes .......................................................... 45
Table 5.1: Comparison between prepared SPION volume fractions and the SPION area fractions as measured using the optical microscope .......................... 63
Table 6.1: Effect of the dry- and wet-processing on the maghemite aggregate size (measured) and their sedimentation and assembly (estimated) ....................... 92
Table 6.2: Summary of the two methods of PNC fabrication in this work ....................... 97
Table 6.3: Geometry, mass, and volume fractions of extracted sections for PNC samples with dry-processed nanoparticles assembled with magnetic fields (300 G DC and 300 G peak 0.05 Hz sinusoidal) ........................................ 103
Table 6.4: Geometry, mass, and volume fractions of extracted sections for PNC samples with wet-processed nanoparticles assembled with magnetic fields (300 G DC and 300 G peak 0.05 Hz sinusoidal) ........................................ 104
Table 6.5: List of PNC samples (magnetically assembled with 30 G DC or 300 G peak 0.05 Hz sinusoidal) inspected using microCT and test parameters ...................... 110
Table 7.1: Electrical resistivity values for the PNC samples with dry-processed maghemite nanoparticles. The volume fraction is indicated by $vf$ .................. 123
Table 7.2: Electrical resistivity values for the PNC samples with wet-processed maghemite nanoparticles. The volume fraction is indicated by $vf$ .................. 123
Table 7.3: Thermal conductivity values for the PNC samples with dry-processed maghemite nanoparticles. The volume fraction is indicated by $vf$ ................ 134
Table 7.4: Thermal conductivity values for the PNC samples with wet-processed maghemite nanoparticles. The volume fraction is indicated by $vf$ ................ 135
Table E.1: Nanoindentation sample list with varying volume fractions assembled with an external magnetic field (300 G DC and 300 G peak 0.05 Hz sinusoidal) .... 183
Table E.2: Elastic modulus and hardness averaged over the 3x3 indentations. The error indicated is represented by the standard deviation of the 9 measurements. 

\begin{center}
\begin{tabular}{|c|c|}
\hline
\textbf{Sample} & \textbf{Elastic Modulus (GPa)} \\
\hline
Sample A & 1.23 \pm 0.05 \\
Sample B & 1.34 \pm 0.07 \\
Sample C & 1.45 \pm 0.09 \\
\hline
\end{tabular}
\end{center}
## Acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1D, 2D, 3D</td>
<td>One-, two-, and three-dimensional, respectively</td>
</tr>
<tr>
<td>A</td>
<td>Axial</td>
</tr>
<tr>
<td>AC</td>
<td>Alternating current</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated total reflection</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>C</td>
<td>Center</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge coupled device</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon nanotube</td>
</tr>
<tr>
<td>CNF</td>
<td>Carbon nanofiber</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current (static)</td>
</tr>
<tr>
<td>DETDA</td>
<td>Diethyltoluenediamine</td>
</tr>
<tr>
<td>DI</td>
<td>Deionized</td>
</tr>
<tr>
<td>DLS</td>
<td>Dynamic light scattering</td>
</tr>
<tr>
<td>DRIFTS</td>
<td>Diffuse reflectance infrared Fourier-transform spectroscopy</td>
</tr>
<tr>
<td>E</td>
<td>Edge</td>
</tr>
<tr>
<td>EDTA</td>
<td>Ethylenediaminetetraacetic acid</td>
</tr>
<tr>
<td>FDD</td>
<td>Focus-to-Detector Distance</td>
</tr>
<tr>
<td>FEMM</td>
<td>Finite element method magnetics</td>
</tr>
<tr>
<td>FOD</td>
<td>Focus-to-Object Distance</td>
</tr>
<tr>
<td>FRP</td>
<td>Fiber-reinforced composites</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier-transform infrared spectroscopy</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>Magnetite</td>
</tr>
<tr>
<td>$\alpha$-Fe$_2$O$_3$</td>
<td>Hematite</td>
</tr>
<tr>
<td>$\gamma$-Fe$_3$O$_3$</td>
<td>Maghemite</td>
</tr>
<tr>
<td>GPS-$\gamma$-Fe$_3$O$_3$</td>
<td>Surface modified (GPS) maghemite</td>
</tr>
<tr>
<td>GPS</td>
<td>3-glycidoxypropyl trimethoxysilane</td>
</tr>
<tr>
<td>H-M</td>
<td>Field strength vs. magnetization</td>
</tr>
<tr>
<td>IPA</td>
<td>Isopropyl alcohol</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>LCR</td>
<td>Inductance-capacitance-resistance</td>
</tr>
<tr>
<td>microCT</td>
<td>Micro computed tomography</td>
</tr>
<tr>
<td>ODE</td>
<td>Ordinary differential equation</td>
</tr>
<tr>
<td>PNC</td>
<td>Polymer nanocomposite</td>
</tr>
<tr>
<td>RMS</td>
<td>Root mean square</td>
</tr>
<tr>
<td>RPM</td>
<td>Revolutions per minute</td>
</tr>
<tr>
<td>SPION</td>
<td>Superparamagnetic iron oxide nanoparticle</td>
</tr>
<tr>
<td>T</td>
<td>Transverse</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TVS</td>
<td>Transient-voltage-suppression</td>
</tr>
<tr>
<td>VSM</td>
<td>Vibrating sample magnetometer</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
</tbody>
</table>
Nomenclature

\[ \begin{align*}
A & \quad \text{Hamaker constant} \\
A_p & \quad \text{Projected nanoindentation area} \\
A_{PNC}, a_{\text{sam}} & \quad \text{Cross-sectional area} \\
a, a_1, a_2, a_3, a_4 & \quad \text{Radius of current loop} \\
a_s & \quad \text{Specific surface area} \\
a_y & \quad \text{Y-intercept} \\
B, B, B_z & \quad \text{Magnetic flux density} \\
B_{thr} & \quad \text{Magnetic threshold} \\
b & \quad \text{Slope} \\
c & \quad \text{BET parameter} \\
d & \quad \text{Aggregate radius} \\
d & \quad \text{Particle diameter} \\
d_h & \quad \text{Interplanar spacing} \\
d_{\text{SPION}} & \quad \text{SPION diameter} \\
E, E & \quad \text{Electric field} \\
E_{es} & \quad \text{Electrostatic repulsive energy} \\
E_m, E_{md}, E_{mds} & \quad \text{Magnetic energy} \\
E_{PNC}, E_m & \quad \text{Reduced elastic modulus of sample and matrix, respectively} \\
E_r & \quad \text{Reduced elastic modulus} \\
E_s & \quad \text{Steric repulsive energy} \\
E_{vdw} & \quad \text{Van der Waals energy} \\
e & \quad \text{Unit charge} \\
F_d, F_{dr} & \quad \text{Drag force due to translation and rotation, respectively} \\
F_m, F_{m,x} & \quad \text{Magnetic force} \\
F_{m,d}, F_{m,ds} & \quad \text{Magnetic dipole force} \\
f & \quad \text{Frequency} \\
g & \quad \text{Gravitational acceleration} \\
H, H & \quad \text{Magnetic field strength} \\
H_c & \quad \text{Magnetic coercivity} \\
H_p & \quad \text{Hardness}
\end{align*} \]
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_{PNC}$, $H_m$</td>
<td>Hardness of sample and matrix, respectively</td>
</tr>
<tr>
<td>$h$</td>
<td>Nanoindentation depth</td>
</tr>
<tr>
<td>$I$</td>
<td>Moment of inertia</td>
</tr>
<tr>
<td>$i$</td>
<td>Current</td>
</tr>
<tr>
<td>$J$</td>
<td>Current density</td>
</tr>
<tr>
<td>$K$</td>
<td>Anisotropic energy density</td>
</tr>
<tr>
<td>$k$</td>
<td>Thermal conductivity</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann’s constant</td>
</tr>
<tr>
<td>$k_m$, $k_f$</td>
<td>Matrix and particle thermal conductivity, respectively</td>
</tr>
<tr>
<td>$k_{PNC}$, $k_{REF}$</td>
<td>Sample and reference thermal conductivity, respectively</td>
</tr>
<tr>
<td>$L_s$, $L_s1$, $L_s2$</td>
<td>Solenoid length</td>
</tr>
<tr>
<td>$l$</td>
<td>Surface-to-surface distance between particles</td>
</tr>
<tr>
<td>$M$, $M$</td>
<td>Magnetization</td>
</tr>
<tr>
<td>$M_r$, $M_s$</td>
<td>Magnetic remanence and saturation, respectively</td>
</tr>
<tr>
<td>$m$, $m_i$, $m_j$, $m$</td>
<td>Magnetic dipole moment</td>
</tr>
<tr>
<td>$m_m$, $m_p$</td>
<td>Particle mass</td>
</tr>
<tr>
<td>$m_{orb}$, $m_{spin}$</td>
<td>Electron orbital and spin moment, respectively</td>
</tr>
<tr>
<td>$m_s$</td>
<td>GPS mass for minimum monolayer covering</td>
</tr>
<tr>
<td>$m_{sam}$</td>
<td>Sample mass</td>
</tr>
<tr>
<td>$m_{wa}$</td>
<td>Molecular weight of cross-linker</td>
</tr>
<tr>
<td>$m_{wi}$</td>
<td>Molecular weight of the internal maghemite</td>
</tr>
<tr>
<td>$m_{ws}$</td>
<td>Molecular weight of functionalization sites</td>
</tr>
<tr>
<td>$N$, $N_1$, $N_2$</td>
<td>Number of turns</td>
</tr>
<tr>
<td>$N_A$</td>
<td>Avogadro’s number</td>
</tr>
<tr>
<td>$n$</td>
<td>Bragg’s law positive integer</td>
</tr>
<tr>
<td>$n_i$</td>
<td>Independent parameter</td>
</tr>
<tr>
<td>$n_m$</td>
<td>Monolayer amount</td>
</tr>
<tr>
<td>$P$</td>
<td>Nanoindentation load</td>
</tr>
<tr>
<td>$P_{max}$</td>
<td>Maximum indentation load</td>
</tr>
<tr>
<td>$P/P_0$</td>
<td>Relative pressure</td>
</tr>
<tr>
<td>$Q$</td>
<td>Amount of gas absorbed</td>
</tr>
<tr>
<td>$q$</td>
<td>Particle charge</td>
</tr>
</tbody>
</table>
$q_1, q_{avg}$  Heat flux

$R$  Resistance

$\hat{r}, r_j$  Vector between the two magnetic dipoles

$r_c$  Magnetic capture radius

$r_{pj}, r_{1}, r_{2}$  Particle radius

$s_{WS}$  Specific wetting surface

$T$  Temperature

$T_m, T_m$  Magnetic torque

$T_x, T_y$  Maxwell stress tensor

$t$  Time

$t_c$  Critical exponent

$t_{sam}, t_{PNC}$  Thickness

$t_w$  Working life

$U$  Potential energy

$V$  Volume

$V_0$  Power law constant

$V_c, V_h$  Magnetic core and hydrodynamic volume, respectively

$V_i$  Voltage

$v$  Particle velocity

$v_{j}, v_{c}$  Sample and percolation volume fraction, respectively

$x, x_{1}, x_{2}, x_{3}, x_{4}$  On-axis distance from the center of a current loop

$\beta$  Ionic strength

$\beta_a$  Percent mass of surface modifier to cross-linker

$\beta_s$  Surface modifier constant

$\gamma, \gamma_k$  Ratio between Brownian motion to gravitational displacement

$\gamma_1$  Brownian motion mean displacement

$\gamma_2$  Gravitational displacement

$\nabla$  Del operator

$\delta$  Length of absorbed molecules

$\delta_a$  Interaggregate separation

$\varepsilon$  Dielectric constant

$\varepsilon_0$  Vacuum permittivity
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\zeta$</td>
<td>Magnetic field distance</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Viscosity</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Angle</td>
</tr>
<tr>
<td>$\theta_b$</td>
<td>XRD scattering angle</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Magnetic potential energy to thermal energy</td>
</tr>
<tr>
<td>$\lambda_b$</td>
<td>Wavelength</td>
</tr>
<tr>
<td>$\mu, \mu_r$</td>
<td>Magnetic and relative permeability, respectively</td>
</tr>
<tr>
<td>$\mu_0$</td>
<td>Permeability of free space</td>
</tr>
<tr>
<td>$\xi$</td>
<td>Surface concentration of absorbed molecules</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Total electric charge density</td>
</tr>
<tr>
<td>$\rho, \rho_m$</td>
<td>Matrix density</td>
</tr>
<tr>
<td>$\rho_{PNC}, \rho_m, \rho_f$</td>
<td>Sample, matrix, and particle electrical resistivity, respectively</td>
</tr>
<tr>
<td>$\rho_s$</td>
<td>Particle density</td>
</tr>
<tr>
<td>$\tau_0$</td>
<td>Larmor frequency</td>
</tr>
<tr>
<td>$\tau_B, \tau_N$</td>
<td>Brownian and Néel relaxation time, respectively</td>
</tr>
<tr>
<td>$\chi, \chi_b, \chi_m$</td>
<td>Magnetic volume susceptibility</td>
</tr>
<tr>
<td>$\psi, \psi_1, \psi_2$</td>
<td>Particle surface potential</td>
</tr>
</tbody>
</table>
Acknowledgements

I would like to thank my advisor Professor Namiko Yamamoto for her continued support and guidance in achieving this milestone in my life. I would also like to thank my committee members, Professor Christine Keating, Professor George Lesieutre, and Professor Raymond Schaak, for their encouraging feedback.

I would not have been able to complete the work in dissertation without the assistance of talented collaborators: Dr. Thomas Juska (ARL), Jeff Long (ECL), Dr. Amira Meddeb (ECL), Professor vonLockette (MACS), Corey Breznak (MACS), Manuel Villalpando (MCL), Gino Tambourine (MCL), Dr. Katya Bazilevskaya (MCL), Professor Amy Marconnet (MTEC), Albrea Alsaati (MTEC), Tim Stecko (XMEN), and Dr. Anna Madra (XMEN).

In addition, I would like to thank my lab mates, Jingyao Dai, Yagmur Atescan, Jatin Haibat, Shreya Trivedi, Ricardo Branco and Charis Lin, for their continued support. I would not have been able to complete the necessary data collection of Chapter 5 without the assistance of David Gao.

I am grateful for the support from the Pennsylvania State University Department of Aerospace Engineering and the Hartz Family Career Development Professorship in Engineering. This material is based upon work supported by the Office of Naval Research under Award No. N00014161217. Any opinions, findings, and conclusions or recommendations expressed in this publication are those of the author and do not necessarily reflect the views of the Office of Naval Research.

Lastly, I would like to thank my family and friends, whom this dissertation is dedicated to.
Chapter 1

Introduction

In the last three decades, fiber-polymer composites have driven aerospace design due to their light weight and high specific strength [1,2], leading to cost reductions between $100 to $2000 per kilogram over their life cycle [3]. Recently, further performance improvement of such composites has been attempted with nanoscale additives (< 100 nm), or nanofillers, to provide so-called polymer nanocomposites (PNCs) (see Figure 1.1). With nanofillers, PNCs can improve upon the mechanical properties of fiber-polymer composites [4,5], including tolerance against delamination, matrix cracking, and fatigue damage, and also to add currently missing electrical and thermal conductivities to protect against electrostatic dissipation and lightning strikes [6].

The effective property enhancement with nanofillers at low volume fractions is enabled by their small size and large interfacial surface area [7–9], in addition to interconnected structures and boundary conditions. Nanofillers, both organic (nanodiamond [10], carbon nanotubes [11], carbon nanofibers [12], and graphene nanosheets [13]) and inorganic (iron oxide [14], silica [15], or silver [16]) have provided PNCs with multi-functional properties such as optical transparency [17,18], thermal stability [19], mechanical strength [20–22], electrical conductivity [12,23], radiation shielding [24], photo [25] or mechanical [26] actuation and more [27–30]. While driven by the advanced properties of nanofillers themselves, such advanced properties of PNCs are also dependent on the structure of the nanofillers within the polymer matrix [31–40]. Structuring of nanofillers can provide anisotropic property control based upon the property of interest, such as anisotropic electrical conductivity due to charge carrier pathway formation [12] or anisotropic mechanical properties due to nanofiller orientation [8,18,41–43]. PNC properties are also affected by their interfaces or boundary conditions between nanofillers and between nanofillers and polymer matrix [18,20,31,44]. Such boundary effects on PNC properties are different for each property; nanofiller interfaces can enhance local plastic deformation and crack deflection improving mechanical properties [15,21,22,45–47], while increasing phonon scattering to reduce thermal conductivity [48–52]. Surface modification of nanofillers can improve the interactions between nanofillers and polymers. Such a modification can further improve PNC mechanical properties as stress is efficiently transferred to the nanofiller [53] or enhance thermal conductivity through a
reduced thermal boundary resistance [54] and even improve thermal stability [55]. Surface modification of the nanofiller is critical not only for property enhancement, but also for improved nanofiller dispersion and suspension within polymer matrices due to their large surface area [7]. While the above demonstrates the usefulness of nanofillers to enhance PNC properties, bulk application of PNCs has not been achieved due to unknown multi-scale structure-property relationships and missing scalable fabrication. PNCs often exhibit smaller property improvements than theoretical predictions when characterized at the macro scale, even with organized implementation of nanofillers [28,48,56,57]. The difficulty in controlling interfaces [51,58], poorly organized nanofillers [59], and weak interphase property control [60,61] all contribute to uncertainty in the structure-property relationships of PNCs. The controlled implementation of the nanofiller, including the precise and tunable tailoring of the nanofiller structures and control of the nanofiller boundary conditions, are critical to study in order to supply bulk, or large-sized, PNCs with organized structures with the desired property enhancement.

Thus, in this work, I aim to provide a novel and potentially scalable method to manufacture PNCs with tailored nanofiller structures, including inter-nanofiller contacts, and improved nanofiller interfaces using oscillating magnetic fields. An oscillating field is expected to produce rotation of the induced nanofiller magnetic moments supplying an additional mechanism to control the structure and interface of nanofillers. Magnetic assembly behaviors are studied both experimentally and theoretically using a model case of superparamagnetic iron oxide nanofillers. Then, the obtained assembly knowledge is used to fabricate sizable PNCs with ferrimagnetic nanofillers and different one-dimensional (1D) nanofiller assembly patterns. The ferrimagnetic nanofillers are also surface modified to have improved interfaces within the selected aero-grade thermoset matrix. The fabricated PNC samples are characterized for their nanofiller structures, and electrical and thermal properties; the obtained data is correlated for structure-interface-property relationships. By overcoming the challenges limiting bulk application of PNCs, such as poor scalability and uncertain structure-property correlations, PNCs can be tailored for application specific designs leading to high performance materials at low density, which is critical for the future advancement of aerospace materials.

The dissertation chapters are organized as follows. In Chapter 2, previous and state-of-the-art work will be discussed about the structure-interface-property relationships of PNCs and about manufacturing techniques for top-down and field-assisted, particularly magnetic, manufacturing of PNCs. In Chapter 3, the objectives and approaches of this PhD work are discussed: scalable, and bulk, manufacturing of PNCs through a novel methodology using oscillating magnetic fields to
organize nanofillers and understand their interface effects. In Chapter 4, review of magnetism and theoretical studies about magnetic nanofiller assembly within polymer matrices by externally applied fields will be discussed. In Chapter 5, experimental studies about magnetic nanofiller assembly will be presented for model superparamagnetic iron oxide nanoparticles in a low viscosity matrix (water) using an external magnetic field. These experimental data are compared with the theoretical studies presented in Chapter 4. In Chapter 6, based on the nanofiller assembly study of Chapter 5, PNCs are fabricated using nanoparticles with stronger magnetic responsiveness (ferrimagnetic iron oxide nanoparticles) and an aero-grade thermoset. Resulting nanofiller structures are characterized using optical microscopy and microCT, and correlated with the parameters of the applied magnetic fields. In Chapter 7, the fabricated PNCs are characterized for their electrical, and thermal properties, and again correlated with the nanofiller structures including interface conditions. Finally, in Chapter 8, summaries of the findings from this work, capabilities and limitations of this magnetic tailoring of PNC structures, are discussed, together with suggestions for future work.

Figure 1.1: Polymer nanocomposites: nanofillers with (or without) a surface modifier coupled to a polymer matrix (not to scale). The nanoparticles can be on the order of 1 nm – 100 nm, while the polymer chain components are typically long and thin (e.g. a thickness of 0.4 nm and length of 204 nm) [62]. Modified from [63].
Chapter 2

Background and Prior Work

As noted in Chapter 1, two challenges exist to achieve bulk application of polymer nanocomposites: unknown structure-interface-property relationships, and missing scalable and precise manufacturing methods. In this chapter, previous and state-of-the-art work on these two topics will be addressed in detail.

2.1 Structure-Interface-Property Relationship Study of PNCs

Properties of PNCs are largely governed by three components, the polymer matrix, the nanofiller, and the nanofiller surface modifier, and their effects are different per composite and per property [9]. While PNC properties are primarily driven by the properties of the nanofiller (rather than those of the matrix), due to their small size scale and large interfacial surface area, the nanofiller structures and their interfaces also have a large influence on PNC properties. Nanofillers can be idealized as a nanosphere or nanoparticle, nanoellipse, nanocube, nanoplatelet, nanorod, nanotube, or nanofiber [64–68]. Nanofillers can be organic (nanodiamond [10], carbon nanotubes [11], carbon nanofibers [12], and graphene nanosheets [13]) or inorganic (iron oxide [14], silica [15], and silver [16]). When designing PNCs, nanofillers are chosen either for their desired material properties or for the ease of implementation (dispersion and compatibility with assembly methods) [69,70]. The dimensional similarity between the polymer matrix chains and the nanofillers produces the so-called nanosize effect [71]. The high surface-to-volume ratio of the nanofiller, which depicts the amount of interfacial surface area available for energy transfer from one domain to another, produces, in most cases, improved and unconventional properties [18,44]. This positive nanosize effect was demonstrated by enhanced fracture toughness of nanoscale, as compared to microscale, silica [15,45–47]. Furthermore, nanofillers have successfully improved the multi-functional properties of PNCs [67] such as flame-retardant abilities [19], fatigue resistance [21], and electrical [12,23] or thermal characteristics [72] due to their nanosize effects. Even with the nanosize effect, poor integration of the nanofiller can result in ineffective or even reduced property enhancement. Therefore, structuring and surface modification of the nanofiller to improve
nanofiller-nanofiller and nanofiller-matrix boundary conditions is necessary to supply PNCs with controllable, and enhanced, properties. Below, the effect of the nanofiller structuring and interfaces on PNC properties will be discussed.

2.1.1 Effect of nanofiller structures on PNC properties

The effect of nanofiller structures, mostly randomly orientated vs. 1D aligned nanofillers, on PNC properties have been studied both in experiments and analyses in the past. Randomly orientated nanofiller has contributed to PNC property improvement, but their effectiveness is less than that of aligned nanofillers due to ineffective boundary conditions [18,42,43]. In early studies of PNCs, nanofillers were often randomly orientated due to their ease of fabrication. These experiments exhibited increased composite modulus due to reinforcement of the matrix [15], improvement of fatigue and/or fracture resistance due to additional toughening mechanisms, such as crack bridging and bifurcation [21], and enhanced transport properties at high volume fractions due to geometrically connecting or networked pathways [20].

As shown in Figure 2.1, assembly of the nanofiller can enhance a wide range of PNC properties over that found for randomly orientated nanofiller due to improved interactions between the nanofillers or their interface and interphase. Modeling the usefulness of nanofiller addition has been conducted, and among them, the multi-scale Mori-Tanaka method has been shown to be effective [73,74] as the method is low cost (reduced computational time) and can accurately model the nanofiller interphases [75]. Using the Mori-Tanaka model, the effects of randomly oriented and organized nanofillers were evaluated; PNCs’ elastic modulus was twice as high when nanofillers were organized than when nanofillers were randomly organized [8]. In addition to the Mori-Tanaka method, three-dimensional finite element simulations using ABAQUS have also shown an increase in the elastic modulus for aligned vs. randomly orientated nanofiller, with the difference growing with increasing volume fractions of the nanofiller [76]; however, issues with modeling nanofiller interphases limit the applicability of such an approach as will be discussed in the next section.

Experimental work has confirmed the trends of these modeled results. Organized nanofillers have been shown to enhance the mechanical properties of PNCs by deflecting propagating crack tips to improve fracture toughness [12], or to improve load bearing characteristics to increase the elastic modulus [59]. Beyond mechanical properties, assembled nanofiller can form percolated networks at lower volume fractions than those found for randomly orientated nanofiller leading to an increase of electrical conductivity by orders of magnitude [12,77,78]. Similar results have been observed with thermal conductivity which was observed to be enhanced with organized vs. randomly
orientated nanofiller as thermal contact resistance is reduced at the interfacial regions [79,80]. Other advanced property enhancements are obtainable with nanofiller assembly, such as a barrier to moisture diffusion [81–83] and high dielectric constants [84], both of which also demonstrate the importance of nanofiller assembly on effective PNC property improvement.

2.1.2 Effect of nanofiller-polymer and nanofiller-nanofiller interfaces on PNC properties

As mentioned above, in addition to nanofiller structures, the nanofiller interfaces and thus their surfaces play a critical role in determining PNC properties. To improve nanofiller dispersion within matrices, nanofiller surfaces are modified. The difficulty in dispersing nanofillers within a polymer matrix has been one of the major challenges in the bulk fabrication of PNCs [69]. Due to the high interfacial surface area of nanofillers, aggregation occurs to minimize surface energy and common dispersion techniques, such as shear mixing, have been found to be ineffective [53,85,86]. Aggregation of the nanofiller will produce negligible improvements to PNC properties [10]. Even worse, excessive concentrations of the nanofiller surface modifier can lead to PNCs with degraded properties, as compared to the unmodified matrix, due to condensed regions of the surface modifier with few bonds available for attachment to the matrix [87]. Another challenge in the bulk fabrication of PNCs is sedimentation of the nanofiller, which can be diminished through surface modification of the nanofiller [88,89]. Thus, modification of the nanofiller surface is critical to provide improved nanofiller dispersion and suspension, and therefore enhanced PNC properties (see Figure 2.2) [18,42,43].

![Figure 2.1](image.png)
A surface modifier can also tune the bonding between the nanofiller and matrix [90–92]. Due to this, modification of nanofiller interfaces and interphases (see Figure 2.3) [93,94] through surface modification has the added benefit of improving the mechanical and transport properties of PNCs. Without a surface modifier, weak interfaces between PNC components can lead to poor, or even reduced, property improvements due to a mismatch between the nanofiller and matrix [10,95,96]. In the past, experiments have shown that enhancement of the nanofiller-matrix interface with a surface modifier can improve the strength (rupture, tensile, impact, and shear) of PNCs due to effective load transfer [53,87,97]. Other effects are possible, such as increased flexibility or elongation of PNCs due to tailoring of the nanofiller interphase to provide reduced hinderance to the polymer chain motion [95]. Proper selection of the surface modifier is important to enhance desired PNC properties. With poor selection of the surface modifier (property mismatch), electrical conductivity, for example, can decreased due to non-conductive interphase regions formed by the surface modifier [98]. On the other hand, proper selection of a surface modifier (property match) can improve electrical conductivity due to charge carrier migration though the conductive interphase regions supplied by the surface modifier [99].

The thermal properties of PNCs with low volume fractions of nanofiller are primarily governed by their interface effects [100]. Thermal conduction in PNCs has been modeled through acoustic phonons, or atomic vibration transmittance [101]. Therefore, thermal boundary resistance, or Kapitza resistance [102], between nanofillers and nanofiller-matrix phases can have a large effect on the thermal conductivity of PNCs [103]. Due to this, thermal conductivity in PNCs does not typically demonstrate percolation behavior [104]. While previous work has demonstrated a linear trend between thermal conductivity and nanofiller volume fraction [105,106], more recent work has demonstrated a nonlinear trend between thermal conductivity and nanofiller volume fraction due to the effects of dispersion and aggregation [107]. Specifically, three regions were identified: an initial increase in the thermal conductivity due to interfacial thermal resistance, a reduction in thermal conductivity due to aggregation, and finally an increase in thermal conductivity due to conducting pathways being formed [107]. Thus, reduction of the interface thermal resistance through aggregation control (surface modification), nanofiller-nanofiller contact (nanofiller assembly to form heat conducting pathways [108]) or reduction of thermal interface contact area (e.g. thinner features to reduce phonon scattering [109]) will improve the thermal conductivity of PNCs.
PNCs with organized micro- or nano-structures, and controllable boundary conditions, are required to maximize the property enhancement with nanofiller implementation. Through control of the nanofiller boundary conditions, effective bonding with the matrix supplies enhanced mechanical strength, thermal stability, elongation, and transport properties. By organizing the nanofiller structures, conducting pathways (electrical and heat) can be formed leading to improvements in the transport properties of PNCs at low volume fractions. Mechanical properties can also be improved by organizing the nanofiller structures due to interactions with materials defects (e.g. dislocations and cracks) and improved nanofiller load bearing capability. Thus, control of the nanostructures, and boundary conditions, are critical during the PNC manufacturing process.

**Figure 2.2:** Effect of surface modification on the uniform dispersion of nanofiller. Modified from [110].

**Figure 2.3:** Different A) interphases and B) interfaces of PNC components.
2.2 Manufacturing of PNCs

2.2.1 Bottom-up vs. top-down

Manufacturing PNCs at the nanoscale can be separated into two main approaches: bottom-up and top-down (see Figure 2.4). Bottom-up manufacturing can be viewed as a synthesis approach whereby nanofiller building blocks are added to a substrate one layer at a time to form nanostructures, typically through self-assembly [112,113]. While homogenously generated nanostructures are possible, the bottom-up manufacturing method has issues with complex structures, defects induced due to thermodynamics, surface preparation, phase separation, and bulk fabrication [114–117]. An example of bottom-up manufacturing is the layer-by-layer assembly of clay nanoparticles to produce a homogeneous, and optically transparent, polymer nanocomposite [17]. Another example is the self-assembly of carbon nanofiber in a polymer matrix through heterocoagulation to achieve electrical percolation at volume fractions less than 2% [118]. In its simplest form, top-down manufacturing incorporates nanofiller directly into the matrix where the nanofillers are broken down, typically through milling, to reduce the nanoscale interaction energies such as the van der Waals force [85,86]. While top-down manufacturing can produce scalable, bulk, mass produced, and easy to fabricate samples [113,119], it is limited by aggregation of the nanofillers, which influences the boundary conditions and the subsequent properties (mechanical, transport, optical, etc.) of the PNC [111]. Thus, the usage of a surface modifier is desirable to

Figure 2.4: The difference in the fabrication of PNCs through the A) bottom-up and B) top-down manufacturing approaches. Modified from [17,111].
control aggregation and therefore the properties of PNCs fabricated using the top-down approach [18,42,43]. The top-down approach to PNC manufacturing is an effective means to produce mass-produced, and bulk, composites which is the focus of this work.

2.2.2 Field-assisted assembly of micro- and nanofillers

The top-down approach can be tailored to incorporate external fields (such as magnetic, electric, or acoustic fields) to create nanoscale structures with desired shapes, characteristics, and boundary conditions [115]. While nanofiller integration by deposition on micro-components (such as fibers and cloths [120–122]) is currently a popular method, field-assisted manufacturing has the balanced benefits of scalability and precise structuring of the nanofiller. Due to the potential of field-assisted manufacturing for the scalable manufacturing of PNCs with controllable nanoscale structures, and therefore interface and property control, this approach is selected for the work of this thesis and is discussed next.

Field-assisted manufacturing is a recent approach to PNC fabrication whereby the nanofillers are assembled prior to cure to give direct control over the micro- or nanostructure without the issues of nonhomogeneous or randomly orientated nanofiller distribution. Field-assisted manufacturing [32] can include the usage of magnetic fields [57], electric fields [22,30], acoustic fields [123], mechanical deformation [124], sedimentation [125] and others [126]. Electric field gradients have been useful for orientation control of CNTs for field effect transistors or piezoresistive devices [23,127], assembly of gold nanoparticles for chemiresistor sensors [38], and the alignment of clay nanofiller to enhance optical transparency and reduce the coefficient of thermal expansion [39]. While electric fields are an effective method to control micro- or nanostructures, it is limited in polymer matrices to low field strengths due to dielectric breakdown of the polymer [12]. Likewise, the application of acoustic waves can produce a highly controllable patterning capability, but is limited due to acoustic dampening and the complexity of the experimental setup which requires patterning device orientation or design changes for different nanoparticle hierarchical organizations [123]. Shear and uniaxial strain has been shown to be an effective means for mechanical assembly of clay nanoplatelets for birefringence control [40] and lead zirconate titanate nanorods for improved dielectric properties [124]. Nevertheless, the multi-dimensional assembly of nanofiller using mechanical deformation is rarely conducted due to its complexity [32,39]. In addition, sedimentation has proven to be a difficult technique to control nanofiller assembly due to issues with direct control over the drying process [125]. On the other
hand, magnetic fields have been shown to be useful for PNC fabrication due to their low power requirements [128], ease of use, high periodicity, and patterning capabilities [41,57]. Thus, this work is conducted using magnetic fields in a field-assisted approach as a cost effective and scalable solution to the bulk manufacturing and tailoring of PNCs.

Nanofiller assembly using oscillating magnetic fields at low frequencies is potentially a solution to the scalable manufacturing of PNCs with tailored nanostructures and nanofiller contacts. Magnetic assembly of nanofillers has been shown to have the benefit of long-range order and periodicity, even in bulk and viscous materials [129–132]. The magnetic assembly of nanofillers has been studied in the past, but knowledge gaps exist to achieve controlled bulk assembly of the nanofillers [32]. In the past, the response of ferromagnetic nanoparticles in solutions against external, static (DC) magnetic fields has been quantitatively evaluated through analytical and experimental studies [133]. An example of previous studies using DC magnetic fields includes the usage of ferrimagnetic materials, such as approximately 0.50 micron sized iron oxide, within the human body for detection, separation, and treatment of cells [133–136]. Also, the alignment of bulk microfillers (spheres [137], rods [57], platelets [57,138], etc.) has been studied using rotating magnetic fields to fabricate sizable (50 mm long) filler-polymer composites with organized microstructures leading to materials with tunable mechanical properties [11,41,57,138]. Effective microplatelet assembly, with optimized platelet geometry and magnetic properties, has been achieved using very small (approximately 10 G) and rotating magnetic fields [57]. In addition, while CNTs have been magnetically assembled at very large field strengths (greater than 70000 G) [139], coating CNT surfaces with iron [140,141] and nickel [142] has been shown to be an energy efficient means for tailoring CNT nanostructures in PNCs. Magnetic fields have also been useful for the assembly of classically non-magnetic materials, such as colloidal ceramics [143].

Further studies are being conducted to understand the influence of frequency on the structuring behavior of magnetic nanofiller. Structuring of colloidal suspensions of superparamagnetic latex nanoparticles were observed to be controlled either via thermal diffusion or the magnetic dipole-dipole interactions of the nanoparticles with pulsed waveforms [144]. In addition, frequency was found to have a coarsening effect on the formed structures. While the effects of gravity decreases due to the nanosize, the hydrodynamic forces are size-dependent, and often diminish nanofiller movement, especially within viscous polymers [23]. Due to this hydrodynamic effect, thermal diffusion of nanofillers in a polymer matrix is limited, leading to pulsed waveforms being a poor choice for this matrix type. However, even with its limited response in viscous matrices, thermal diffusion is still an effective mechanism to counteract sedimentation.
Heterodyned magnetic fields have been shown to mimic the effect of thermal diffusion at high frequencies, but high energy consumption remains an issue when using this technique for the scalable manufacturing of PNCs [145]. Due to reorientation of the nanofiller magnetic moment when placed within an oscillating magnetic field, techniques incorporating high frequency fields have found applications in timed [146] and ruptured [147] drug delivery due to heating of the magnetic nanofiller. Localized heating of magnetic nanofiller due a high field frequency has also been the source of much investigation, such as the treatment of cancers through magnetic hyperthermia [148–155]. However, localized heating of the nanofiller is not desirable in the manufacturing of PNCs due to its effect on the matrix viscosity and cure cycle, making controlled and tailorable nanostructuring difficult at high field frequencies. The interaction between rotating magnetic fields and fluid viscosity has also been investigated for magnetic colloidal suspensions demonstrating a maximum rotational frequency threshold, above which viscous dissipation produces undefined colloidal structures [156]. Therefore, in addition to heating, practical limitations exist on the frequency of the applied field in order to achieve tailorable magnetic nanofiller structures in viscous polymers.

Much still remains unknown about magnetic nanofiller assembly using oscillating magnetic fields with varying parameters such as field frequency, field waveform type, field flux density, nanofiller concentration, nanofiller susceptibility and matrix viscosity. Variations to the nanofiller structures will affect the nanofiller boundary conditions, and thus the properties of PNCs manufactured using field-assisted assembly.

### 2.3 Applications of PNCs with Magnetic Nanofiller

Recently, PNCs consisting of organized magnetic nanofillers have been studied [41] for applications in sensors, storage devices, and other electromagnetic components [157], and in electromagnetic shielding [158] and actuation [26]. Electromagnetic shielding is critical in aerospace defense applications to protect against electromagnetic interference (for example, from electromagnetic pulses) [159]. Electromagnetic absorption, and control over the resonance peak, is a technique where specific electrical frequencies can be attenuated to prevent electromagnetic interference – this technique has been achieved through the usage of magnetic iron oxide within a thermoplastic matrix for frequencies up to 30 GHz [160]. Electromagnetic dissipation is another critical topic in aerospace design; reduction in the energy dissipated during lightning strikes is
important to prevent damage to aerospace components, which is responsible for at least 40 aerospace accidents [161].

Other than electromagnetic absorption and shielding, a wide variety of applications for PNCs with magnetic nanofillers exists. In antenna design, improvements to the electrical conductivity and dielectric constant are desirable [162,163], and these properties have been shown to increase with the addition of magnetic nanoparticles to a polymer matrix [164]. The incorporation of magnetic iron oxide into a polymer matrix is an effective, and instantaneous, method to measure variations in humidity through hydroxyl formation on the nanofiller surface which produces additional free electrons [165]. Magnetically saturated PNCs can be used for magnetic actuation devices [166], such as magnetically response microfluidic gates [167], with their response dependent upon the nanofiller volume fraction [14,168,169]. While the above demonstrates several applications possible with magnetic nanofillers, more is attainable with scalable manufacturing processes and enhanced control over the nanofiller interfaces and interphases.
Chapter 3

Objectives and Approach

The benefits of tailored PNCs for anisotropic property enhancement were discussed in Chapter 1 and past work depicting the challenges and limitations in the bulk fabrication of tailored PNCs were discussed in Chapter 2. Technology gaps still exist in the controlled implementation of magnetic nanofillers within high viscosity matrices to produce novel materials with tailored anisotropic properties. Magnetic nanoparticle assembly, especially using low-frequency oscillating fields, can potentially be a solution to scalable and tailorable fabrication of PNCs, yet many unknowns are still left in order to achieve such a novel fabrication method.

3.1 Objectives

To counteract the challenges and limitations and to develop novel scalable methods to manufacture tailorable PNCs, the objectives of this dissertation are listed below and also summarized in Figure 3.1.

I. To obtain an understanding about the assembly of magnetic nanoparticles using oscillating magnetic fields:
   - The effect of the external magnetic flux density, frequency, and waveform type, and nanoparticle concentration and magnetic response, on nanoparticle assembly in matrices with low viscosity.
   - The tailorability of one-dimensional (1D) nanoparticle patterns, structures, or assemblies using oscillating magnetic fields and its limitations.

II. To demonstrate tailorability and scalability of 1D structured PNCs and their properties using oscillating magnetic fields:
   - Control of the nanoparticle boundary conditions (interface or interphase) using oscillating magnetic fields and chemical surface modification.
   - Correlation between the tailored 1D nanoparticle structures with the PNC properties.
III. To develop a design space for tailored PNCs using oscillating magnetic fields:

- Limitations of magnetic nanoparticle structuring – particle dispersion (aggregation and sedimentation), high volume fractions, external field control, and high viscosity matrices.
- The advantages in controlling inter-particle boundary conditions.

3.2 Approach

The approaches to address the three objectives stated above are listed below.

3.2.1 Quantitative study of nanoparticle assembly using oscillating magnetic fields

First, in order to obtain an understanding about the assembly of magnetic nanoparticles using oscillating magnetic fields (Objective I), both experimental and simulation studies were conducted to capture correlations between resulting nanoparticle assembly patterns and oscillating magnetic field parameters. Control of nanoparticle assemblies allows for the tailoring of the interphases and interfaces between particle-particle and particle-matrix interactions, and thus the properties of PNCs. Tailored interfacial/interphase interactions can improve mechanical properties due to effective load transfer, increase thermal conductivity due to a reduction in thermal contact resistance, or even reduce electrical resistivity due to the formation of charge carrier pathways [58,95,97,99,170–173]. Various methods have been studied in the past to integrate nanoparticles
into polymer matrices, and application of oscillating magnetic fields has demonstrated potential to provide precise tailoring of nanoparticles [174]. For example, superparamagnetic latex nanoparticles (525 nm) of iron oxide were magnetically assembled in deionized water using a non-symmetric, pulsed, magnetic field; interactions between the magnetic attraction dipole forces and thermal diffusion led to constant coarsening of the assemblies over time [144]. Yet, much still remains unknown about how nanoparticle assembly patterns, their contacts, and thus PNC properties, are affected by the parameters of the oscillating magnetic field (frequency, flux density, and waveform), of the nanoparticles (shape and concentration), and of the matrix (viscosity). For example, nanoparticle assembly using oscillating magnetic fields of lower frequency (< 0.3 Hz) has not been explored [144]. Usage of a symmetric oscillating magnetic field, instead of pulsed field, is expected to dampen the influence of thermal diffusion, while still allowing for additional control over the nanoparticle assemblies.

In this work, both experimental and simulation work was conducted to understand nanoparticle assembly using oscillating magnetic fields at low frequency. First, an experimental set-up was designed to evaluate the real-time assembly of nanoparticles – a digital optical microscope, in conjunction with a solenoid pair in series, was used to collect images of the 1D assembly of the nanoparticles for different parameters (magnetic flux density, frequency, waveform, concentration, and particle type) and their ranges [128,175]. As a model case, superparamagnetic iron oxide nanoparticles (SPIONs) were selected since the SPIONs do not have remnant magnetization, allowing quantification of the results without correlation to pre-existing nanoparticle magnetization. Deionized water was selected as the matrix to limit the influence of the matrix, namely hydrodynamic drag, and to ensure that nanoparticle assembly occurred within a reasonable amount of time due to the number of experiments performed. The nanoparticle volume fractions were kept low (< approximately 1 vol%) for easier observation of the nanoparticle assemblies in real-time under the microscope. The assembly sizes were quantitatively measured from the captured microscope images to evaluate critical field parameter ranges. The obtained knowledge of magnetic SPION assembly was compared and verified with the magnetic assembly of ferrimagnetic nanoparticles (Fe₃O₄ or magnetite) in DI water. Second, magnetic assembly of nanoparticles was also studied theoretically. Due to its size (< 30 nm), the nanoparticles were approximated as having a single magnetic domain [176,177] and thus modeled to have uniform magnetization without the presence of magnetic domains. Theories behind the assembly of single magnetic domain particles were formulated through the correlation between the interaction energies, magnetic dipole forces, thermal energy, gravitational forces, and hydrodynamic drag. In
addition, COMSOL simulations were performed to better understand the interactions between the magnetized nanoparticles and the matrix viscosity, which is a useful technique to quantify the feasibility of nanoparticle assembly in higher viscosity matrices.

3.2.2 Fabrication and characterization of tailored one-dimensional iron oxide thermoset nanocomposites

Second, in order to demonstrate tailorability and scalability of 1D structured PNCs and their properties using oscillating magnetic fields (Objective II), PNCs were fabricated with different assembly patterns with varying magnetic fields. Instead of SPIONs, ferrimagnetic iron oxide ($\gamma$-Fe$_2$O$_3$ or maghemite) nanoparticles were used to overcome the hydrodynamic drag present in the selected aerospace grade polymer matrix (bisphenol-f matrix with a diethyltoluenediamine cross-linker). Previously, PNCs have been structured using pulsed, static or rotating external magnetic fields with tailored nanoparticle boundary conditions [11,41,57,141]. Yet, several challenges still exist, especially when working life, the time before the thermoset starts to cure, is limited: poor nanofiller dispersion (or nanofiller aggregation and sedimentation) and large hydrodynamic drag due to the viscous matrix.

In this work, magnetic structuring of PNCs was demonstrated in a scalable manner by 1) improving nanoparticle dispersion with a surface modifier and 2) evaluating the differences between 1D nanoparticle assemblies within the viscous matrix. The fabricated sizable PNCs were characterized for their nanoparticle structures using optical microscopy and microCT, and correlated with the measured PNC properties (electrical and thermal). Dispersion of the nanoparticles was improved through the usage of a silane coupling agent (GPS, 3-glycidyloxypropyl trimethoxysilane), providing an interface between the nanoparticles and the cross-linking agent. Nanoparticle functionalization was conducted in two ways: dry-processing (dried and broken down using a mortar and pestle prior to mixing with the curing agent) and wet-processing (ball milled and centrifuged prior to mixing with the curing agent). The dry- and wet-processed nanoparticles were magnetically assembled within the polymer matrix between a solenoid pair (magnetic field gradient) and Helmholtz coil (uniform magnetic field), respectively. The nanoparticle assemblies were evaluated using optical microscopy and microCT to assess the effect of the manufacturing parameters. The anisotropic transport (electrical and thermal) properties of the manufactured PNCs were evaluated (axial vs. transverse), and were correlated with the nanoparticle structures.
3.2.3 Development of a design space to direct future work in the tailorable fabrication of polymer nanocomposites using oscillating magnetic fields

Third, in order to develop a design space for tailored PNCs using oscillating magnetic fields (Objective III), the knowledge obtained above (magnetic assembly, and structure-interface-property relationships) was extrapolated. The tailorability and limitations of magnetic assembly were identified in the form a guideline, in relation to the parameters of nanoparticles (magnetic properties, size, etc.), of magnetic fields (frequency, waveform, strength, etc.), and of matrix (viscosity).
Chapter 4

Theoretical Studies of the 1D Magnetic Assembly of Superparamagnetic Nanoparticles

In this chapter, the theoretical aspects of magnetic nanoparticle assembly are discussed. First, magnetism will be briefly reviewed including common magnetic nomenclature, magnetic material types, and generalized magnetic fields by a solenoid pair. Second, magnetic assembly behaviors are analytically studied for superparamagnetic nanoparticles within a magnetic field generated by a solenoid pair. The effects of relevant forces and energies on superparamagnetic iron oxide nanoparticle (SPION) assembly are evaluated. These studies are conducted to be directly comparable with the experimental studies about the magnetic assembly of SPIONs to be discussed in Chapter 5. Based on this study, capabilities and limitations are evaluated about the tailorable behavior of magnetic nanoparticle assembly. Third, in addition to the above analytical studies, COMSOL simulations are performed to study the magnetic interactions between a pair and multiple particles with a single magnetic domain.

4.1 Brief Review of Magnetism

4.1.1 Classical theory of electromagnetism

The scientific investigation into magnetism begins with William Gilbert. In 1600, Gilbert published *De Magnete, Magneticisque Corporibus, et De Magna Magnete Tellure* (On the Magnet and Magnetic Bodies, and on That Great Magnet the Earth) theorizing that the earth itself is a weak magnetic, which is the basis for compasses pointing north. In 1800, Joseph-Louis Lagrange, followed by Carl Gauss, proposed that the net electric flux through any closed surface was equal to a constant time the net electric charge contained within that closed surface, as described in Equation 4.1.

\[
\nabla \cdot E = \frac{\rho}{\varepsilon_0}
\]

(4.1)
\( \nabla \) is del operator, \( \mathbf{E} \) is the electric field (V/m), \( \rho \) is the total electric charge density (C/m\(^3\)), and \( \varepsilon_0 \) is the vacuum permittivity (8.854 x 10\(^{-12}\) F/m). More specifically, a static electric field points away from positive charges and towards negative charges. Therefore, electric field lines begin at positive charges and end at negative charges. This relationship became known as Gauss’s Law and also as the first equation in the classical theory of electromagnetism. The first link between current and magnetism was proposed by Hans Oersted in 1820. Biot and Savart closely followed his work by deriving the first experimental relationship between magnetic field (strength and direction) and electric current as shown in Equation 4.2. The magnetic field (T) at a distance \( \zeta \) (m) is given by:

\[
B(\zeta) = \frac{\mu_0}{4\pi} \int_C \frac{id\mathbf{l} \times \mathbf{\zeta}}{|\mathbf{\zeta}|}
\]

(4.2)

\( \mu_0 \) is the permeability of free space (4\(\pi\) x 10\(^{-7}\) H/m), \( i \) is the steady current (A), and \( d\mathbf{l} \) (m) is a vector along path C. This equation is only valid for static magnetic fields. The Biot-Savart law is based on the assumptions that the current element is infinitely thin (e.g. filament), that the contour is closed, and that electric flow and the magnetic field are generated within the same material. Carl Gauss proposed in 1830 that the divergence of a magnetic field is zero (see Equation 4.3), implying that a magnetic field is a solenoidal vector field or that magnetic monopoles do not exist. In other words, magnetic fields are composed of two poles, north and south, and any flux line from one pole leads to the other pole, and vice versa as shown in Figure 4.1.

\[
\nabla \cdot \mathbf{B} = 0
\]

(4.3)

\( \mathbf{B} \) is the magnetic flux density (T). This relationship is known as Gauss’s Law for Magnetism, and also as the second equation in the classical theory of electromagnetism.

**Figure 4.1:** Gauss’s law for magnetism: the divergence of the magnetic field is zero – magnetic monopoles do not exist.
Early in the 1830s electromagnetic induction was discovered by Michael Faraday and Joseph Henry. The primary theory used in devices such as transformers, the theory was generalized by Maxwell to state that the curl of the electric field is proportional to a time varying magnetic field and became known as the Maxwell-Faraday law and is the third equation in the classical theory of electromagnetism:

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$$  \hspace{1cm} (4.4)

$t$ is the time (s). James Maxwell effectively corrected Ampere’s law to account for time-varying electric fields in 1861, where a magnetic field around a loop is related to the electric current passing through the loop as shown in Equation 4.5, where $\mathbf{J}$ is the current density ($A/m^2$). Based on this relationship, a generated magnetic field is orientated normal to either an electric current, a time varying electric field, or the combination of the two that produced it (as given by the right-hand rule). This equation is known as Ampere’s circuit law with Maxwell’s addition and also as the fourth equation in the classical theory of electromagnetism.

$$\nabla \times \mathbf{B} = \mu_0 \left( \mathbf{J} + \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t} \right)$$ \hspace{1cm} (4.5)

Oliver Heavyside derived the relationship describing the electromagnetic force (N) applied to a charged particle in motion in 1889:

$$\mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B})$$ \hspace{1cm} (4.6)

$q$ is the particle charge (C) and $\mathbf{v}$ is the particle velocity (m/s). In a magnetic field, the force applied to a current carrying object is directed orthogonal to the velocity of the charge and the magnetic field direction. This equation is referred to as the Lorentz force law and is the basis for classical definitions of the electric and magnetic field. In 1928, Werner Heisenberg proposed the theory for permanent magnetic materials where the lowest-energy configuration of electron spins, and nearest neighbor interactions, aligned parallel leading to a so-called ferromagnetic state in magnetic materials, to be discussed next.
4.1.2 Characterization of magnetic materials

Magnetic materials are materials that respond to an external magnetic field. A magnetic nanoparticle will move along a magnetic field gradient [133,178] and an elastomer with embedded magnetic particles will deform or actuate due to an external magnetic field [179,180]. The type of magnetic material determines how the material will respond to a magnetic field – for example, diamagnetic and ferromagnetic materials will be repulsed and attracted by an external magnetic field, respectively. By understanding magnetic materials, and their responses, structuring, for example, of magnetic nanoparticles within a matrix can be tailored providing a methodology for control of nanoparticle interfaces. Magnetic materials are composed of domains where electron spins (and orbitals) are aligned, but never in contact (the Pauli exclusion principle). These electrons act as miniature current coils, leading to magnetic fields being generated orthogonal to their plane of spin. An infinitesimally small current loop is referred to as a magnetic dipole moment (see Figure 4.2A), and applies a torque to a body. Regions within materials where magnetic dipole moments are aligned in the same direction are referred to as domains. Here, domains should not be confused with grains; many magnetic domains can be within a single grain boundary, and several small grains can be within a magnetic domain. The magnetic dipole moment \( m \) (A/m\(^2\)) is defined as a vector which, in conjunction with the external magnetic flux density \( B \) (T), produces a magnetic torque (N-m):

\[
T_m = m \times B
\]  

(4.7)

The potential energy (J) of a magnetic dipole moment is given as:

\[
U = -m \cdot B
\]  

(4.8)

The potential energy of a magnetic dipole is minimum when the magnetic dipole moment is in the same direction as \( B \), and maximum (\( U = 2mB \)) when antiparallel to the direction of \( B \) (see Figure 4.2B). Thus, the magnetic dipole moment will align with the external magnetic field direction to minimize potential energy. Magnetic domains are formed to minimize the magnetostatic energy. When a magnetic field is applied to a material with magnetic domains, the magnetic domains will re-orient and align with the external field direction. In some cases, during reorientation, the magnetic domains will become pinned to material defects leading to a
The superposition effect between adjacent and aligned magnetic domains in which the material becomes magnetized (see Figure 4.3).

![Figure 4.2](image1.png)

**Figure 4.2:** A) A hypothetical magnetic dipole moment, and B) minimum and maximum energy states.

![Figure 4.3](image2.png)

**Figure 4.3:** A) Randomly orientated regions of uniform magnetic dipole moments, and B) alignment of the domain magnetic moments with application of an external magnetic field – the material becomes magnetized.

The temperature dependence of magnetic materials is of importance in this work since phase changes can transform magnetic materials to non- or weakly magnetic materials. The formation of spontaneous magnetic domains will occur below the Curie temperature in ferromagnetic and ferrimagnetic materials which produces a state of permanent magnetization in a material. Above the Curie temperature, induced magnetization is only possible due to thermal energy randomizing electron spin orientations. The Curie temperature of several materials is given in Table 4.1. Of interest is the Curie temperature of maghemite (\(\gamma\)-\(\text{Fe}_2\text{O}_3\)). Due to maghemite being thermally unstable and phase changing to the alpha phase (hematite, \(\alpha\)-\(\text{Fe}_2\text{O}_3\)) at approximately 250°C, estimation of the Curie temperature is difficult [181]. While this is not an issue with the cure cycle selected in Chapter 6 (up to 121 °C), it may be an issue if maghemite is sintered at temperatures above 250 °C for estimation of transport properties of the nanofiller.
The magnetization of a material (A/m) is defined as the sum of the magnetic dipole moments throughout a material:

\[ M = \lim_{\Delta V \to 0} \frac{1}{\Delta V} \sum_{i=1}^{n} m_i \]  

(4.9)

\( V \) is the volume (m³). Therefore, the magnetization \( M \) of a material with randomly orientated magnetic dipoles can lead to weak or zero magnetization. In some materials a favored crystallographic orientation exists in which magnetization has a preferred direction, or an easy axis or easy direction. Magnetization of these materials in directions other than their preferred direction requires an energy input greater than their anisotropic energy barrier, refer to [183] and [184] for more details. The magnetic flux density (T) is composed of two components as shown in Equation 4.10. The first, \( H \), is the external, applied, magnetic field strength (A/m). The second, \( M \), is the magnetic field produced due to the magnetization of a material. Thus, the total magnetic field is a superposition of the magnetic field produced from an external source and the summation of a material’s internal magnetic dipoles. In addition, the magnetic flux density in free space is simply \( B = \mu_0 H \).

\[ B = \mu_0 (H + M) \]  

(4.10)

A common method to characterize magnetic materials is with a vibrating sample magnetometer (VSM), and the magnetic material classes can be categorized by the field-magnetization (H-M) plots. A magnetic sample is placed within a uniform magnetic field and vibrated as shown in Figure 4.4A. The induced voltage in the pickup coils is measured and correlated with the material magnetization, \( M \). The resulting magnetization for different magnetic field strengths, \( H \), are then plotted (see Figure 4.4B). Depending on the magnetic material type,

<table>
<thead>
<tr>
<th>Material</th>
<th>Curie Temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>770</td>
</tr>
<tr>
<td>Alnico (Aluminum-Nickel-Cobalt)</td>
<td>850</td>
</tr>
<tr>
<td>Ba-Fe (Barium-Iron)</td>
<td>600</td>
</tr>
<tr>
<td>Sm-Co (Samarium-Cobalt)</td>
<td>700</td>
</tr>
<tr>
<td>Ne-Fe-B (Neodymium-Iron-Boron)</td>
<td>300</td>
</tr>
<tr>
<td>Maghemite ((\gamma)-Fe₂O₃)</td>
<td>250-900</td>
</tr>
</tbody>
</table>

Table 4.1: Curie temperatures of ferromagnetic materials.
different magnetic hysteresis are observed. The magnetic saturation, $M_s$, is the maximum magnetization of the material and represents when the largest number of magnetic dipole moments are aligned. The magnetic remanence, $M_r$, indicates the amount of magnetization present when the external magnetic field has been removed. The magnetic coercivity, $H_c$, represents the resistance of a material to being demagnetized. A material with a high magnetic coercivity value is referred to as a ‘hard’ magnetic material (hard to demagnetized). In permanent magnets and magnetic disc drives, for example, it is desirable to have a high coercivity value to resist demagnetization. Conversely, a material with a low coercivity value is referred to as a ‘soft’ magnetic material. A low coercivity value is useful in applications where a material needs to be magnetized and demagnetized repeatably, such as transforms and electric motors.

\[
\chi_m = \frac{M}{H} \quad (4.11)
\]

The volume magnetic susceptibility, or magnetic susceptibility, is defined as the ratio of the magnetization of a material, $M$, to the external field strength, $H$, as shown in Equation 4.11.

The magnetic susceptibility indicates how easily a material can become magnetized and is a fundamental property of the material. The magnetic susceptibility of a material is dependent upon the temperature due to thermal reorientation of the magnetic dipole moments. As discussed above, at temperatures greater than the Curie temperature [185], long range order of the magnetic dipole moments is lost. One caveat is antiferromagnetic materials – these materials lose their long-range

![A) Vibrating sample magnetometer experimental setup and B) typical H-M plot of a ferromagnet produced by the VSM.](image-url)
order above the so-called Néel temperature [186]. When long range magnetic dipole order is lost, all materials (with the exception of diamagnetic materials) behave as a paramagnetic material (see Figure 4.5). In general, it is preferred to write the magnetic susceptibility into a different form. Substitution of Equation 4.11 into Equation 4.10, and rearranging leads to:

\[
B = \mu_0 (1 + \chi_m)H = \mu_0 \mu_r H = \mu H
\]  

(4.12)

\(\mu\) is the magnetic permeability (H/m), and \(\mu_r\) is the relative magnetic permeability, which is the ratio of the material’s magnetic permeability and the permeability of free space. The magnetic permeability, \(\mu\), is a useful quantity as it’s easy to measure experimentally.

![Figure 4.5: Dependence of magnetic susceptibility on temperature. Modified from [187].](image)

4.1.3 Magnetic material types

The types and classification of magnetic materials is typically given in terms of the relative magnetic permeability, \(\mu_r\). Thus, magnetic material types are distinguished by the orientation and strength of their magnetic domains. A useful summary of the properties of magnetic materials is given in Table 4.2 [188], where \(m_{\text{spin}}\) and \(m_{\text{orb}}\) are the magnetic moments due to the electron spin and orbital, respectively. Below, five different type of magnetic materials are explained: diamagnetism, paramagnetism, ferromagnetism, antiferromagnetism, and ferrimagnetism. Superparamagnetism is explained separately in Section 4.1.4.
Diamagnetic materials are characterized by their relative magnetic permeability of less than or equal to 1 and no long range order of the magnetic dipole moments [189]. Diamagnetic materials are repulsed by an external magnetic field. Unlike other forms of magnetism, the susceptibility of diamagnetic materials is constant with temperature. Diamagnetism occurs in all materials to a certain extent, with other forms of magnetism producing a much greater magnetization. A non-magnetic material is diamagnetic with a relative magnetic permeability of approximately 1. Superconducting materials are highly diamagnetic with a relative magnetic permeability close to 0 leading to these material types ‘levitating’ when placed on top of an external magnetic field. One common atomic model for diamagnetic materials is that their magnetic dipole moments cancel under normal conditions, but in the presence of an external field the dipoles produced by the orbiting electrons are smaller than the dipoles produced by the electron spins leading to a net effect which repels external magnetic fields [182]. An example H-M plot for diamagnetic materials, along with relative magnetic permeability values, is shown in Figure 4.6. The matrices of Chapters 5, 6, and 7 are diamagnetic which will slightly diminish the effect of the external field.

![Figure 4.6: A) H-M plot and B) relative magnetic permeability of common diamagnetic materials [182].](image-url)
Paramagnetic materials are characterized by their relative magnetic permeability greater than 1 and their magnetic dipole moments having no long-range order. Due to randomization of the orientation of the magnetic dipole moments, the relative magnetic permeability of paramagnetic materials is slightly greater than 1. This leads to paramagnetic materials being weakly attracted to external magnetic fields (typically, these materials are considered as non-magnetic). At temperatures greater than the Curie temperature (Néel temperature for anti-ferromagnetic materials) all materials, with the exception of diamagnetic materials, become paramagnetic. The magnetic dipole moments of paramagnetic materials readily align with external magnetic fields, adding to the overall field strength (albeit with low magnetization). Upon removal of the field, paramagnetic materials exhibit no remanent magnetization. An example H-M plot for paramagnetic materials, along with relative magnetic permeability values, is shown in Figure 4.7. The aluminum mold of Chapters 6 and 7 is paramagnetic.

\[
\begin{array}{c|c}
\text{Material} & \mu_r > 1 \\
\hline
\text{Air} & 1.00000036 \\
\text{Oxygen} & 1.0000019 \\
\text{Aluminum} & 1.000021 \\
\text{Tungsten} & 1.000068 \\
\text{Platinum} & 1.00029 \\
\end{array}
\]

**Figure 4.7:** A) H-M plot and B) relative magnetic permeability of common paramagnetic materials [182].

Ferromagnetic materials are characterized by their large, positive, values of relative magnetic permeability and long-range order of the magnetic dipole moments such as bulk iron (see Figure 4.8). As such, ferromagnetic materials will tend to magnetize in the direction of the external field and produce large magnetizations. As previously discussed, this large magnetization in ferromagnetic materials is due to the formation of magnetic domains, or regions where the magnetic dipole moments align, to minimize magnetostatic energy (see Figure 4.3). Due to the pinning of the magnetic domain walls to material defects during magnetization, some ferromagnetic materials can be permanently magnetized. An example H-M plot for a ferromagnetic material is shown in Figure 4.4B; ferromagnetic materials are one of the few magnetic materials to demonstrate a hysteresis in their magnetization curves. Due to this hysteresis, ferromagnetic materials are
distinguished by their magnetic coercivity values to determine whether they are ‘hard’ or ‘soft’ magnetic materials. A few examples of the relative magnetic permeability of ‘hard’ and ‘soft’ ferromagnetic materials are shown in Table 4.3.

![Alignment of magnetic moments](image)

**Figure 4.8**: Orientation of the magnetic dipole moments in ferromagnetic materials; long range order of the magnetic dipoles is observed. Adopted from [189].

**Table 4.3**: Properties of soft and hard ferromagnetic materials [182].

<table>
<thead>
<tr>
<th>Type</th>
<th>Material</th>
<th>Relative Permeability, $\mu_r$</th>
<th>Magnetic Coercivity, [A/m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soft</td>
<td>Silicon iron (3% Si)</td>
<td>55000</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>Iron (0.2% impure)</td>
<td>9000</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>Nickel</td>
<td>600</td>
<td>-</td>
</tr>
<tr>
<td>Hard</td>
<td>Alnico (Aluminum-Nickel-Cobalt)</td>
<td>3.5</td>
<td>60000</td>
</tr>
<tr>
<td></td>
<td>Ba-Fe (Barium-Iron)</td>
<td>1.1</td>
<td>240000</td>
</tr>
<tr>
<td></td>
<td>Ne-Fe-B</td>
<td>1.05</td>
<td>800000</td>
</tr>
</tbody>
</table>

Antiferromagnetic materials are characterized by their magnetic dipole moments being of approximately equal magnitude and alternating in direction as shown in Figure 4.9. Due to the arrangement of their magnetic dipole moments, antiferromagnetic materials produce a net zero magnetic moment. The antiferromagnetic ordering disappears at temperatures greater than the Néel temperature. Similar to the behaviors observed at the Curie temperature, magnetic dipole moments of antiferromagnetic materials become randomized at temperatures above the Néel temperature due to thermal rearrangement leading to a parametric material response. The Néel temperatures of several antiferromagnetic materials are listed in Table 4.4. Of interest is the alpha phase of iron oxide ($\alpha$-Fe$_2$O$_3$, hematite). Unlike other antiferromagnets, hematite demonstrates two transitions: (1) the Morin transition temperature, and (2) Néel transition temperature. Below the Morin transition temperature hematite demonstrates perfect antiferromagnetic behavior. Above the Morin transition temperature (~10 °C), the hematite structure has magnetic dipole moments slightly canted with respect to the crystal structure, producing weak magnetization. Above the Néel temperature (675 °C), hematite becomes a paramagnetic material. For this work, it is important to note that
gamma phase iron oxide ($\gamma$-Fe$_2$O$_3$, magnetite) phase changes into hematite at approximately 250°C.

![Magnetic moments alternate](image)

**Figure 4.9:** Orientation of the magnetic dipole moments in antiferromagnetic materials; long range order of the magnetic dipoles is observed. Adopted from [189].

**Table 4.4:** The Néel temperature for several antiferromagnetic materials [190].

<table>
<thead>
<tr>
<th>Material</th>
<th>Néel Temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO</td>
<td>-157</td>
</tr>
<tr>
<td>FeO</td>
<td>-75</td>
</tr>
<tr>
<td>CoO</td>
<td>18</td>
</tr>
<tr>
<td>NiO</td>
<td>252</td>
</tr>
</tbody>
</table>

Ferrimagnetic materials are characterized by their alternating orientations of their magnetic moments, but with unequal magnitude (see Figure 4.10). Due to the orientation of their magnetic moments, ferrimagnets have weaker relative magnetic permeability than ferromagnets as shown in Table 4.5. Ferrimagnetic materials demonstrate the similar behaviors as ferromagnetic materials, namely a Curie temperature, magnetic hysteresis, magnetic domains, and magnetic remanence. Ferrimagnetic materials are useful as they are typically powders and can be compressed or tailored into any desired shape, and exhibit low power losses making them useful for high frequency transformers and radio antennas [182]. As will be demonstrated in Chapter 6, ferrimagnetic materials can be magnetized at very low magnetic flux densities (~ 10 G or 0.001 T, about an order of magnitude above the earth’s magnetic field). Both magnetite (Fe$_3$O$_4$) and gamma phase iron oxide ($\gamma$-Fe$_2$O$_3$) are ferrimagnetic materials.

![Magnetic moments alternate and are unequal](image)

**Figure 4.10:** Orientation of the magnetic dipole moments in ferrimagnetic materials; long range order of the magnetic dipoles is observed. Adopted from [189].
4.1.4 Superparamagnetic materials

Superparamagnetic materials are characterized by the thermal reorientations of their magnetic moments. Reduction of the size of a body beyond a certain critical point leads to the formation of a single magnetic domain due to competing interactions between the magnetostatic energy and the energy to form domain walls [192]. A single domain magnetic particle has uniform magnetization directed along the easy axis [193]. The direction of the magnetic dipole moment for these single domain magnetic bodies does not stay constant, but undergoes fluctuations or relaxations due to thermal energy. Therefore, the magnetization of a collection of these bodies is zero when no external field is present, but a very large directional magnetization occurs when an external field is applied. Therefore, superparamagnetic materials do not exhibit a magnetization hysteresis. These bodies or particles are referred to as superparamagnetic since they behave as paramagnetic materials but with much larger magnetizations [189]. The primary particle type investigated in Chapter 5 are superparamagnetic iron oxide nanoparticles (SPIONs) because of their large magnetizations enabling assembly at a relatively low magnetic field (approximately 10 G) and without the influence of magnetic remanence. Due to these particles having a single magnetic domain, the discussion below and the calculation of the forces of interest in Section 4.3 is conducted assuming spherical SPIONs with uniform magnetization and characteristics of the SPIONs investigated in Chapter 5.

Relaxation of the SPION magnetic moments can occur through two different mechanisms as shown in Figure 4.11: (1) Brownian or (2) Néel relaxation [194,195]. If the SPIONs physically rotate while their magnetic moments stay at a fixed crystallographic orientation, then they have undergone Brownian relaxation. Conversely, if the SPION magnetic moments rotate internally, such that the magnetic domains switch direction without physical rotation of the SPIONs, then they have undergone Néel relaxation. In general, both mechanisms may occur, and the dominate mechanism is classically defined as the one with the smaller time scale. The linear response theory

<table>
<thead>
<tr>
<th>Material</th>
<th>Relative Permeability, $\mu_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Zn-Co (Ceramic Magnetics, N40)</td>
<td>15</td>
</tr>
<tr>
<td>Type 61 (Fair-Rite)</td>
<td>125</td>
</tr>
<tr>
<td>Mn-Zn (Ferroxcube Corp, 3F45)</td>
<td>900</td>
</tr>
</tbody>
</table>

Table 4.5: Relative magnetic permeability of several ferrimagnetic materials [191].
is commonly used to evaluate the Brownian and Néel relaxation times [196]. This theory is only valid if SPION magnetization varies linearly with the external field as shown in Equation 4.13, where $V_c$ is the SPION magnetic core volume ($\text{m}^3$), $T$ is the temperature (K), and $k_B$ is Boltzmann’s constant ($1.381 \times 10^{-23} \text{J/K}$). For the SPIONs investigated in Chapter 5, $M_s |\mathbf{B}|V$ is maximum at an external magnetic field strength of 100 G and, in this condition, is less than $k_B T$.

$$M_s |\mathbf{B}|V_c < k_B T$$ (4.13)

The Brownian relaxation time is given by Equation 4.14, where $\eta$ is the matrix viscosity (Pa·s, $0.89 \times 10^{-3}$ Pa·s for water), and $V_h$ is the hydrodynamic volume ($\text{m}^3$). Here, the Brownian relaxation time is found to be $3.4 \times 10^{-6}$ s for a SPION of Chapter 5 (a spherical particle of 15 nm diameter with a hydrodynamic diameter of 21.4 nm following Jeyadevan [197]).

$$\tau_B = \frac{3\eta V_h}{k_B T}$$ (4.14)

The Néel relaxation time is given by Equation 4.15, where $K$ is the anisotropic energy density ($\text{J/m}^3$, commonly used as 13500 J/m$^3$ for iron oxide [198]), and $\tau_0$ is the Larmor frequency (s, estimated as $4.64 \times 10^{-20}/\sqrt{V}$ s or $3.5 \times 10^{-8}$ s per Leliaert et al. [199]). The Néel relaxation time is found to be $1.3 \times 10^{-5}$ s for the SPIONs of Chapter 5 (spherical particle of 15 nm diameter).

$$\tau_N = \tau_0 e^{KV/k_B T}$$ (4.15)
Therefore, since τ_B is less than τ_N, Brownian relaxation will be the dominant relaxation mechanism for the SPIONs investigated in Chapter 5, and the SPIONs will physically rotate with changes to the external magnetic field as long as the SPIONs are not physically constrained (see Figure 4.12). The SPIONs of this work form aggregates to minimize surface free energy. It is hypothesized that the SPIONs will rotate within the aggregates themselves since no visual observation of physical rotation of the aggregates or assemblies was found under an optical microscope. In this context, rotation of the SPIONs within the aggregates will produce a high field gradient on the transverse surfaces of the aggregates during rotation, as discussed in Section 4.4.

![Figure 4.12](image)

**Figure 4.12:** Brownian and Néel relaxation times for the 15 nm diameter SPIONs.

### 4.2 On-Axis Magnetic Field Between Solenoid Pair

For a solenoid pair (such as those used in Chapter 5), an external magnetic field gradient produced between the solenoid pair will impose external forces on any magnetic material between the pair to migrate towards the pole locations (see Section 4.3). Therefore, estimation of the magnitude of any external gradient produced between a solenoid pair is critical to better understand these applied forces. A direct approach is taken to estimate the on-axis magnetic field between a solenoid pair below, which was not easily found in the literature. The geometry of the solenoid pair is shown in Figure 4.15.

An alternate form of the Biot-Savart relationship given in Equation 4.2 is the differential form shown in Equation 4.16 where \( \mu_0 \) has been replaced by \( \mu \) to account for the influence of the
core material and $\theta$ is the angle between the current element, $dl$, and the magnetic flux density, $dB$ (see Figure 4.13).

$$dB = \frac{\mu i (dl) \sin \theta}{4\pi \xi^2}$$ \hspace{1cm} (4.16)

![Diagram showing the Biot-Savart relationship for a current element.]

**Figure 4.13**: Biot-Savart relationship for a current element.

Integration of Equation 4.16 over a circular current loop yields the magnetic flux density at any point along the axis of the loop:

$$B_x = \frac{\mu i}{2} \frac{a^2}{(a^2+x^2)^{3/2}}$$ \hspace{1cm} (4.17)

$a$ is the radius of the current loop (m), and $x$ is the on-axis distance from the center of the loop (m). The relationship shown in Equation 4.17 can be integrated over a range of axial values to give the on-axis magnetic field for a finite, straight, thin shell solenoid. First, rewrite Equation 4.17 into the form shown in Equation 4.18, where the differential current, $di$, is written in terms of the differential length, $dx$, the number of turns, $N$, and the length of the solenoid, $L_s$ (m). Integrating Equation 4.18 from $x_1$ (m) to $x_2$ (m), the resulting on-axis magnetic flux density of a thin, finite-length solenoid is given by Equation 4.19, where the nomenclature for $x_1$ and $x_2$ are shown in Figure 4.14.

$$dB_x = \frac{\mu i}{2} \frac{a^2}{(a^2+x^2)^{3/2}} = \frac{\mu (Ndx)}{2 L_s} \frac{a^2}{(a^2+x^2)^{3/2}} = \frac{\mu N i}{2 L_s} \frac{a^2 dx}{(a^2+x^2)^{3/2}}$$ \hspace{1cm} (4.18)

$$B_x = \frac{\mu N i}{2 L_s} \left( \frac{x_2}{(a^2+x_2^2)^{1/2}} - \frac{x_1}{(a^2+x_1^2)^{1/2}} \right)$$ \hspace{1cm} (4.19)
The on-axis magnetic field can be determined for a solenoid with finite thickness by integrating Equation 4.19 with respect to the radius (here, $a$). Integrating Equation 4.19 from the inner radius, $a_1$ (m), to the outer radius, $a_2$ (m), yields the resulting on-axis magnetic field as shown in Equation 4.20 and Equation 4.21. The nomenclature for $a_1$ and $a_2$ are shown in Figure 4.14.

\[
B_x = \int_{a_1}^{a_2} \frac{\mu N_i}{2L_s} \frac{da}{a_2-a_1} \left\{ \frac{x_2}{(a^2+x_2^2)^{1/2}} - \frac{x_1}{(a^2+x_1^2)^{1/2}} \right\} \tag{4.20}
\]

\[
B_x = \frac{\mu N_i}{2L_s(a_2-a_1)} \left\{ x_2 \ln \left( \frac{(a_2^2+x_2^2)^{1/2}+a_2}{(a_1^2+x_2^2)^{1/2}+a_1} \right) - x_1 \ln \left( \frac{(a_2^2+x_1^2)^{1/2}+a_2}{(a_1^2+x_1^2)^{1/2}+a_1} \right) \right\} \tag{4.21}
\]

![Figure 4.14: Geometry of finite thickness solenoid.](image)

The on-axis magnetic field between a pair of solenoids in series is determined through the superposition of the on-axis magnetic field of a pair of finite length and thickness solenoids. Thus, the magnetic field on-axis between a solenoid pair is given by Equation 4.22, where $L_{s1}$ and $L_{s2}$ are the length of the left and right solenoid, respectively, $\mu_1$ and $\mu_2$ are the magnetic permeability of the left and right solenoid, respectively, $N_1$ and $N_2$ are the number of turns of the left and right solenoid, respectively, and $a_3$, $a_4$, $x_3$, and $x_4$ are as shown in Figure 4.15.

\[
B_x = \frac{\mu_1 N_1 l}{2L_{s1}(a_2-a_1)} \left\{ x_2 \ln \left( \frac{(a_2^2+x_2^2)^{1/2}+a_2}{(a_1^2+x_2^2)^{1/2}+a_1} \right) - x_1 \ln \left( \frac{(a_2^2+x_1^2)^{1/2}+a_2}{(a_1^2+x_1^2)^{1/2}+a_1} \right) \right\} + \\
\frac{\mu_2 N_2 l}{2L_{s2}(a_4-a_3)} \left\{ -x_4 \ln \left( \frac{(a_4^2+x_4^2)^{1/2}+a_4}{(a_3^2+x_4^2)^{1/2}+a_3} \right) + x_3 \ln \left( \frac{(a_4^2+x_3^2)^{1/2}+a_4}{(a_3^2+x_3^2)^{1/2}+a_3} \right) \right\} \tag{4.22}
\]
The magnetic field between the solenoid pair used in this work (see Chapter 5) has the following parameters (separation of 0.155 m):

\[
\begin{align*}
    a_1 &= a_3 = 0.0325 \text{ m}, \\
    a_2 &= a_4 = 0.0389 \text{ m}, \\
    L_{s1} &= L_{s2} = 0.148 \text{ m}, \\
    N_1 &= N_2 = 570 \\
    i &= 5 \text{ A}, \\
    \mu &= \mu_0 = 1.257 \times 10^{-6} \text{ Tm/A}
\end{align*}
\]

The resulting on-axis magnetic field between the identical solenoid pair is shown in Figure 4.16A. The simulated magnetic field produced between the solenoid pair above using FEMM software \[200\] is shown in Figure 4.16B. Comparison of the on-axis magnetic flux density at the center of the solenoids between Equation 4.22 and the FEMM software demonstrates an error of approximately 3.3\% (19.2 G using Equation 4.22 and 19.9 G using FEMM software) for the derived on-axis magnetic field. Note that the measured magnetic flux density between the solenoid pair of Chapter 5 using a gaussmeter (Lakeshore model 425) was found to be approximately 18.4 G (approximately 4.3\% error).
4.3 Forces and Energies Applied to SPIONs in Magnetic Fields

The assembly behavior of SPION aggregates in an oscillating magnetic field is not well understood. Due to different interaction energies, the SPIONs of Chapter 5 will aggregate into relatively large sizes (< 5 µm) to minimize surface free energy. The assembly of SPION aggregates using oscillating magnetic fields is governed by the forces produced by electrostatic interactions, van der Waals interactions, inter-particle magnetic interactions, steric interactions, thermal energy, external magnetic field, hydrodynamic drag, and gravitational forces. Of these, the coupled interactions between the inter-particle magnetic forces and thermal energy are important to ensure that SPION assemblies are formed, and gravitational forces, hydrodynamic drag, and thermal energy to avoid sedimentation. Below, the relative forces and energies of interest to the assembly of SPION aggregates in an oscillating magnetic field are discussed. Here, the SPIONs are assumed to be spherical, have a single magnetic domain [176], and thus have uniform magnetization with no magnetic remanence. SPIONs refer to individual nanoparticles, aggregates refer to the initial SPION groupings, and assembly refer to the assembly of aggregates.
4.3.1 Interaction energies

The interaction energies are those from particle-to-particle interactions. These energies are composed of the dipole forces (van der Waals and electrostatic interactions), magnetic dipole forces (induced inter-particle interactions), and steric repulsion (surfactant or surface modification chemistry). The non-magnetic dipole forces and steric repulsion are important in colloidal chemistry to avoid nanoparticle aggregation; additional information beyond that discussed here can be found in the literature [201,202].

An attractive interaction, the van der Waals attractive force will produce SPION aggregation. The van der Waals interaction energy (\(J\)) between two identical spheres is given as [192]:

\[
E_{vdw} = -\frac{A}{6} \left\{ \frac{2}{l^2 + 4l} + \frac{2}{(l+2)^2} + ln \left( \frac{l^2 + 4l}{l^2 + 4l+4} \right) \right\}
\]  (4.23)

\(l\) is the surface-to-surface distance between the particles (m), and \(A\) is the Hamaker constant (J). While the Hamaker constant is not affected by temperature, it is influenced by the selected matrix type [203]. The Hamaker constant for iron oxide is approximately 36 \(10^{-21}\) J in water [203]. Due to the \(l\) dependence of the van der Waals equation, an infinite amount of energy is required to separate two particles [192]. Therefore, modification of the Hamaker constant is necessary – for example, ball milling nanoparticles in the presence of a solvent and surface modifier, or surfactant, as discussed in Chapter 6, can effectively fragmentate SPION aggregates.

The steric interactions due to a surface modifier will repulse two particles due to compression of the surfactant atoms surrounding the particle. The steric repulsive energy (\(J\)) can be approximated as [189]:

\[
E_s = \frac{k_b T \pi d^2 \xi}{2} \left\{ 2 - \frac{s+2}{t} ln \left( \frac{1+t}{1+s/2} \right) - \frac{s}{t} \right\}
\]  (4.24)

\(d\) is the particle diameter (m), \(s = 2l/d\), \(t = 2\delta/d\), \(\delta\) is the length of the absorbed molecules (m), and \(\xi\) is the surface concentration of the absorbed molecules (m\(^{-2}\)). The limiting condition of maximum repulsion energy for a thick coating can be solved as \((E_s)_{max} = k_b T \pi d^2 \xi / 2\). For particles within a matrix, overlap of the electrical double layer can lead to a second repulsion mechanism. The energy associated with repulsive electrostatic forces (\(J\)) is given as [201]:
\[ E_{es} = \frac{4\pi \varepsilon \varepsilon_0 r_1 r_2}{r_1 + r_2} \left\{ \psi_1 \psi_2 e^{\exp(-\kappa l)} - \frac{1}{4} (\psi_1^2 + \psi_2^2) e^{\exp(-2\kappa l)} \right\} \]  

(4.25)

\[ \kappa^{-1} = \frac{\varepsilon \varepsilon_0 k_B T}{2 N_A \beta e^2} \]

\( \varepsilon \) is the dielectric constant of the matrix, \( \varepsilon_0 \) is the permittivity of free space (8.854x10^{-12} C/V-m), \( r_1 \) and \( r_2 \) are the respective particle radius (m), \( \psi_1 \) and \( \psi_2 \) are the respective particle surface potentials (mV), \( N_A \) is Avogadro’s number (6.02 x 10^{23} mol^{-1}), \( \beta \) is the ionic strength (M), and \( e \) is the unit charge (1.602 x 10^{-19} C).

SPIONs placed within an external magnetic field will become magnetized. The magnetization of the SPIONs will lead to an induced magnetic field produced around the SPIONs. By modeling the SPION as a single magnetic dipole moment, the induced magnetic interactions between the SPIONs can be determined. The interaction energy (J) between a collection of SPIONs is shown in Equation 4.26, where \( i \) is the \( i^{th} \) particle, \( j \) is the \( j^{th} \) particle, \( r_{ij} \) is the vector pointing between the \( i^{th} \) and \( j^{th} \) particle magnetic cores, and \( m_i \) and \( m_j \) are the magnetic moment dipole vectors for the \( i^{th} \) and \( j^{th} \) particles, respectively. For two SPIONs, or interacting magnetic dipoles, Equation 4.26 can be simplified to Equation 4.27 [189]. For two identical magnetic dipoles pointing in the same direction, with an angle between the magnetic dipole vectors of 0, Equation 4.27 can be simplified even further as shown in Equation 4.28. The magnetic moment of SPIONs can be determined through VSM testing, as will be discussed in Chapter 5, or using theoretical predictions such as those that can be found in literature [204–206].

\[ E_m = \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{\mu_0}{4\pi |r_{ij}|^3} \left( m_i \cdot m_j - \frac{3}{|r_{ij}|^2} (m_i \cdot r_{ij})(m_j \cdot r_{ij}) \right) \]  

(4.26)

\[ E_{md} = \frac{\mu_0}{4\pi |r|^3} \left( m_1 \cdot m_2 - \frac{3}{|r|^2} (m_1 \cdot r)(m_2 \cdot r) \right) \]  

(4.27)

\[ E_{mds} = -\frac{\mu_0 |m|^2}{2\pi |r|^3} \]  

(4.28)
The net interaction between the energies discussed here is shown in Figure 4.17. The contribution to the repulsive forces from the steric repulsion is dependent upon the $\delta$, the amount of surface modifier coating the SPIONs. For larger separations between particles, magnetic dipole attraction governs the particles response due to a $1/r^3$ variation. In addition, the SPION aggregates of Chapter 5 have been observed to disperse or diffuse upon removal of the external magnetic field indicating that the interaction energies at the micron scale (electrostatic, van der Waals, and steric) are less dominant than the induced magnetization of the SPIONs. Therefore, only the interaction energies associated with the induced magnetic dipole will be considered for the SPION assembly behaviors in Section 4.4.

### 4.3.2 Magnetic forces

In addition to the interaction energies discussed in Section 4.3.1, an external magnetic field will impose additional forces onto the SPIONs. Classically, the magnetic force applied to a magnetic dipole $m$ is given by Equation 4.29 [204].

$$
F_m = \nabla (m \cdot B) = (B \cdot \nabla) m + (m \cdot \nabla) B + B \times (\nabla \times m) + m \times (\nabla \times B) 
$$

(4.29)

If a point-like magnetic dipole is assumed, then $\nabla m = 0$ and $\nabla \times m = 0$. In addition, for a source-free space, $\nabla \times B = 0$ by Maxwell’s equation (Equation 4.5). Thus, the force on SPIONs
due an external magnetic field (N) can be approximated by Equation 4.30. For a magnetic dipole, or SPION, located between a solenoid pair, such as that described in Section 4.2, and with a magnetic moment orientated along the external magnetic field direction, the force can be approximated as one-dimensional. In this case, Equation 4.30 reduces to the form shown in Equation 4.31.

\[ F_m = (m \cdot \nabla)B \]  
(4.30)

\[ F_{m,x} = m \frac{\partial B_x}{\partial x} \]  
(4.31)

Incidentally, in the absence of an external magnetic flux density gradient, the sole attractive energy between SPIONs are those discussed in Section 4.3.1. The force between a magnetic dipole pair can be determined by calculating the magnetic field due to a magnetic dipole and then using Equation 4.29. Conversely, the force can be determined using Equation 4.27 since \( F = -\nabla E \) for a conservative force (assuming a static magnetic field). Regardless, the force between a magnetic dipole pair (N) is given in Equation 4.32 \[207\], where \( \hat{r} \) is the unit vector pointing between the two magnetic dipoles. If the magnetic moments are assumed to be equal, aligned and in the same direction, the magnetic force between a dipole, or SPION, pair can be estimated as in Equation 4.33.

\[ F_{m,d} = \frac{3\mu_0}{4\pi|r|^4} \left( (\hat{r} \times m_1) \times m_2 + (\hat{r} \times m_2) \times m_1 - 2\hat{r}(m_1 \cdot m_2) + 5\hat{r}[(\hat{r} \times m_1) \cdot (\hat{r} \times m_2)] \right) \]  
(4.32)

\[ F_{m,dx} = \frac{3\mu_0 m^2}{2\pi|r|^4} \]  
(4.33)

The two magnetic forces are compared in Figure 4.18. Here, the magnetic moment is estimated from Equation 4.9 as \( m = MV \), where \( V \) is the volume of the SPIONs. For a 15 nm SPION, the magnetization is estimated from VSM testing in Chapter 5 to be approximately 2000 A/m at a magnetic flux density of 20 G. Therefore, the magnetic moment of the SPIONs is estimated to be approximately \( 1 \times 10^{-21} \) A-m\(^2\). The gradient in the magnetic flux density is 0.02 T/m over the test region at a field flux density of 20 G, as tested in Chapter 5. Comparison between the magnetic forces indicate that the induced magnetic dipole forces on the SPIONs in Chapter 5 are
approximately three orders of magnitude greater than the external field forces over the test region when the SPIONs are separated by a distance of 100 nm. Therefore, the forces due to the external field gradient are ignored for the analysis of the SPION assembly behaviors.

**Figure 4.18**: Comparison between the magnetic dipole and external field gradient forces.

### 4.3.3 Magnetic and thermal interactions

Assembly of SPION aggregates is dependent upon the interaction between magnetic and thermal energy. Depending on the size of the SPION aggregates, the magnetic capture radius, defined as the inter-aggregate distance when magnetic interactions are less than the energies associated with thermal diffusion, is a useful parameter to determine the likelihood of assembly. If a SPION aggregate pair are at a separation greater than the magnetic capture radius, thermal diffusion will control the motion of the SPION aggregates; conversely, if the aggregate pair are closer than the magnetic capture radius, the energies associated with magnetic attraction are greater than those for thermal diffusion and the SPION aggregates will attract. The magnetic capture radius \( r_c \) is given by Equation 4.34 [144], where \( \lambda \) is the dimensionless parameter relating magnetic potential energy to the thermal energy of the SPION aggregates, and \( c \) is the SPION aggregate radius (m).

\[
r_c = 2c\lambda^{1/3}
\]

(4.34)

The dimensionless parameter \( \lambda \) can be defined as shown in Equation 4.35, where \( H \) is the magnetic field strength (A/m) [144].
The magnetic capture radius is plotted in Figure 4.19 for varying magnetic flux densities and spherical SPION aggregate diameters. The susceptibility is selected to be 0.610 based upon the VSM measurement data in Chapter 5. The propensity for assembly is highly dependent upon the size and separation of the SPION aggregates; as SPION aggregates attract, the size of the resulting assembly, and the inter-assembly separation, increase.

Of interest is the minimum magnetic flux density such that SPION assembly does not occurred, herein referred to as the magnetic threshold. Rearrangement of Equation 4.34 in terms of the magnetic flux density is shown in Equation 4.35, where $\delta_0$ (m) is the separation between SPION aggregates. For magnetic flux densities below the magnetic threshold, thermal diffusion controls the reorientation of the SPION assemblies making effective control over the assembly morphologies difficult, in addition to free SPION aggregates present within the matrix. For example, for the SPIONs used in this work (see Chapter 5), an average separation between SPION aggregates of 1 µm size was estimated to be approximately 7 µm at a 0.04 vol % concentration in DI water. For these conditions, a magnetic threshold of approximately 13 G is found. This threshold is verified as shown in Figure 5.9 in Chapter 5.

$$B_{th} = \sqrt{\frac{9 \delta_0^2 \mu_0 k_B T}{8 \pi c^2 \chi^2}}$$

(Figure 4.19): The magnetic capture radius for SPION aggregates of various size based upon VSM data of Chapter 5.
4.3.4 Gravitational, hydrodynamic, and thermal interactions

The interaction between gravitational, hydrodynamic, and gravitational forces is important to control gravitational sedimentation. For SPION aggregates smaller than a certain threshold, thermal energy or Brownian diffusion will randomize aggregate motion arresting sedimentation of the aggregates. In addition, hydrodynamic forces will dampen sedimentation of the aggregates. The mean displacement for Brownian motion can be estimated using Equation 4.36 [208], where \( t \) is the time (s), \( \eta \) is the matrix viscosity (Pa\-s), and \( c \) is the particle aggregate diameter (m). The displacement due to gravitational forces assuming Stokes drag and terminal velocity is shown in Equation 4.37 [208], where \( \rho_s \) and \( \rho_l \) are the density of the particle and matrix (kg/m\(^3\)), respectively, and \( g \) is the acceleration due to gravity (9.81 m/s\(^2\)).

\[
\gamma_1 = \sqrt{\frac{4k_BTt}{3\pi^2\eta c}}
\] (4.36)
\[
\gamma_2 = \frac{(\rho_s-\rho_l)gc^2}{18\eta}t
\] (4.37)

A useful comparison, or mean percent ratio, between the Brownian motion to gravitational sedimentation is classically given as shown in Equations 4.37 and 4.38 [208,209], where a large percentage in \( \gamma_k \) indicates that Brownian motion will arrest particle sedimentation.

\[
\gamma = \frac{36}{(\rho_s-\rho_l)gc^2} \sqrt{\frac{2k_BT\eta}{3\pi\tau}}
\] (4.37)
\[
\gamma_k = \frac{100\gamma}{1+\gamma}
\] (4.38)

In many cases, the matrix type, temperature, and particle density are difficult to vary. Therefore, control of the SPION aggregate size is useful to prevent gravitational sedimentation, for example by using a ball mill with a solvent and surface modifier, or through chemical precipitation [189]. For comparison, the percent ratio between Brownian and gravitational motion, \( \gamma_k \), is shown in Table 4.6 for varying temperature, particle diameter, and matrix viscosity. The particles are a model SPION aggregate with a density of 5240 kg/m\(^3\). The matrix in Table 4.6A is selected to be a bisphenol-f epoxy (EPON 862 as discussed in Chapter 6) with a density of 1167 kg/m\(^3\) and a
viscosity dependence on temperature equal to that shown in Figure 6.11. The matrix is selected to have a density of 1000 kg/m³ in Table 4.6B. A total analysis time of 30 minutes is selected. As expected, as the aggregate diameter increases, the gravitational effects on the SPION aggregates increases. In the epoxy matrix selected, Brownian effects are greater than those of gravitational for aggregate sizes of 0.500 µm or less. Above this aggregate size, sedimentation is likely – this effect is amplified during magnetic assembly due to the SPION assemblies having sizes larger than their aggregates.

Table 4.6: Percent ratio of Brownian and gravitational motion for a model SPION aggregate after 30 minutes.

<table>
<thead>
<tr>
<th>A)</th>
<th>Aggregate Diameter [µm]</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>η (T)</td>
<td>0.500</td>
<td>1.00</td>
<td>2.50</td>
<td>5.00</td>
</tr>
<tr>
<td>Temp [°C]</td>
<td>γ_k [%]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>88.20</td>
<td>56.93</td>
<td>11.80</td>
<td>2.31</td>
</tr>
<tr>
<td>40</td>
<td>75.02</td>
<td>34.67</td>
<td>5.10</td>
<td>0.94</td>
</tr>
<tr>
<td>55</td>
<td>61.96</td>
<td>22.36</td>
<td>2.83</td>
<td>0.51</td>
</tr>
<tr>
<td>70</td>
<td>50.74</td>
<td>15.40</td>
<td>1.81</td>
<td>0.32</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>B)</th>
<th>Aggregate Diameter [µm]</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>70 °C</td>
<td>0.100</td>
<td>0.500</td>
<td>1.00</td>
<td>5.00</td>
</tr>
<tr>
<td>η [Pa-s]</td>
<td>γ_k [%]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.001</td>
<td>86.61</td>
<td>10.37</td>
<td>2.00</td>
<td>0.04</td>
</tr>
<tr>
<td>0.1</td>
<td>98.48</td>
<td>53.63</td>
<td>16.98</td>
<td>0.36</td>
</tr>
<tr>
<td>1.0</td>
<td>99.51</td>
<td>78.53</td>
<td>39.27</td>
<td>1.14</td>
</tr>
<tr>
<td>10.0</td>
<td>99.85</td>
<td>92.04</td>
<td>67.16</td>
<td>3.53</td>
</tr>
</tbody>
</table>

4.3.5 Magnetic moment reorientation and hydrodynamic drag

The hydrodynamics of the SPIONs is investigated to better understand the relationship between rotation of the SPIONs and the applied field frequency. Here it is assumed that the SPIONs are not constrained and will undergo a Brownian relaxation mechanism (physical rotation of the particles to align their magnetic moments as discussed in Section 4.1.4). Assuming only viscous drag and the external magnetic field act on the SPIONs, or magnetic potential energy as given by Equation 4.8, the equation modeling rotation of the SPIONs (rad) using Stokes’ drag [210] is given by Equation 4.39, where I is the SPION moment of inertia (kg-m²), r_p is the SPION radius (m), and θ is the angle between the SPION magnetic moment and the external field direction (rad).

\[ I \ddot{\theta} + 8\pi r_p^3 \eta \dot{\theta} + |m||B|sin\theta = 0 \]  
(4.39)
Equation 4.39 is solved numerically to determine the influence of the matrix viscosity, magnetic flux density, and field frequency on rotation time of a model SPION (spherical, 15 nm diameter). In Figure 4.20, how a model SPION magnetic moment rotates to the external field ($\theta: \pi \rightarrow 0$) over time is plotted with relevant varying external field parameters (flux density and waveform) and matrix viscosity. Here, the SPIONs have a density of $5240 \text{ kg/m}^3$, and an approximate magnetic moment of $10^{-21} \text{ A-m}$ (similar to that discussed in Section 4.3.2). For numerical stability, the initial orientation of the SPIONs magnetic moment is offset from $\pi$ by $10^{-5}$ rad. The matrix viscosity is chosen to match the matrix types in Chapter 5 (0.89 cP, water) and Chapter 6 (70 cP, EPON 862 at the working temperature of 70°C). In addition, magnetic flux densities of less than 100 G are selected to match the experimental parameters of Chapter 5, and

Figure 4.20: Calculated Brownian rotation angle of a model spherical SPION over time in oscillating magnetic fields: A) magnetic moment rotation slowed down by smaller flux density (top), by sinusoidal waveform (middle), and by higher matrix viscosity (bottom), and B) slow magnetic moment rotation (top) or incomplete rotation (middle and bottom) with increasing field oscillation frequency. Adopted from [211].
since ultra-high magnetic responses of nanoparticles have been found below this flux density [212]. The time for the SPIONs to complete rotation is longer with external fields of small strength and with a sinusoidal waveform, and in more viscous matrices (see Figure 4.20A). Such conditions should help promote transverse assembly (in the direction orthogonal to the external field direction) as discussed in Section 4.4. Meanwhile, as illustrated in Figure 4.20B, as the frequency increases, the SPION magnetic moment cannot catch up with the external field changes and thus may not rotate which will limit transverse assembly. Therefore, to ensure complete rotation of the SPION magnetic moments, and to promote transverse assembly, in addition to lateral assembly, magnetic field oscillation with low frequency (< approximately 10 Hz) need to be applied to tailor SPION assembly in higher viscosity matrices.

As an addendum to the above analysis, a small cylindrical magnet (5 mm x 2 mm, Ni-Si ferromagnet, approximately 90 G remanent field) is placed centered within the solenoid pair described in Chapter 5. An oscillating sinusoidal waveform (0.05 Hz, 35 G peak) is generated across the magnet. The magnet is observed to physically rotate with the external field such that it’s
magnetization is aligned with the external field direction, see Figure 4.21. In addition, rotation of the magnet is observed to have a delayed response, similar to the findings of Figure 4.20, especially for a sinusoidal waveform, between switching of the external field direction and rotation of the magnetic moment, or magnetization. Specifically, the magnet described here was found to switch its magnetization direction at approximately 50% of the peak field strength, compared to approximately 80% and 20% peak field strength for the SPIONs of Figure 4.20 in a matrix with viscosity of 70 cP and 0.89 cP, respectively.

4.4 Analysis of SPION Assembly in Static and Oscillating Magnetic Fields

Based upon the discussion in Section 4.3, in the presence of a uniform external magnetic field, SPION assembly is due to inter-aggregate magnetic attraction only since magnetization of the SPION aggregates will produce local, induced, non-uniform magnetic fields. The interaction energies, and forces from the external magnetic field gradient, are small compared to the induced magnetic forces at the micron scale and therefore are not discussed here. Meanwhile, both the hydrodynamic drag forces and thermal diffusion are important to (1) ensure rotation of the SPIONs prior to the field switching, (2) enable SPION aggregate assembly within the desired time, and (3) guarantee that control of the SPION assembly morphology is dependent upon the external field conditions and not thermal diffusion. Below, the mechanisms for SPION aggregate assembly due to induced magnetic forces are discussed for a static and oscillating external magnetic field; these mechanisms will be verified by comparing them with experimental observation as will be discussed in Chapter 5.

4.4.1 SPION assembly using static magnetic field

As illustrated in Figure 4.22, upon application of a magnetic field, magnetic moments of the SPIONs align along the field direction. When the distance between neighboring spherical aggregates is smaller than the capture radius, see Section 4.3.3, magnetic attraction overcomes thermal diffusion, and the aggregates form needle-like, elongated assemblies along the field direction (lateral assembly) due to the locally induced fields [213]. The assembly size grows when stronger magnetic fields are applied or with particles of higher susceptibility. As the assemblies become larger and more anisotropic in shape, the locally induced field at the assembly tips becomes stronger promoting additional assembly [183]. Once the assemblies become large enough,
neighboring assemblies exhibit head-to-tail attraction to make longer assemblies, or occasionally zippering to produce wider (and longer) assemblies [214]. Similar assembly behaviors have been observed with colloidal suspensions [144] where assemblies consisting of single chains of colloids are formed along the field direction due to induced magnetic dipole-dipole interactions. The assembly size grows until free aggregates and assemblies are depleted within the capture radius of the larger assemblies. The time required until all free aggregates and assemblies are depleted within the capture radius is dependent upon the hydrodynamic drag – as an example, complete depletion occurs within 15 minutes for a DI water matrix and a SPION volume fraction of 0.04% at a magnetic flux density of 50 G (see Figure 5.6).

![Figure 4.22](image.png)

**Figure 4.22:** Schematic of SPION assembly using a static magnetic field: A) SPION aggregate with zero magnetic remanence due to randomly orientated magnetic moments, B) reorientation of SPION magnetic moments along the external static field direction forming a high, locally induced magnetic field gradient, and C) needle-like anisotropic SPION aggregate due to lateral assembly. Not to be scaled; more particles exist within the aggregates and assemblies.

### 4.4.2 SPION assembly using oscillating magnetic field

A time-varying magnetic field initially magnetizes the SPION aggregates along the field direction, and upon switching the applied field direction, the SPIONs will reorient their magnetic moments along the new field direction [194,195] as illustrated in Figure 4.23. Upon field switching, the SPION aggregates magnetic moments are 180° out-of-phase with the external magnetic field, and thus in a high energy state. Reorientation of the SPION magnetic moments is necessary to minimize the SPION magnetic moment potential energy (see Equation 4.8). As discussed in Section 4.1.4, Brownian relaxation (physical particle rotation) occurs faster than Néel relaxation (magnetic domain redefinition) assuming linear response theories. Thus, if unconstrained, the SPIONs will physically rotate with changes to the applied magnetic field, and will produce a large, albeit temporary, local field gradient in the directional orthogonal to the external field direction.
(transverse direction). In this case, transverse assembly is promoted to form wider (and longer) assemblies. For effective transverse assembly using oscillating magnetic fields, the SPIONs need to reorient their magnetic moments with the changing field’s orientation fast enough to complete SPION rotation and assembly as discussed above. In other words, transverse assembly will not be effective if the field switching occurs too frequently (high frequency). Magnetic moment rotation will occur faster with larger magnetic fields, with less gradual field transition (square over sinusoidal), or with smaller-sized particles of larger susceptibility, which should promote transverse assembly. In addition, the length of the SPION assemblies is dependent upon the field frequency – if the frequency is too high, there will not be enough time for lateral assembly to occur and the length of the SPION assemblies will be reduced.

The combination of the lateral and transverse assembly is expected to contribute to the tailorability of nanoparticle assembly, which will be verified experimentally in Chapters 5 and 6. Transverse assembly can be introduced by the field oscillation as long as the magnetic moments of the SPIONs have sufficient time to respond to the field oscillation and the SPIONs can complete rotation and assemble.
Figure 4.23: Schematics of SPION assembly behaviors as a magnetic field is applied and as the field direction is switched. Not to be scaled; more particles exist within the aggregates and assemblies. Adopted from [211].
4.5 Simulation of SPION assembly in static magnetic fields

Simulations are conducted to model a simplified two-dimensional (2D) case of single-domain, induced magnetic interactions under a static and uniform magnetic field. COMSOL is selected as the multiphysics simulation software due to its ability to couple physics-based systems [215]. The purpose of these simulations is to verify the static assembly trends postulated in Section 4.4.1, and to provide a guideline on how to set up COMSOL simulations to model magnetic interactions between homogenous circular particles. The governing equation relating the translation of a homogenous circular particle within an external magnetic field is shown in Equations 4.40 and 4.41 for the x- and y-directions, respectively, where $r_p$ is the particle radius (m), $m_p$ is the mass of the particle (kg), and $T_x$ and $T_y$ are the Maxwell stress tensor [189] integrated over the particle surface in the x- and y-directions, respectively (N).

$$6\pi\eta r_p \frac{dx}{dt} + m_p \frac{d^2x}{dt^2} - T_x = 0$$  \hspace{1cm} (4.40)

$$6\pi\eta r_p \frac{dy}{dt} + m_p \frac{d^2y}{dt^2} - T_y = 0$$  \hspace{1cm} (4.41)

Figure 4.24: COMSOL simulation domain for magnetic particle interaction.
Here, only the hydrodynamic drag forces and the magnetic interactions are considered based on the discussions in Section 4.3. Therefore, in the presence of a uniform and static magnetic field, the only attractive force acting on the particles is the induced magnetization of the particles. The equations above are directly applied within COMSOL’s ordinary differential equation (ODE) module to simulate the motion of magnetic 2D particles. A model situation of idealized circular, isotropic iron particles are used for simplicity. The relative magnetic permeability is set as 30000. The particles are placed within a water matrix, and the domain length and particle radius are selected to be 1000 µm and 20 µm, respectively. The external magnetic field is set at a static value of 50 G. The magnetic fields, global ODEs, and moving mesh modules are coupled to simulate motion of the magnetic particles. The force acting on the particles is solved via the magnetic fields’ module using the Maxwell stress tensor. Automatic remeshing is enabled to ensure no mesh

**Figure 4.25:** Simulation setup for moving magnetic particle interactions.
distortion during particle motion. A summary of the simulation domain is shown in Figure 4.24. The simulation is set up as shown in Figure 4.25 and using the following procedure:

I. Create the geometry.
   a. Define the fluid domain length (1000 µm).
   b. Define the particle size and placement.
   c. Specify an infinite domain around the fluid domain.
II. Specify the properties of the matrix and particles.
III. Add a global ODE module.
   a. For each particle, specify the x- and y-direction equations of motion. For example, using COMSOL notation, the x-direction equation of motion is given in Equation 4.42 and based upon Equation 4.40. \( xp1t \) is the partial derivative of the x-displacement of particle 1 (here, \( xp1 \)) with respect to the time and \( xp1tt \) is the second partial derivative of the x-displacement of particle 1 with respect to time. \( mf1.Forcex_F1 \) is the magnetic force from the magnetic fields module \( mf1 \) in the x-direction (\( Forcex \)) on particle 1 (here, the magnetic force on the particle is named \( F1 \)). This couples the magnetic fields module to the ODE module.

\[
6\pi \eta_p (xp1t) + m_p(xp1tt) - mf1.Forcex_F1 = 0 \quad (4.42)
\]

IV. Add a moving mesh module.
   a. Fix the infinite domain.
   b. Specify a zero-mesh prescribed displacement at the domain boundary.
   c. Select free deformation for the fluid domain.
   d. For each particle in the domain, specify a prescribed deformation as the x- and y-displacements solved for by the ODE (for example, this would be \( xp1 \) for the particle above in Equation 4.42 for the x-direction). This couples the moving mesh module to the ODE module.
   e. For each particle in the domain, specify a prescribed mesh displacement at the particle boundaries as the x- and y-displacements solved for by the ODE.
V. Add a magnetic fields module.
   a. Created the desired magnetic field (in this case, a uniform DC field).
   b. For each particle, set a force calculation (which couples with the ODE module).
VI. Create an initial condition by setting up a stationary study to first complete with only the magnetic fields module.

VII. Set up a transient study to use the results from the stationary study as an initial condition, with all the modules being used (ODE to moving mesh to magnetic fields).
   a. Turn on automatic remeshing.

First, as discussed in Section 4.3.2, a uniform external magnetic field will produce no forces on a homogenous magnetic particle. As shown in Figure 4.26, it is verified that a magnetic particle does not translate in a uniform magnetic field since the external magnetic field gradient is zero.

![Figure 4.26](image)

**Figure 4.26:** The magnetization (top) of one iron particle in a DC magnetic field of 50 G; the vectors represent the direction of the magnetic field, the legend represents the magnetic flux density in Gauss, and the axis are in µm. The displacement (bottom) of the iron particle with respect to time.
Second, the attraction between two particles due to the interaction between their induced magnetic fields is investigated for different particle orientations and separations (see Figure 4.27). Due to the magnetization of the particles, a gradient in the magnetic flux density is produced between the particles leading to attraction or repulsion. Repulsion is the dominant mechanism when the particles are placed vertically due to their magnetization directions being parallel – attraction of magnetic particles in the vertical, or transverse, direction can be enhanced through reorientation of the external field direction as discussed in Section 4.4.2. Attraction between the particles is enhanced when the particles are placed horizontal, similar to the discussions in Sections 4.3.2 and 4.4.1 that magnetic particle aggregates tend to attach head-to-tail forming long chains along the magnetic field direction. As shown in Figure 4.28, and as discussed in Section 4.3.3, the magnetic capture radius plays a critical role; with a DC magnetic field of 50 G, if the distance between the particles is larger than approximately 190 μm (as determined via simulations), the two particles do not attract or attract at a very slow rate due to weak interparticle forces which is a function of interparticle distance and also of the magnetic field and the fluid viscosity.

**Figure 4.27**: Interaction between a pair of 2D, homogenous magnetic particles at different orientations: A) slight repulsion, B) slight attraction, and C) attraction between the particles due to interactions between their induced magnetic fields.
Third, simulations were conducted with a collection of 10 particles. The particle radius was reduced to 10 µm and the relative magnetic permeability to 1.61 to model the SPIONs of Chapter 5. The magnetic field was also increased to 100 G. Since no contact model is incorporated into the simulation, the simulation stops as soon as contact between a particle pair occurs. As shown in Figure 4.29, induced magnetic attraction between the particles will cause the particles to assemble along the field direction. The closer, and more horizontal, the particles are orientated, the quicker assembly occurs. Improvements to this simulation methodology using COMSOL could be made by incorporating contact mechanics, rotation of the particles, the addition of an oscillating external field, and additional randomized forces due to thermal effects.

Figure 4.28: The attraction between two iron particles at 200 µm (top) and 170 µm (bottom) separation.
Figure 4.29: Induced magnetic dipole interactions between 10 2D iron particles at a magnetic flux density of 100 G. The dashed arrows indicate the particle direction of motion. The legend is in Gauss, and the axis are in µm.
Chapter 5

Experimental Study of 1D Magnetic Assembly of Nanoparticles

In this chapter, experimental studies about the magnetic assembly of nanoparticles will be discussed, including the effects of the nanoparticles (superparamagnetic vs. ferrimagnetic, volume fraction, and particle size) and the applied fields (frequency, magnetic flux density, and waveform). The usage of superparamagnetic nanoparticles enables direct comparison to the magnetic assembly theories discussed in Chapter 4. Previous work regarding assembly tailorability of superparamagnetic nanoparticles has primarily been focused on pulsed waveforms to tailor inter-assembly contacts through the balancing of thermal diffusion and induced magnetization [144], as discussed in Chapter 3. Here, oscillating magnetic fields are investigated for their added tailorability to the nanoparticle structures with transverse assembly uniquely introduced through the usage of low frequencies and small magnitude magnetic fields which is useful to precisely control nanofiller contacts. The results discussed here are extended in Chapters 6 and 7 to the fabrication of tailored polymer nanocomposites with controllable nanoparticle interfaces and thus resulting transport properties. The work of this chapter has been published in [211].

5.1 In Situ Observation of the Magnetic Assembly of Superparamagnetic Nanoparticles

The primary nanoparticle type studied here are spherical, superparamagnetic iron oxide nanoparticles (SPIONs, Sigma-Aldrich I7643) supplied in an aqueous suspension (50 mg per ml in 1 mM EDTA, pH 7.0). These nanoparticles are amine-terminated to maintain particle suspension. As found in transmission electron microscopy (TEM) images (see Figure 5.1), the average particle size is between 15 nm and 20 nm. These nanoparticles were optically observed to homogeneously aggregate to the size of roughly 1 μm to 5 μm as shown in Figure 5.2 due to the nanoparticle interaction energies as discussed in Section 4.3.1.
The magnetic properties of the SPIONs were characterized using a vibrating sample magnetometer (VSM, MicroSense Vibrating Sample Magnetometer) as shown in Figure 5.3. The iron oxide solution was diluted in deionized (DI) water to a particle volume fraction of 0.08 vol% and housed in a container of volume $6.77 \times 10^{-2}$ ml. The solution container was inserted between a pair of solenoids and then vibrated in a uniform magnetic field from $-1200$ kA/m to $+1200$ kA/m. An anhysteretic response was found verifying the superparamagnetic behavior of the particles; therefore, the net magnetization of the SPIONs is zero (no remanent magnetization) with no external magnetic field due to thermal energy randomizing the magnetic moment directions. The magnetic saturation ($M_s$) was measured as 20.6 emu/g (108 kA/m). The initial magnetic susceptibility was estimated by measuring the slope of the magnetization curve at the zero field.

Figure 5.1: TEM images of the as-received SPIONs at different magnifications: A) 5800x and B) 79000x.

Figure 5.2: Optical microscope images of the SPIONs dispersed in a DI water matrix at volume fractions of A) 0.04 and B) 0.08 vol%.
condition ($\chi = \frac{dM}{dH}|_{H \to 0}$ [216]) and was found to be approximately 1.59, in agreement with work done on the magnetic properties of iron oxide nanoparticles [217, 218]. The slope of the magnetization curve at the zero field condition is also useful to estimate the magnetic diameter of the SPIONs [219–222]. As shown in Equation 5.1, the SPION magnetic diameter is calculated as approximately 14 nm, slightly less than that found from the TEM images due to a magnetic “dead” layer surrounding the nanoparticles [223], where $k_B$ is Boltzmann’s constant ($1.381 \times 10^{-21}$ J/K), $T$ is the temperature (293 K), and $\mu_0$ is the permeability of free space ($4\pi \times 10^{-7}$ H/m). As discussed in Section 4.1.4, Brownian relaxation is the dominant mechanism for reorientation of the SPION magnetic moments, and therefore the SPIONS will physically rotate with changes to the applied magnetic field.

$$d_{SPION} = \left\{ \frac{18k_BT(dM/dH)_0}{\pi\mu_0M_s^2} \right\}^{1/3}$$  \hspace{1cm} (5.1)

**Figure 5.3:** VSM of the SPIONs demonstrating the saturation magnetization and no magnetic hysteresis.

Magnetic assembly of the SPIONs in an aqueous solution was conducted under an optical microscope so that particle assembly behaviors can be captured in real time (see Figures 5.4 and 5.5). The SPION solution was diluted in DI water to four different particle volume fractions: 0.02%, 0.04%, 0.06% and 0.08%. The volume fractions were kept relatively small for observation of nanoparticle assembly and inter-nanoparticle distances under an optical microscope. Local nanoparticle area fractions in the optical microscope images are higher than these average volume fractions due to settling of the nanoparticles since the microscope objective was focused on the
bottom of the sample. Settling of the SPION aggregates occurs when their sizes are larger than 150 nm (see Section 4.3.4). Thus, the local area fractions were calculated from the captured images (see Table 5.1). The diluted solutions were ultrasonicated for 5 minutes and then encapsulated in a slide (KOVA Glasstic) with a height of 0.1 mm and a chamber volume of 6.6 μL. The magnetic assembly set-up is shown in Figure 5.4. A solenoid pair in series were used to produce a nearly uniform magnetic field across the encapsulated solution. The solenoid pair (570 turns, 14.8 cm length, 6.51 cm inner diameter, 16-gauge enameled wire, 410 stainless steel core) were driven by a bipolar power supply (Kepco BOP 20-10M, ±20 V, ±10 A). The driving signal was controlled via a function generator (BK Precision, 4014B) which is capable of producing square, sinusoidal, and triangle waveforms with a frequency range of 0 to 12 MHz and resolution of 0.01 Hz. The magnetic flux density was measured using a gaussmeter (LakeShore Model 425) placed next to the sample and was monitored with an oscilloscope (BK Precision 5105B). The diluted nanoparticle solution was mounted and centered, and along axis of the solenoid pair.

Figure 5.4: A) Digital image and B) schematic of the magnetic assembly set-up.
Table 5.1: Comparison between prepared SPION volume fractions and the SPION area fractions as measured using the optical microscope.

<table>
<thead>
<tr>
<th>Volume Fraction (%)</th>
<th>Area Fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>7.5</td>
</tr>
<tr>
<td>0.04</td>
<td>8.9</td>
</tr>
<tr>
<td>0.06</td>
<td>10.4</td>
</tr>
<tr>
<td>0.08</td>
<td>11.7</td>
</tr>
</tbody>
</table>

Real-time images of nanoparticle magnetic assembly were captured using a digital optical microscope (Olympus BX51WI) during the first 15 minutes of the field application. This assembly time was selected because nanoparticle assembly did not noticeably change beyond 15 mins when monitored up to 30 mins (see Section 5.1.1). Here, aggregates refer to the initial SPION groupings as shown in Figure 5.2, and assembly refers to the assembled line features after magnetic field application (see Figure 5.5). Microscope images were collected before magnetic field application and after 5, 10, and 15 minutes of the field application. The applied magnetic field was varied about the waveform (sinusoidal and 50% duty cycle square), magnetic flux density ($\pm 10$ G, $\pm 50$ G, and $\pm 100$ G), and frequency (static, and up to 5 Hz). A root mean square (RMS) magnetic flux density was selected for the sinusoidal waveforms: 10 G (14.1 G peak), 50 G (70.7 G peak) and 100 G (141.4 G peak). A minimum magnetic flux density of 10 G was selected since an ultrahigh magnetic response has been observed at that magnitude in the past [57]. The magnetic field frequency range was limited to below 5 Hz for control of the Brownian magnetic moment reorientation mechanism [137] as discussed in Section 4.3.5. A symmetric waveform (square and sinusoidal) was selected such that nanoparticle assembly is further controlled through switching of the external field rather than thermal diffusion as found in previous work [144]. In addition to measurement with the gaussmeter, spatial distribution of the magnetic flux density between the solenoids was studied in Section 4.2. As given in Equation 4.30, a gradient in the external magnetic field provides additional forces to move the nanoparticles towards the pole locations. The sample location and the distance between the two solenoids were set so that the field gradient across the sample was limited to 5% to minimize these forces (see Section 4.3.2). For example, with application of a current of 2 A, the solenoid pair, 10 cm apart, provided a magnetic flux density of 75 G between the solenoid pair and with a $\pm 5\%$ spatial variation across a 2 cm area.
5.1.1 Magnetic assembly time

Tests were conducted to evaluate the sensitivity of assembly morphology about the field application time. A magnetic field of 80 G was applied for up to 30 minutes at a SPION volume fraction of 0.06%. The case of a DC or static (80 G) and 50% duty cycle square AC (pulsed from 0 to 80 G, and oscillating from -80 G to 80 G) magnetic fields were investigated. As for the DC field, little to no changes were observed with the SPION assembly morphology after approximately 15 minutes of magnetic field application (see Figure 5.6A and 5.6B). Likewise, as shown in Figure 5.6C and 5.6D, as for the oscillating AC fields, a consistent SPION assembly morphology was observed after 15 minutes of field application. While a pulsed AC field produced slightly coarser morphologies after 15 minutes of field application, no significant changes to the morphology were found up to 23 minutes (Figure 5.6E and 5.6F). Thus, a maximum field application time of 15 minutes was selected to produce steady morphologies for the DC and oscillating AC magnetic fields.

Figure 5.5: Optical microscope images of SPION aggregate assembly in DI water due to application of an external magnetic field.
5.1.2 Image processing of magnetic assembly behaviors

The optical microscope images captured after 15 mins of the field application were processed using Matlab (see Appendix A) following the procedure given below in order to quantitatively evaluate assembly morphology as a function of the parameters:

**Figure 5.6:** Assembly morphology variations of 0.06% volume fraction SPIONs in DI water with time. A) and B) demonstrate morphology variations for a DC field at 15 and 30 minutes, respectively. C) and D) represent variations for an oscillating 0.1 Hz AC field at 15 minutes and 25 minutes, respectively. E) and F) represent variations for a pulsed 0.1 Hz AC field at 15 minutes and 23 minutes, respectively.
i. The microscope image is converted to grayscale.

ii. The center region of the image is extracted due to a circular lensing effect near the edges of the image (see Figure 5.7A).

iii. The image is partitioned and a threshold is selected for each partition based upon the standard deviation of the grayscale pixel intensity values in the partition.

iv. The partition thresholds are recombined and Gaussian smoothing is applied to the threshold matrix to ensure no discontinuities between partitions.

v. The threshold matrix is then applied to the grayscale image to produce a black and white image.

vi. Each assembly is assigned a numerical label and assemblies below a specified size are removed to correct for image processing artifacts – typically less than 10% of the mean assembly size, although no more than 20% of the mean assembly size.

vii. Each assembly is stored into an array, and the size, length, and width of the assembly is calculated (see Figure 5.7C). The average size, length, width, and separation between all the assemblies in the image is then found.

viii. The results are then converted to μm using the microscope calibration data and output (see Figure 5.7B).

The above image processing algorithm outputs the characteristic dimensions of the assemblies (Figure 5.7C): assembly density, and the average assembly size, width, length, and separation for each image. An image was collected for each parametric condition, and the characteristic dimensions were averaged over approximately 100-1000 assemblies for each sample or condition; example histograms are shown in Appendix B. To ensure accuracy of the image processing technique, the lengths as calculated via the algorithm were compared with the length measured directly from the optical microscope images. The lengths calculated from the algorithm were, on average, approximately 3% greater than those directly measured from microscope images. This discrepancy is attributed to a transition region found between the assemblies and the matrix which produces a slight shadowing in the optical microscope images; this shadowing is responsible for slightly larger assemblies in the algorithm.
5.2 Experimentally Observed Magnetic Assembly Behaviors

The SPION assembly behaviors discussed in Chapter 4 were confirmed in real-time experimental observation. Prior to magnetic field application, nanoparticles were dispersed as shown in Figure 5.2. Following the discussion in Section 4.4.1, when a static magnetic field is applied the aggregates become magnetized, stretching along the field direction as shown in Figure 4.22 and confirmed in Figure 5.8A. For a colloidal suspension, such as those used by Swan et al [144], assemblies of single particle thickness are initially formed along the field direction due to induced magnetic dipole-dipole interactions. However, for nanoparticle aggregates, assemblies with thicknesses of hundreds of nanoparticles across are formed along the field direction due to the induced field gradient formed around the assemblies [213]. Rearrangement of the assemblies into needle-like shapes leads to an anisotropic magnetic response with higher induced magnetic fields at the assembly tips. This leads to neighboring assemblies zippering or being attracted head-to-tail along the field direction as confirmed in Figure 5.8B [214].
An average separation between SPION aggregates of 1 µm size was estimated to be approximately 7 µm at a 0.04% volume fraction in DI water. For these conditions, the magnetic threshold is calculated as 13 G per the discussion of Section 4.3.3; this threshold magnetic flux density is also verified. As shown in Figure 5.9A, free aggregates are left unassembled with an external magnetic flux density of 10 G, whereas full assembly of all free aggregates occurs for a flux density of 50 G, Figure 5.9B. Therefore, the parametric studies in Section 5.3 are evaluated with an external magnetic flux density greater than 10 G to accurately compare quantitatively SPION assembly features without the presence of free aggregates in the matrix. As discussed in

**Figure 5.8:** Optical microscope images of SPION assembly in DI water (0.04 vol%): A) needle-like assemblies upon static field application and B) zippering.

**Figure 5.9:** Optical microscope images of SPION assembly in DI water (0.04 vol%): A) free aggregates in matrix due to magnetic field below the threshold, B) full assembly of aggregates due to an increased magnetic field, and C) reduction in assembly length due to an increased field frequency.
Section 4.4.2, limitation of assembly length with higher frequency is also confirmed: the assembly lengths are longer with application of a 0.1 Hz field than those with an application of a 5 Hz field as shown in Figure 5.9C. No visual rotation of the aggregates was observed under the optical microscope, supporting the assumption that the SPIONs rotate within the aggregates.

5.3 Parametric Studies of Magnetic Assembly

In this study, the assembly characteristic dimensions (length, width, and separation) were measured with varying external magnetic field parameters (50 to 100 G flux density, 0 to 5 Hz field frequency, and square and sinusoidal waveforms). The influence of the SPION volume fraction on assembly morphology is also investigated (0.02% to 0.08% volume fraction). In addition, the effect of increased particle size, and therefore enhanced magnetic response, is demonstrated for ferrimagnetic nanoparticles (magnetite, Fe₃O₄). Due to an oscillating magnetic field producing rotation of the local, induced, magnetic field, it is expected that an oscillating magnetic field will enhance transverse assembly, producing thicker and more separated assemblies as compared to a static field (Section 4.4). Furthermore, an increased particle size is expected to produce larger assemblies due to an enhanced capture radius (see Section 4.3.3).

5.3.1 Effects of magnetic field frequency and flux density

The magnetic assembly behavior of SPIONs within DI water are summarized with varying frequency (static, 0.1 Hz, 1 Hz, and 5 Hz, 50% duty cycle square waveform) and magnetic flux density (10 G, 50 G, and 100 G) in Figure 5.10A for the exemplary case of a nanoparticle volume fraction of 0.04%. The average characteristic dimensions of the assemblies were extracted by processing these images, as summarized in Figures 5.10B through 5.10D; a 95% bootstrap confidence interval based upon the mean parameter values is indicated in the figures.
As shown in Figure 5.10, with a DC magnetic field, an increase in the magnetic flux density produced additional magnetization of the assemblies, and therefore an enhanced magnetic capture.

**Figure 5.10**: A) Selected optical microscope images of SPION assemblies in DI water (0.04 vol%) using a square oscillating magnetic field with varying flux density and frequency. Corresponding characteristic dimensions of the SPION assemblies for the 50 G and 100 G flux densities: average B) separation, C) length, and D) width. A 95% bootstrap confidence interval based upon the mean parameter values is indicated in the figures.

As shown in Figure 5.10, with a DC magnetic field, an increase in the magnetic flux density produced additional magnetization of the assemblies, and therefore an enhanced magnetic capture.
radius, leading to increased head-to-tail magnetic bonding in the field direction. These forces resulted in longer, but thinner assemblies aligned along the field direction. Upon introduction of a frequency component to the magnetic field, the separation between assemblies increased by approximately 32% at 0.1 Hz, but plateaued for frequency values above 1 Hz. While a linear trend was observed at 50G, an in-depth study of the frequency trend at 50 G found that the average separation between assemblies was steady above a frequency of 0.12 Hz, see Figure 5.11. A similar trend was found for the assembly width and length; a frequency of 0.1 Hz produced an increase of approximately 24% and 60% for the average width and length, respectively, from DC, with a plateauing effect for frequencies above 1.0 Hz. These assembly trends caused by the magnetic field frequency can be attributed to local field gradients in the induced magnetic flux density during reorientation of the nanoparticle magnetic moments, or introduction of the transverse assembly mechanism (see Section 4.4.2). As demonstrated by Figure 4.23, rotation of the induced magnetic flux density gradients produces additional forces, facilitating nanoparticles aggregates or assemblies to further migrate in the transverse direction. It is hypothesized that at frequency values higher than tested here the response of the nanoparticle magnetic moments will become limited leading to no significant changes in the assembly separation or width as discussed in Section 4.3.5. The assembly length is sensitive to small changes in the frequency of the external magnetic field. A frequency of 0.1 Hz produced an increase in the assembly length of approximately 40% from a DC field, whereas a decreasing trend was found for frequencies higher than 0.1 Hz. Frequencies of 1 Hz or higher produced an increased assembly density, leading to a larger number of assembly and a more homogeneous assembly morphology in the image processing region. It is hypothesized that this occurs due to reduced propensity for head-to-tail magnetic bonding of the assemblies since switching of the nanoparticle magnetic moments occurs too rapidly for additional aggregates or assemblies to translate along the induced magnetic field gradient.

Low frequency structuring is of interest due to the smaller currents required to produce the magnetic field which leads to reduced heating (viscous and hysteresis [149]) of the nanoparticles during reorientation and reduced power consumption. The parametric trends for very low frequency assembly morphology variations is shown in Figure 5.11 for a volume fraction of 0.04% and magnetic flux density of 50 G. A 50% duty cycle square waveform was applied and two data sets were collected at each frequency to better resolve the error between data sets. Similar to the trends previously discussed, an increase of approximately 50% in the assembly separation was seen immediately upon the addition of a frequency component to the external magnetic field, with the change degree diminishing as the frequency increases beyond 0.12 Hz. The assembly length was
found to increase by approximately 70% when frequency is increased to 0.04 Hz from DC; similarly, the overall size of the assemblies was observed to increase by approximately 84%. The assembly length was again found to decrease beyond the lowest applied frequency of 0.04 Hz, which correlates to an increasing trend in the number of the assemblies in the image processing region and a more homogenous assembly morphology. The largest increase of 74% in separation is observed with the field oscillation of 0.2 Hz, and the largest increase of 16% in width is observed with the field oscillation of 0.04 Hz. Thus, oscillating magnetic fields within the small frequency range (< 0.1 Hz) are key to achieving SPION assemblies that contrast those achieved by static fields.

**Figure 5.11**: Characteristic dimensions of SPION assemblies (0.04% volume fraction in DI water) using a square oscillating magnetic field (50 G) below 1 Hz. A 95% bootstrap confidence interval based upon the mean parameter values is indicated in the figure.
Tailoring polymer nanocomposites at low magnetic flux densities is of interest due to the reduced energy required for structuring. Morphology variations for magnetic flux density are shown in Figure 5.12. With increasing magnetic flux density, thinner and less separated assemblies are found due to an increased induced magnetization at the assembly tips and thus an increase in the zippering or head-to-tail magnetic bonding. As the magnetic flux density increases, and the induced anisotropic magnetization at the assembly tips becomes greater, additional zippering between larger sized assemblies occurs leading to an increase in the length of the assemblies. The magnetization of the assemblies is related to the size of the assemblies and the applied magnetic field, up to the saturation magnetization. As the magnetization increases, the magnetic moment of the aggregates, and subsequently the assembly anisotropic magnetization increases. At very low

Figure 5.12: Dependence of the characteristic dimensions on magnetic flux density for a SPION volume fraction of 0.04%. A 95% bootstrap confidence interval based upon the mean parameter values is indicated in the figure.
magnetic flux densities, the assembly magnetization, or magnetic capture radius, is not sufficient enough to overcome thermal diffusion and complete assembly of all the free aggregates does not occur as demonstrated at a flux density of 10G (see Section 5.2).

5.3.2 Effects of magnetic field waveform

As discussed in Section 4.3.5, in addition to the field frequency, the magnetic waveform type influences rotation of the SPIONs magnetic moments. A sinusoidally, as opposed to square, varying field was shown (see Figure 4.20) to produce a delayed rotation of the magnetic moments which was hypothesized to promote transverse assembly leading to wider and more separated assemblies. The parametric trends for a sinusoidally varying field are shown in Figure 5.13B for a SPION volume fraction of 0.02% in DI water. For comparison, the parametric trends for a square waveform at a volume fraction of 0.04% in DI water is also shown in Figure 5.13A; the morphology differences between the volume fractions discussed here (0.02 vol% versus 0.04 vol%) are only expected to impact the length and width of the assemblies (higher volume fractions leading to larger values), and not the separation, as discussed in Section 5.3.3. As the frequency decreases, the separations produced by the sinusoidal waveform increase, while the separations produced by the square waveform decrease. This discrepancy can be attributed to the SPION rotation behavior differences due to the waveform type (see Figure 4.20). With the gradual transition of the sinusoidal waveform, the SPIONs have a delayed rotation and thus have enough time to complete transverse assembly which also increases the separation between assemblies. Meanwhile, with the abrupt transition of the square waveform, the SPIONs rotate to briefly promote transverse assembly, but then quickly align their magnetic moment with the new field direction, and thus have more time to complete lateral assembly. This effect is most evident at very low frequencies. For example, at a frequency of 0.1 Hz, the sinusoidally varying field produced assemblies with an average separation of approximately 45 µm, whereas the average separation was determined to be approximately 19 µm for a square field. In addition, the impact of the magnetic flux density is more pronounced for a sinusoidal waveform, as compared to a square waveform, at frequencies at or below 1 Hz, which is possibility due to more free aggregates being located in the transverse direction and thus an increase in the magnetic flux density will increase the magnetic capture radius in directions other than laterally, especially for induced fields with delayed rotation.

Compared with SPION assemblies achieved with the static field, the assembly morphology by the sinusoidal oscillating field exhibited changes by as much as 43% increase for the length (100
G, 0.1 Hz), 56% for the width (100 G, 0.05 Hz), and 139% for the separation (100 G, 0.05 and 0.1 Hz). Such line assembly patterning capability will be effective to tailor, for example, transport properties of PNCs: with the same nanofiller volume fraction, thin, long, and dense line features are more likely to extend across the sample size with minimum interfaces and thus boundaries resistance, resulting in higher thermal transport properties.

Figure 5.13: Characteristic dimensions of SPION assemblies in DI water using oscillating magnetic fields of varying magnetic flux density, frequency, and waveform: A) 0.04 vol%, square waveform and B) 0.02 vol% sinusoidal waveform. A 95% bootstrap confidence interval based upon the mean parameter values is indicated in the figure.
5.3.3 Effects of nanoparticle volume fraction

The influence of the nanoparticle volume fraction on assembly morphology is important to achieve connectivity percolation at low volume fractions. Figure 5.14 demonstrates morphology variations of the SPION assemblies for volume fractions of 0.04%, 0.06%, and 0.08% using a square waveform. The volume fraction variation has the effect to produce longer, wider, but similarly separated assemblies on average. Specifically, an approximately constant separation was found between assemblies for all volume fractions, with increased separation found for increasing frequency up to 1 Hz, and a plateauing of the separation occurring for frequencies above 1 Hz. This trend can be better understood by investigating the morphology changes in the assembly length and width with increasing SPION volume fraction. Both the assembly length and width increased with increased volume fractions, which led to larger assemblies on average. For example, SPIONs with a volume fraction of 0.08% produced assemblies on average three times the size of those formed with SPION of the 0.04% volume fraction. The length change of the assemblies was more sensitive to volume fraction variations than those found for width changes, implying additional SPION aggregates or assemblies are more likely to migrate in the lateral direction as opposed to the transverse direction. Due to the increase in the size of the assemblies, fewer assemblies within the image processing region were found. At a frequency of 0.1 Hz, a volume fraction of 0.08% produced 50% fewer assemblies compared to a volume fraction of 0.04%. Therefore, the combination of larger assemblies, fewer assemblies within the magnetic capture radius, and additional SPIONs migrating in the lateral direction leads to an approximately constant separation for all volume fractions. In addition, it is hypothesized that at higher volume fractions, 1% or greater, the volume fraction will have a notable influence on the separation leading to reduced separation due to assemblies having lengths that span the entirety of the sample domain and thus additional assemblies will migrate in the transverse direction as opposed to the lateral direction.
Effects of nanoparticle type

Ferrimagnetic nanoparticles (see Section 4.1.3) are more magnetically responsive than SPIONs, although with magnetic remanence. The increased magnetic response of ferrimagnetic nanoparticles will produce an increased magnetic capture radius leading to larger nanoparticle assemblies. Thus, ferrimagnetic nanoparticles can provide stronger inter-particle magnetic forces to overcome hydrodynamic drag and achieve connectivity percolation, and therefore are suitable for assembly in viscous polymers. To apply the above knowledge about SPION assembly to a different magnetic nanoparticle type, ferrimagnetic iron oxide nanoparticles (US Research Nanomaterials, US7568, Fe₃O₄, supplied 20% weight in water) were selected. The ferrimagnetic nanoparticles are approximately 25 nm in diameter (see Figure 5.15A) and therefore 50% larger.

Figure 5.14: Characteristic dimensions of SPION assemblies in DI water using oscillating magnetic fields with square waveform of varying SPION volume fractions.

5.3.4 Effects of nanoparticle type

Ferrimagnetic nanoparticles (see Section 4.1.3) are more magnetically responsive than SPIONs, although with magnetic remanence. The increased magnetic response of ferrimagnetic nanoparticles will produce an increased magnetic capture radius leading to larger nanoparticle assemblies. Thus, ferrimagnetic nanoparticles can provide stronger inter-particle magnetic forces to overcome hydrodynamic drag and achieve connectivity percolation, and therefore are suitable for assembly in viscous polymers. To apply the above knowledge about SPION assembly to a different magnetic nanoparticle type, ferrimagnetic iron oxide nanoparticles (US Research Nanomaterials, US7568, Fe₃O₄, supplied 20% weight in water) were selected. The ferrimagnetic nanoparticles are approximately 25 nm in diameter (see Figure 5.15A) and therefore 50% larger.
than the previously used SPIONs. Due to this, as shown in Figure 5.15B, the ferrimagnetic nanoparticles have a magnetic saturation (60 emu/g) approximately three times greater than that of the SPIONs. The ferrimagnetic nanoparticles aggregate to sizes of approximately 1-5 µm due to the interaction energies (see Chapter 4.3.1). The nanoparticles were diluted in deionized water to a volume fraction of 0.04% and then ultrasonicated for 5 minutes. As before, the solution was then encapsulated in a slide (KOVA Glasstic) and mounted centered, and along the axis, of the solenoid pair. The experimental set-up is the same as before, as shown in Figure 5.4.

**Figure 5.15:** A) TEM image and B) VSM plot of ferrimagnetic Fe₃O₄. Taken from www.us-nano.com (US7568).

To evaluate the effect of the nanoparticle size, or the nanoparticle magnetic response, on assembly morphology, comparisons were made between the ferrimagnetic iron oxide nanoparticles and the SPIONs, see Figure 5.16. With the static field application (50 G, 10 min), the Fe₃O₄ assembly length (139 µm) and separation (61 µm) were much larger than those of SPION assemblies (25 µm length and 18 µm separation) at the same volume fraction (0.04 vol %). With the stronger magnetic susceptibility of Fe₃O₄, the capture radius increased and thus head-to-tail assembly was promoted, resulting in longer assemblies with larger separation. An unexpected trend was observed when the field oscillation was turned on (0.05 Hz, 50 G, square waveform); the Fe₃O₄ assembly length decreased (45 µm), while the SPION assembly length always increased with the square field oscillation, especially in the low frequency range, as discussed previously. It should be noted that this Fe₃O₄ assembly length (45 µm by the square waveform with 0.05 Hz and 50 G) is comparable with the SPION assembly length achieved with the similar oscillating field (37 µm by the square waveform with 0.1Hz and 50 G). In addition, the Fe₃O₄ assembly separation (106 µm
by the square waveform with 0.05 Hz and 50 G) is much larger than those of Fe$_3$O$_4$ assembly by the static field (61 µm by the static field of 50 G) and of the SPION assembly achieved with the similar oscillating field (23 µm by the square waveform with 0.1 Hz and 50 G). Assuming that magnetic moment reorientations can be completed with this low frequency field oscillation (0.05 Hz), this unexpected trend can be attributed to two possible mechanism. First, due to their larger magnetic susceptibility, transverse assembly is enhanced and free aggregates are effectively attracted to the assemblies, leading to the separations between assemblies becoming larger than the capture radius, effectively prohibiting head-to-tail and/or zippering assembly. Second, the magnetic assembly time was not long enough to ensure that the assembly morphology was steady. By increasing the field strength to 100 G, the Fe$_3$O$_4$ assembly length increased (121 µm by the square waveform with 0.05 Hz and 100 G) while keeping the separation relatively large (89 µm) because the capture radius was increased and thus the head-to-tail and/or zippering assembly were promoted. This assembly study confirmed that the magnetic properties of the nanofillers play a large role in assembly formation by inter-assembly attraction rather than by aggregate attraction to assemblies. This capability to lengthen assemblies is effective to achieve connectivity percolation within PNCs and thus higher transport properties. Further studies should be conducted to explore more tailorability of ferrimagnetic nanofiller assembly, for example to decrease the separation while maintaining assembly lengths.

**Figure 5.16**: Magnetic assembly comparison of A) SPIONs and B) ferrimagnetic Fe$_3$O$_4$ (both 0.04 vol% in DI water) by optical microscope images and measured characteristic dimensions.
The influence of a sinusoidal waveform (50G peak, 0.05 Hz) on assembly characteristics of the ferrimagnetic nanoparticles (Fe₃O₄ at a volume fraction of 0.04% in DI water) is shown in Figure 5.17 after 10 minutes of the field application. ‘Breathing’ of the ferrimagnetic assemblies was observed due a combination of thermal diffusion or reorientation of the nanoparticles and the nanoparticles magnetic remanence during the minimum field condition leading to constant variations of the length of the assemblies. The assemblies were observed to reduce to 80% of their maximum length near the minimum field condition. Unlike the assembly variations with SPIONs, diffusion and magnetic remanence of the ferrimagnetic nanoparticles during the minimum field condition leads to a coarsening of the assemblies with time, similar to observations in Swan et. al [144]. Compared to the SPION assemblies, the ferrimagnetic assemblies are approximately 300% wider, but 20% the length at the same field conditions. The cyclic assembly morphology variations, including coarsening, of the ferrimagnetic nanoparticles is hypothesized to be prevalent only in low viscosity matrices due to a limiting of Brownian diffusion during the minimum field condition in high viscosity matrices. Thus, ‘breathing’ of ferrimagnetic assemblies due to a sinusoidal waveform is not expected in polymer matrices.

![Figure 5.17: ‘Breathing’ of ferrimagnetic nanoparticle (Fe₃O₄ at 0.04% volume fraction in DI water) assemblies due to a sinusoidal waveform at an external magnetic field of 50 G, frequency of 0.05 Hz, and assembly time of 10 minutes. The time between each successive image (A-E) is approximately 2 seconds. (F) Ferrimagnetic nanoparticle assembly morphology for a 50% duty cycle square waveform at the above assembly parameters – ‘breathing’ of the assemblies is not observed.](image-url)
5.4 Summary of Magnetic Nanoparticle Parametric Studies

Magnetic assembly behavior of nanoparticles has been studied parametrically with model SPIONs, and symmetric and oscillating magnetic fields, and the study was applied to the magnetic assembly of ferrimagnetic nanoparticles. The field parameters were varied (flux density, frequency, and waveform) to demonstrate the tailorability of anisotropic nanoparticle structuring and fabrication in an energy efficient (< 100 G) manner and in a short time (15 mins). The magnetic assembly behavior of the SPIONs was observed to be dominated by inter-aggregate attraction caused by induced, local, non-uniform magnetic fields. Oscillation of the external magnetic field produced increased separation and coarsening of the assemblies due to rotation of the induced field. The lower frequency range (< 0.1 Hz) was found to produce highly tailorable assemblies due to balancing between lateral (along the field direction) and transverse assembly mechanisms leading to more separated, longer, and wider assemblies on average. The tailorability of assemblies can be enhanced through the use of a sinusoidal field, as opposed to a square field, due to an increased phase delay between the nanoparticle’s magnetic moments and the external field direction. Also, the magnetic flux density has been shown to be effective at enhancing the head-to-tail assembly mechanism due to an increased magnetization of the nanoparticles. The tailorability of nanoparticle assemblies using an oscillating field was also verified for ferrimagnetic nanoparticles; due to the increased viscosity of polymer matrices, rotation of the local, induced field is limited and thus nanoparticles with increased magnetization are required to ensure rotation of the nanoparticles prior to the field switching. However, ferrimagnetic nanoparticle assembly with oscillation of the external magnetic field requires longer assembly time than that for a static field, possibility due to the increased capture radius and thus additional time required for complete aggregate or assembly translation.
Chapter 6

Fabrication of 1D Tailored Polymer Nanocomposites using Magnetic Fields

In this chapter, fabrication processes will be discussed about one-dimensionally (1D) tailored polymer nanocomposites (PNCs) using static and oscillating magnetic fields to evaluate scalability and tailorable of this magnetic structuring method for PNCs (Objective II). As was discussed in Chapter 2, and as will be confirmed in Chapter 7, magnetic assembly uniquely tunes interface and interphase conditions within iron oxide assemblies, influencing transport (electrical and thermal) properties of PNCs. The novel usage of an oscillating magnetic field enables additional control over the iron oxide assembly morphologies producing thicker, but more separated assemblies as confirmed in Chapters 4 and 5. The theoretical discussions of Chapter 4 and the parametric findings of Chapter 5 are incorporated to tailor maghemite assemblies within a thermoset matrix.

The challenges of PNC fabrication include 1) the larger effect of hydrodynamic forces and 2) nanoparticle suspension and dispersion due to the higher viscosity of the polymer matrix as compared to DI water. More magnetically responsive ferrimagnetic maghemite nanoparticles are used to increase magnetic forces in order to counteract hydrodynamic forces. In order to reinforce suspension and dispersion, nanoparticles are surface treated and fragmentated with two different methods: wet-processing using ball milling and dry-processing using a mortar and pestle. Optical and microCT evaluation of the nanoparticles assemblies within the polymer matrix is conducted to correlate the manufacturing parameters (magnetic flux density, frequency, waveform, and field gradient) to the observed, and expected, assembly morphologies. Property characterization of these fabricated samples will be discussed in Chapter 7.
6.1 Preparation of Maghemite Nanoparticles

6.1.1 Characterization of maghemite nanoparticles

Maghemite, or gamma-phase iron oxide ($\gamma$-Fe$_2$O$_3$), was selected as the nanofiller for PNC fabrication, over SPIONs, due to their stronger magnetic responsiveness. Maghemite also readily couples with the selected surface modifier as will be discussed in Section 6.1.2. The maghemite nanoparticles in powder form were purchased from US Research Nanomaterials (US3200) in 100g quantities. While the company provides particle information, the as-received maghemite nanoparticles were again characterized about their particle size (including its distribution and associated particle surface areas), material phase and associated magnetic properties as these nanoparticles can potentially alter their conditions during shipping, handling, and storage.

First, the particle size of as-received maghemite nanoparticles and their aggregates were measured. Like SPIONs, maghemite nanoparticles form aggregates due to the interaction energies as discussed in Section 4.3.1. The size of the maghemite aggregates needs to be small to minimize gravitational sedimentation and to control the size of the resulting assemblies when exposed to an external magnetic field. As shown in Table 4.6, for the as-received nanoparticles in a bisphenol-F matrix, the percent ratio between Brownian translation and gravitational sedimentation, $\gamma_k$, is calculated at room temperature after 30 minutes; the ratio decreases (from 88%, 57%, and to 2%) as the aggregate diameters increases (from 0.50 µm, 1.00 µm, and to 5.00 µm, respectively). Based on this calculation, the goal was to decrease the aggregate size to less than approximately 0.5 µm to avoid sedimentation. On the other hand, a large aggregate size is useful to increase the magnetic capture radius (see Section 4.3.3) to enhance magnetic assembly; the capture radius is proportional to the square of the aggregate diameter. For the as-received maghemite in a bisphenol-F matrix, an aggregate diameter of 5.00 µm will produce a magnetic capture radius 100 times greater than that of an aggregate with a diameter of 0.50 µm (140 µm vs. 1.4 µm for a magnetic susceptibility of 4.9 and at a temperature of 70 °C). A large capture radius is effective in continuous structuring along the assembly direction, together with the external field strength and the particle magnetic susceptibility.

Transmission electron microscopy (TEM, Philips EM 420, 120 kV) images of the as-received nanoparticles are shown in Figure 6.1; the particles were drop cast onto a Lacey carbon grid. The individual nanoparticles are roughly spherical with a diameter of approximately 15 to 25 nm. Aggregate sizes were evaluated from optical microscope images (Olympus BX51WI) of the as-received maghemite in DI water (0.04 vol %) focused on the bottom slide plane where the largest
aggregates settle. The upper bound for the aggregate size was estimated to be approximately 10 µm (see Figure 6.2A).

![Figure 6.1: TEM images of the maghemite nanoparticles at different scales: A) nanoparticles within an aggregate, B) multiple aggregates, and C) large aggregates.](image)

To obtain a more accurate size measurement of nanoparticles below 1 µm, dynamic light scattering (DLS) was used. By focusing a laser on the as-received maghemite aggregates in DI water (0.04 vol%), the time rate intensity variations of the scattered light can be measured and correlated to the Brownian velocity leading to estimates of the aggregate hydrodynamic diameter [224]. DLS (Zetasizer Nano ZS, 173° measurement angle) is a technique sensitive to aggregates that are suspended within a matrix and represents a lower bound for the aggregate size. Errors with this methodology are primarily associated with accurate measurement of the temperature due to its effect on Brownian diffusion (1° error in temperature is correlated with a 2% error in aggregate size) and errors associated with the detection angle (1° error in detection angle is correlated with a 0.1% error in aggregate size for systems with a 173° measurement angle). In Figure 6.3, the averaged DLS measurement results are given about three consecutive tests at a temperature of 25 °C (± 0.1 °C). The mean for the aggregate size was estimated to be approximately 0.58 µm with a standard deviation of 0.081 µm. Therefore, even the lower bound size range of the as-received
maghemite aggregates (approximately 0.35 – 0.83 µm) is not entirely below the desired aggregate size range calculated above (< 0.5 µm), and thus sedimentation will likely occur. Aggregate size reduction will be discussed in Section 6.1.2.

Second, magnetic properties of the as-received maghemite nanoparticles were measured using vibrating sample magnetometry (VSM, MicroSense); see Section 4.1.2 for details on VSM methodology. Maghemite is a ferrimagnetic material (see Section 4.1.3) with small coercivities and thus low power loss. Due to their non-zero magnetic remanence, maghemite nanoparticles will not disperse upon removal of the external field, unlike SPIONs. This trend causes aggregation, but is useful to maintain nanoparticle assembly morphology during the post-cure step in fabricating PNCs. VSM measurement (± 1200 kA/m) was conducted on a 0.066 g sample of the as-received maghemite as shown in Figure 6.4. The saturation magnetization, magnetic coercivity, and remanent magnetization were measured as $M_s = 66$ emu/g, $H_c = 1226$ A/m, and $M_r = 1.1$ emu/g. The measured $M_s$ is approximately three times greater than that of the SPIONs measured in Chapter 5 ($M_s = 21$ emu/g). The initial magnetic susceptibility was measured from the slope of the magnetization curve at the zero-field condition as approximately $\chi_i = 4.9$.

![Figure 6.3: DLS results of the as-received and ball-milled maghemite nanoparticles dispersed in water; each plot is the average value over three consecutive measurements.](image)
Third, the maghemite phase was partially verified through X-ray diffraction (XRD, PANalytical Empyrean X-Ray Diffractometer). Due to the large number of iron oxide phases \[225\], verification that the phase is maghemite is important to direct surface modification of the nanoparticles. XRD is conducted through the generation of x-rays in a cathode ray tube (cobalt), which are filtered (to produce monochromatic radiation), concentrated, and directed towards a sample. The x-rays diffract based upon the crystal lattice. By scanning the sample over an angle of 2\(\theta\), all possible lattice diffraction directions can be obtained and when constructive interference occurs a peak in the intensity is found. These peak intensity angles can be related to the lattice constant of the material by Bragg’s law as shown in Equation 6.1; \(n\) is a positive integer, \(\lambda_b\) is the wavelength of the source (Å), \(d_b\) is the interplanar spacing or d-spacing (Å), and \(\theta_b\) is the scattering angle (degree). Typically, the d-spacing values are compared against a database of known samples to determine the material phase.

\[
2d_b\sin\theta_b = n\lambda_b \tag{6.1}
\]

An approximate 0.1 g sample of the as-received maghemite was placed within the test chamber and a cobalt source (\(\lambda_b = 1.789\) Å) emitted x-rays over a 2\(\theta_b\) angle (\(\pm 0.03^\circ\) 2\(\theta\)) of 85\(^\circ\). The resulting diffraction peaks and corresponding d-spacing of each peak based on Equation 6.1 are shown in Figure 6.5. The diffraction peaks are verified to be that of either maghemite or magnetite \[226,227\], with the tetragonal lattice structure and lattice constants of 8.332 Å and 25.113 Å. Determination of whether the phase is maghemite or magnetite is discussed in Section 6.1.2.2.
Fourth, the specific surface area of the as-received maghemite was measured using Brunauer-Emmett-Teller (BET, ASAP 2420) theory. BET theory relates the amount of gas absorption on the surface of nanoparticles to the nanoparticle specific surface area. The specific surface area of the nanoparticle is of interest to determine the required amount of surface modifier needed to coat the nanoparticles. The as-received maghemite (0.554 g) was evaluated at a bath temperature of 77.4 K with nitrogen (N\textsubscript{2}) as the adsorbate and an equilibrium interval of 10 s. Per ISO 9277, the amount of gas absorbed ($Q$, mmol/g) is given by Equation 6.2, where $P/P_0$ is the relative pressure, $n_m$ is the monolayer amount (mmol/g), and C is the BET parameter. As shown in Figure 6.6, the left side of Equation 6.2 is plotted against the relative pressure to determine the monolayer amount, $n_m$. The monolayer amount is calculated using Equation 6.3, where $a_y$ is the y-intercept value and b is the slope of the BET surface area plot. The specific surface area ($a_s$, m\textsuperscript{2}/g) for N\textsubscript{2} as the adsorbate is calculated as shown in Equation 6.4. The specific surface area for the as-received maghemite was measured as approximately 79.1 m\textsuperscript{2}/g. If the nanoparticles are assumed to be nonporous and spherical, and $\rho_s$ is the density of maghemite (4900 kg/m\textsuperscript{3}), the diameter of the nanoparticles can be estimated as $d = 6/(\rho_s a_s) \approx 16$ nm which is in agreement with the TEM images.

$$\frac{1}{Q(P_0/P-1)} = \frac{1}{n_m C} + \frac{C-1}{n_m C P_0}$$

(6.2)
\[ n_m = \frac{1}{a_y + b} \]  
\[ a_s = 97.6n_m \]  

Figure 6.6: BET surface area plot for the as-received maghemite nanoparticles.

6.1.2 Silane surface modification of maghemite nanoparticles

Application of a surface modifier (also known as a surfactant or coupling agent) to the surface of the as-received maghemite is beneficial to stabilize the surface of the maghemite aggregates. This application limits the interaction energies (see Section 4.3.1) and thus can control aggregate size [110,228–230]. In addition, a surface modifier can reduce sedimentation through a gradient in surface tension due to non-uniform coatings (the so-called Marangoni flow) [88,89]. Due to a diamagnetic effect of surface modifiers, the net magnetization of surface modified nanoparticles decrease to some extent [231–233]. In addition to the benefits of aggregate and sedimentation control, the surface modifier is expected to enhance the mechanical properties of fabricated PNCs due to bonding and effective load transfer between the nanoparticle and matrix [53,87,234].

Here, a silane surface modifier, 3-glycidyloxypropyl trimethoxysilane (GPS, Sigma-Aldrich), was selected to coat maghemite particles. The chemical processes are illustrated in Figure 6.7. GPS is compatible with the polymer matrix (bisphenol-F type, EPON 862, miller-stephenson), the cross-linking agent (diethyltoluenediamine, DETDA, Epikure W, miller-stephenson), and the maghemite nanoparticles used in this work (see Section 6.2). The mass of GPS required for a minimum monolayer covering on the maghemite surface is calculated using Equation 6.5, where...
\( m_m \) is the mass of the maghemite (g) and \( sws \) is the specific wetting surface of the surface modifier (331 m\(^2\)/g for GPS). Therefore, to ensure at least a minimum coating of GPS over the maghemite nanoparticles, the mass of the surface modifier to the mass of the as-received maghemite needs to be a minimum of 24% (for \( a_s = 79.1 \) m\(^2\)/g as calculated from the BET measurement above).

\[
m_s = \frac{m_m a_s}{sws}
\] (6.5)

### 6.1.2.1 Processing

Two different processes, with the same chemistry (see Figure 6.7) but with different fragmentation methods, were followed to bond the surface modifier to the maghemite surface [235]: dry-processing and wet-processing. The major difference between the dry- and wet-processes is that the Hamaker constant, a matrix dependent material constant proportional to the van der Waals interaction energy [236], was modified during wet-processing leading to control over the resulting aggregate size as discussed in Section 4.3.1. Since the Hamaker constant was not modified during dry-processing, the maghemite aggregate size following this process was expected to be similar to that of the as-received maghemite.

The dry-process consists of three steps. First, GPS (2% by weight) was mixed with ethanol (as catalyst, 95% by volume) and DI water (5% by volume), and ultrasonicated (Branson Ultrasonics, CPX-952-117R) at 60 °C for one hour to hydrolyze the silane. Second, the as-received maghemite (\( \gamma \)-Fe\(_2\)O\(_3\)), already hydrolyzed in the atmosphere, was added (6% by weight) to the hydrolyzed silane solution and ultrasonicated at 60 °C for two hours. This weight percentage of maghemite is greater than that required to ensure a monolayer covering of the surface modifier (here, the mass of GPS to the mass of maghemite is approximately by 32%, greater than the 24% required for monolayer coverage). Third, the surface modified nanoparticles (GPS-\( \gamma \)-Fe\(_2\)O\(_3\)) were centrifuged (Benchmark Scientific, C3100, 2000 RPM for 10 minutes) out of the solution and dried in an oven at 80 °C for 24 hours to facilitate covalent bond formation.
Meanwhile, the wet-process uses ball-milling. In the presence of a solvent and surface modifier, ball-milling is an effective technique to diminish nanoparticle interaction energies and fragmentate aggregates as discussed in Section 4.3. The as-received maghemite (6% by weight) was ball-milled in a planetary ball-mill (Tencan, XQM-0.4A) for 70 hours in the presence of a solvent (ethanol, 95% by volume), DI water (5% by volume), and the surface modifier (GPS, 2% by weight). To prevent re-aggregation of the nanoparticles due to heating, the ball mill ran at 300 RPM and cycled through 6 minutes clockwise, 3 minutes pause time, 6 minutes counter-clockwise,

**Figure 6.7:** Idealized process to attached the silane surface modifier GPS to the surface of the maghemite aggregates: A) the chemical structure of the selected surface modifier GPS, B) hydrolysis of the surface modifier, C) hydrogen bond formation with the maghemite aggregates, and D) covalent bond formation due to a loss of water. Modified from [231].
and 3 minutes pause time. A 7:1 ratio of the milling media (zirconia, 0.9 mm) to the powder was used. In addition, the ball-milling containers were filled approximately 40% full to ensure high impact forces. The ball-milled, and surface modified, maghemite was then stored in the milling matrix to be used for PNC fabrication.

6.1.2.2 Characterization

The effectiveness of GPS surface modification and of dry- vs. wet-processing was evaluated by measuring the aggregate size, sedimentation, and the surface chemistry condition of the surface modified maghemite nanoparticles.

The aggregate sizes were measured using both optical microscopy and DLS after dry- and wet-processing as summarized in Table 6.1. When compared with the as-received maghemite aggregate sizes (0.58 µm – 10 µm, see Section 6.1.1), the surface modified aggregate sizes were smaller for the wet-processed nanoparticles, with little to no change for the dry-processed nanoparticles since the interaction energies were not modified: 0.58 µm to 10 µm for dry-processed nanoparticles (see Figure 6.2B), and 190 nm to 1 µm for wet-processed nanoparticles (see Figures 6.2C and 6.3). While the wet-processed nanoparticles have aggregate sizes below the sedimentation threshold of 0.5 µm, the dry-processed nanoparticles do not. To accurately investigate the sedimentation threshold for the processed nanoparticles, the percent ratio between Brownian translation and gravitational sedimentation, \( \gamma_k \), was calculated. As discussed in Section 4.3.4, this value represents the ratio of Brownian (thermal) diffusion to gravitational sedimentation. Aggregates with \( \gamma_k \) close to 100% will randomly diffuse and therefore stay suspended, whereas when \( \gamma_k \) is close to 0% sedimentation is likely. For the dry-processed nanoparticles, \( \gamma_k \) values below 50% were calculated for all sizes, indicating sedimentation will occur. However, this analysis does not incorporate the effects of the surface modifier, which will arrest the effects of sedimentation as discussed above. On the other hand, the wet-processed nanoparticles had a calculated \( \gamma_k \) near 100% at their lower size range, and approximately 15% at their upper size range. Including the effects of the surface modifier on sedimentation reduction, the wet-processed nanoparticles were not expected to settle. The magnetic capture radii for the dry- and wet-processed nanoparticles were also calculated at a temperature of 70 °C, magnetic field of 300 G, and magnetic susceptibility of 4.9 (see Section 6.1.1). The upper bound magnetic capture radius was found to be large (5 mm) for the dry-processed nanoparticles due to their aggregate size. Therefore, these nanoparticles are expected to form assembly even with larger inter-aggregate distances, and therefore to form longer assembly and thus pathways throughout the PNC samples leading to percolation. On the other hand,
the upper bound capture radius for the wet-processed nanoparticles is much smaller (54 µm), which may limit assembly formation soon after the field application, and thus may not form conductive pathways in the fabricated samples.

**Table 6.1:** Effect of the dry- and wet-processing on the maghemite aggregate size (measured) and their sedimentation and assembly (estimated).

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>As-Received/ Dry-Processing</th>
<th>Wet-Processing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aggregate Size ($c$)</td>
<td>580 nm – 10 µm</td>
<td>190 nm – 1 µm</td>
</tr>
<tr>
<td>Sedimentation ($\gamma_k$, 30 min at 70 cP)</td>
<td>41% – 0.06%</td>
<td>92% – 15%</td>
</tr>
<tr>
<td>Capture Radius ($r_c$, 300 G, 70 °C)</td>
<td>18 µm – 5 mm</td>
<td>2 µm – 54 µm</td>
</tr>
</tbody>
</table>

Attachment of the silane surface modifier to the maghemite surface (GPS-$\gamma$-Fe$_2$O$_3$) was evaluated using Fourier-transform infrared spectroscopy (FTIR, Bruker Vertex 70). By directing an infrared source towards the nanoparticles, FTIR measures resonance wavelengths due to phonon absorption. The resonance wavelengths are then correlated to known molecular vibrational and rotational states. Attenuated total reflection (ATR) was first conducted to verify the maghemite phase, the presence of hydroxyl groups on the as-received maghemite, and the presence of organic groups on the surface modified maghemite. As shown in Figure 6.8, the absorbance peaks observed at 548, 625, 687, and 724 cm$^{-1}$ correlate well to the classical high frequency modes of gamma phase iron oxide (589, 620, 687, and 725 cm$^{-1}$) [237]. In addition, the shoulder at 625 cm$^{-1}$ indicates that the phase is maghemite, not magnetite, as this wavelength is a characteristic of maghemite and previous work in literature has demonstrated that this shoulder can be used to distinguish between a maghemite or magnetite phase [226]. An O-H stretch (3600 – 3200 cm$^{-1}$) was found on the as-received maghemite indicating the presence of hydroxyl groups: $Fe_2O_3 + H_2O \leftrightarrow FeO(OH)$. Organics, specifically C-H bonds and the epoxy ring group, were found on the surface modified GPS-$\gamma$-Fe$_2$O$_3$ nanoparticles indicating the presence of the surface modifier. However, observation of these peaks only indicates that these materials exist within the inspected samples. Thus, diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) was conducted to verify that the surface modifier was bonded to the maghemite surface, instead of agglomerated around the nanoparticles (see Figure 6.9). After surface treatment, the peak associated with the Fe-O-H stretch became non-existent indicating that the as-received maghemite hydroxyl groups were consumed during the reaction to bond the surface modifier with the nanoparticle surface, and confirming the surface modifier attachment with the nanoparticles.
Reduction of sedimentation by surface modification was evaluated by inspecting distribution of the surface modified nanoparticles within PNCs fabricated using a bisphenol-F.

**Figure 6.8**: ATR FTIR absorbance spectrum of the A) as-received maghemite, B) GPS surface modifier, and C) the surface modified maghemite nanoparticles (GPS-γ-Fe₂O₃) using the dry-process. The peak wavenumber were obtained from [87,228,229,238–240].

**Figure 6.9**: DRIFTS absorbance spectrum of the A) as-received maghemite, and B) surface modified maghemite nanoparticles (GPS-γ-Fe₂O₃) using the dry-process.

Reduction of sedimentation by surface modification was evaluated by inspecting distribution of the surface modified nanoparticles within PNCs fabricated using a bisphenol-F.
matrix; details about this fabrication process will be discussed in the next section. A 0.3 vol % of the three maghemite nanoparticles (as-received, GPS-γ-Fe₂O₃ using dry-processing, and GPS-γ-Fe₂O₃ by wet processing) were separately mixed with the cross-linking agent Epikure W (1.9 g) and ultrasonicated at 60 °C for 2 hours. The bisphenol-F resin (EPON 862) was then added (7.2 g, 100:26.4 mass ratio) to the resulting mixture, which was ultrasonicated at 60 °C for 30 minutes. The mixture was then poured into a mold (1.9 cm x 1.9 cm x 0.95 cm) and cured following the standard cycle (70 °C for 30 minutes, 121°C for one hour and 171°C for two hours). After post-cure, a diamond saw was used to extract a 1-mm-thick cross-section from the center of each sample, see Figure 6.10A. The extracted cross-sections were polished for visual inspection, and the thickness of the sedimentation layer at the bottom was measured. As compared in Figure 6.10B, the sedimentation thickness decreased from approximately 80 µm for the as-received maghemite to approximately 32 µm after the dry-processing, even though dry-processing did not decrease the aggregate size. As explained above, a non-uniform coating of the surface modifier will produce a surface tension gradient over the aggregate surface limiting sedimentation. Meanwhile, almost no sedimentation was observed with the wet-processed nanoparticles. The decreased aggregate size increased Brownian diffusion, while reducing gravitational sedimentation, which effectively enhanced nanoparticle suspension.

![Figure 6.10](image)

**Figure 6.10**: PNC samples prepared to investigate the effect of a surface modifier on reducing nanoparticle sedimentation: A) schematics showing the cut section location, and B) optical microscope images showing the sedimentation (lighter regions) close to the bottom surface of the PNC samples consisting of the as-received and dry- and wet-processed surface modified maghemite nanoparticles.
An aerospace grade thermoset (bisphenol-F type resin, EPON 862) was selected as the matrix in this work due to its high mechanical properties and low viscosity at the working temperature (approximately 70 cP at 70 °C). The viscosity of the resin (as measured using a Brookfield Viscometer, RVTDV-IICP) is shown in Figure 6.11. The chemical structure of the resin, DETDA cross-linker (Epikure W) and their attachment to the surface modifier are illustrated in Figure 6.12. The additional amount of cross-linker needed due to the epoxy groups on the surface modified nanoparticle surfaces can be estimated by assuming spherical aggregates. Assuming functionalization sites exist surrounding the surface modified maghemite, but not internal (see Figure 6.7D), the molecular weight of these functionalization sites was estimated \((mw_s = 215 \text{ g/mol per epoxy group for maghemite and GPS, } C_6H_{11}O_3SiFe)\). The molecular weight of the internal maghemite was approximated \((mw_i = 160 \text{ g/mol for maghemite, } Fe_2O_3)\). Knowing the molecular weight of the cross-linker \((mw_a = 45 \text{ g/mol per anime hydrogen for DETDA})\), the percent mass of the surface modified nanoparticles to the cross-linker can be calculated as shown in Equations 6.6 and 6.7, where \(c\) and \(r_p\) are the radius (m) of the aggregates and nanoparticles, respectively. For an aggregate diameter of 500 nm, and a nanoparticle diameter of 20 nm, the mass percent is calculated to be 3.1%. Therefore, due to the small mass fraction found here, additional cross-linker was not considered, and the standard stoichiometric mass ratio of 100:26.4 (resin: cross-linker) was used.

It is important to note that the surface modification process, and cross-linker and resin bonding, as demonstrated in Figure 6.7 and Figure 6.12, and discussed above, are idealized. It is assumed that hydroxyl groups are present uniformly around the nanoparticle aggregate surface, and these groups are only present at the surface. However, grafting density at the aggregate surface is not likely to be 100%, in addition to imperfect bonding due to non-uniform hydroxyl distribution, which may limit bonding between the nanoparticles and the resin leading to diminished property improvement.

\[
\beta = \frac{mw_i \left( c^3 - r_p^3 \right) + mw_s \phi}{r_p^3} \times 100\% \quad (6.6)
\]

\[
\phi = \left( c^3 - \left[ c - r_p \right]^3 \right) / r_p^3 \quad (6.7)
\]
Below, two different methods to conduct the surface modification, mixing, and assembly of maghemite nanoparticles in the epoxy matrix are summarized in Table 6.2. For both these processes, a non-magnetic aluminum mold with dimensions of 1.91 cm x 1.91 cm x 0.95 cm was used (see Figure 6.13C). The standard cure cycle was followed for all fabricated PNCs: (1) 70 °C working temperature for 1 hour, (2) 121 °C cure temperature for 1 hour, and (3) 171 °C post-cure temperature for 2 hours. The working life was split between heated ultrasonication (Branson Ultrasonics, CPX-952-117R, 30 minutes) and magnetic assembly (30 minutes) to ensure dispersion of the nanoparticles and allow enough time for the nanoparticles to assemble within the matrix due

**Figure 6.11**: The viscosity vs. temperature of EPON 862 (bisphenol-F type).

**Figure 6.12**: Chemical structures of A) bisphenol-F, B) DETDA and C) idealized bonding of the bisphenol-F resin with DETDA and DETDA with the surface modified maghemite nanoparticles (GPS-γ-Fe₂O₃).
to the large hydrodynamic forces. Heating of the mold was conducted through a heat pad (Omega, SRFG-203/10) contacting the bottom side of the mold and powered through an AC power supply (BK Precision, 1653A). A mold release spray (Mann, Ease Release 200) was applied to the mold surfaces prior to fabrication for easy removal of the fabricated PNCs. In all cases, the mold was placed at the center of the generated magnetic field. Below, the details about the two processes are discussed.

### Table 6.2: Summary of the two methods of PNC fabrication in this work.

<table>
<thead>
<tr>
<th>Surface Modification</th>
<th>Dry Process</th>
<th>Wet Process</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ultrasonicate ethanol, GPS, and DI water at 60°C for 1 hour</td>
<td>Ball mill as-received maghemite with ethanol, DI water, and GPS for 70 hours at 300 RPM and room temperature</td>
</tr>
<tr>
<td></td>
<td>Ultrasonicate the as-received maghemite with the above solution for 2 hours at 60°C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Centrifuge particles out of solution and dry at 80°C for 24 hours</td>
<td></td>
</tr>
<tr>
<td>Dispersion</td>
<td>Ultrasonicate the cross-linking agent and the dry processed particles at 60°C for 2 hours</td>
<td>Centrifuge ball milled mixture and decant the solution</td>
</tr>
<tr>
<td></td>
<td>_centrifuge the wet processed particles and DETDA by ultrasonication for 5 minutes</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Add EPON 862 and ultrasonicate at 60°C for 30 minutes</td>
<td>vacuum the mixture at room temperature for 20 minutes, 60°C for 20 minutes, and 120°C for 20 minutes</td>
</tr>
<tr>
<td>Assembly and Fabrication</td>
<td>Solenoid pair (300 G DC and 300 G peak 0.05 Hz sinusoidal)</td>
<td>Ultrasonicate the mixture at 60°C for 30 minutes</td>
</tr>
<tr>
<td></td>
<td>Helmholtz coil pair (300 G DC and 300 G peak 0.05 Hz sinusoidal)</td>
<td>Add EPON 862 and ultrasonicate at 60°C for 30 minutes</td>
</tr>
<tr>
<td></td>
<td>Working: Apply field for 30 minutes at 70°C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cure: Apply field for 60 minutes at 121°C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Post-cure: 120 minutes at 171°C</td>
<td></td>
</tr>
</tbody>
</table>

6.2.1 Solenoid magnetic assembly of dry-processed maghemite nanoparticles

The dry-processed nanoparticles were assembled within the matrix using a magnetic field generated by a solenoid pair. The solenoid experimental set-up is illustrated in Figure 6.13. The solenoid pair (Pasco Scientific, SE-7585, with 416 stainless steel core) is centered, in series, and powered by a bipolar power supply (Kepco, BOP 50-8ML). A function generator (BK Precision,
4014B) is connected to the power supply for current control of the waveform. A TVS diode is connected in parallel across the power supply to limit currents below the maximum allowed. The generated magnetic field was verified using a gaussmeter (Lakeshore, Model 425 with probe 425-HMMT-6J04-VR) and a 3.5% variation in the external field was observed across the mold. Specifically, the magnetic flux density gradient was measured to be approximately 0.11 T/m over the mold length (1.91 cm), which will induce migration of the dry-processed nanoparticles towards the magnetic poles. The temperature of the mold was measured using an infrared thermometer (Omega, HHC 210). While not used here, the experimental setup is also capable of vibration through a connected shaker. This experimental setup is capable of magnetic flux densities up to 600 G and frequencies up to 5 Hz. The magnetic field generated using a solenoid pair in series inevitably has the field gradient.

![Image of experimental setup](image)

**Figure 6.13:** Magnetic assembly set-up using a solenoid pair: digital images of A) experimental components, B) solenoids and C) mold, and D) schematic.

The cross-linking agent was first mixed with the dry-processed nanoparticles (volume fractions of 0.5%, 2.0%, and 5.0%) and ultrasonicated (60 °C for two hours) to facilitate bonding between the curing agent amine and the epoxy group attached to the surface modified nanoparticles. Epon 862 was then added and ultrasonicated (60 °C for 30 minutes) to enhance dispersion of the nanoparticles. The mixture was then poured into the mold, centered and along axis of the solenoid
A one-dimensional magnetic field (300 G DC and 300 G peak 0.05 Hz sinusoidal) was applied to the mixture for 30 minutes at 70 °C. A sinusoidal field at 0.05 Hz was selected to enhance the transverse assembly mechanism for the nanoparticles within a high viscosity matrix as discussed in Sections 4.3.5 and 5.3.2. After assembly, the mixture was cured following the standard cycle (121°C for one hour and 171°C for two hours).

6.2.2 Helmholtz coil magnetic assembly of wet-processed maghemite nanoparticles

The wet-processed nanoparticles were assembled within the matrix using a magnetic field generated by a Helmholtz coil. A Helmholtz coil, unlike a solenoid pair, can generate a uniform magnetic field and will therefore produce no additional forces on the nanoparticles due to an external field gradient. The experimental set-up is illustrated in Figure 6.14. A custom designed triaxial Helmholtz coil (Micro Magnetics, 208 VAC, 50-60 Hz, 30 A) is connected to three bipolar power supplies (Kepco, BOP 50-8ML and BOP 100-10MG along the x- and y-directions, and the z-direction, respectively). The coils are capable of producing a region with uniform magnetic field over 3.8 cm (x-direction) x 6.4 cm (y-direction) x 8.9 cm (z-direction). The generated magnetic field is controlled via LabVIEW software provided by the coil manufacture. In this work, one Helmholtz coil pair (x-direction) was used to generate a one-dimensional magnetic field. The generated magnetic field was verified using a gaussmeter (Lakeshore, Model 425 with probe 425-HMMT-6J04-VR) and a 0.0% variation in the external field was observed across the mold. Therefore, the Helmholtz coil pair does not produce a measurable gradient in the magnetic flux density and thus the wet-processed particles will not migrate towards the magnetic poles. The temperature of the mold was measured using an infrared thermometer (Omega, HHC 210). This experimental set-up is capable of magnetic flux densities up to 300 G, 250 G, and 180 G in the x-, y-, and z-directions, respectively. In addition, the coils are capable of frequencies up to 1 Hz.

The wet-processed nanoparticles were separated from the milling matrix via centrifugation (at 2000 RPM for 10 minutes), and then decanted. The cross-linking agent was then added to the wet-processed particles (volume fractions of 0.5%, 1.0%, 2.0%, 3.0% and 5.0%) and then stirred by hand for 30 seconds, followed by room temperature ultrasonication for 5 minutes. Removal of excess milling matrix was conducted by vacuuming (BestValueVacs, RS-1, -28 in Hg) the mixture at elevated temperatures: 20 minutes at room temperature, 20 minutes at 60 °C, and 20 minutes at 120 °C. At each temperature it was verified that no bubbles were present in the mixture. The mixture was then again ultrasonicated (60 °C for 30 minutes) to disperse the nanoparticles, and Epon 862 was added and further ultrasonicated (60 °C for 30 minutes). The mixture was then
poured into the mold and centered within the triaxial Helmholtz coil. A one-dimensional magnetic field (300 G DC and 300 G peak 0.05 Hz sinusoidal) was applied to the mixture for 30 minutes at 70°C. The mixture was then cured following the standard cycle (121°C for one hour and 171°C for two hours).

6.3 Microstructure Inspection of 1D-Tailored Polymer Nanocomposites

The microstructures of the fabricated PNCs were inspected to evaluate sizes and distribution of the assembled GPS-$\gamma$-Fe$_2$O$_3$ nanoparticles. To inspect the cross-sections, and to prepare for property characterization in Chapter 7, sample slices were extracted from the fabricated PNCs. A diamond saw was used to cut approximately 1-mm-thick samples. Due to the expected anisotropic and non-homogenous assembly characteristics of the dry-process (sedimentation and field gradient from the solenoids), these PNCs had samples extracted at four different locations as indicated in Figure 6.15: transverse (T) vs. axial (A), and edge (E) vs. center (C). In addition, the dry-processed PNC samples were sanded down to cross-sectional dimensions of approximately 5 mm x 5 mm as shown in Figure 6.15, with the bottom and top of the samples being removed to diminish the effect of sedimentation and minimal nanoparticle assemblies. The wet-processed PNCs were extracted at two different locations as indicated in Figure 6.15: transverse (T) vs. axial
(A), both at the center (C). These samples were not reduced in size due to their expected homogenous distribution, and the cross-sections were approximately 10 mm x 10 mm in size. The nomenclature for the sample designation is shown in Figure 6.16.

**Figure 6.15:** Schematic showing sections extracted from PNCs fabricated using nanoparticles with dry- and wet-processes for characterization. The nanoparticle assemblies are orthogonal to the cross-sectional plane for the axial (A) direction, and parallel to the cross-sectional plane for transverse (T) direction.

**Figure 6.16:** Nomenclature designation for the fabricated PNCs.

<table>
<thead>
<tr>
<th>Manufacturing Process:</th>
<th>Waveform Type:</th>
<th>Extracted Location:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry</td>
<td>DC</td>
<td>C - Center</td>
</tr>
<tr>
<td>Wet</td>
<td>Sine</td>
<td>E - Edge</td>
</tr>
</tbody>
</table>

**Bulk VF-Process-Field-Waveform-Direction-Location**

<table>
<thead>
<tr>
<th>Bulk Volume Fractions:</th>
<th>Field Magnetic Flux Density:</th>
<th>Nanoparticle Assembly Direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>300</td>
<td>A - Axial</td>
</tr>
<tr>
<td>1.0</td>
<td>R - No Field</td>
<td>T - Transverse</td>
</tr>
<tr>
<td>2.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Example: 2-Dry-300-DC-C-T = 2.0% bulk volume fraction PNC sample fabricated using dry-processing at 300 G DC and taken from the center of the sample with the nanoparticle assemblies orientated in the transverse direction.
The PNC samples were polished to ensure that the nanoparticle assemblies were exposed and not covered by the polymer matrix, which may limit property characterization. The dry-processed samples were attached to a metallic puck using a bonding agent (Crystalbond, 555) and each cross-section was manually polished with water as the lubricant and using 800 grit silicon carbide sandpaper until optical inspection indicated removal of the saw marks, followed by 1200 grit silicon carbide sandpaper (approximately 4.5 µm surface roughness) until a uniform mirror finish was achieved. The wet-process samples were machine polished down to approximately 0.04 µm. The wet-process samples were attached to a metallic puck using a bonding agent (Crystalbond, 555) and then were placed within an automated polishing machine (Allied High-Tech Products, Multiprep) at 150 RPM and 13 N with a propylene glycol lubricant (Allied High-Tech Products, Redlube). A 600 grit silicon carbide sandpaper was first used until the saw marks were removed and the sample surface was level. This was followed by 800 grit silicon carbide sandpaper for 2 minutes, 1200 grit silicon carbide sandpaper for 2 minutes, 3 µm polycrystalline diamond suspension for 5 minutes, 1 µm polycrystalline diamond suspension for 5 minutes, and 0.04 µm colloidal silica suspension for 5 minutes. This process was performed on both sample cross-sections.

### 6.3.1 Local nanoparticle volume fraction measurements

Due to variation of the nanoparticle structures within the fabricated PNCs, the sample volume fractions deviate from the original bulk volume fractions. The sample volume fractions (%) were calculated as shown in Equation 6.8, where \( m_{\text{sam}} \) is the measured mass of the sample (g), \( \rho_{\text{um}} \) is the density of the unmodified matrix (0.0114 g/mm\(^3\) for EPON 862 and Epikure W), \( \rho_s \) is the density of the nanoparticles (4.9 g/cm\(^3\) for maghemite), \( a_{\text{sam}} \) is the cross-sectional area of the samples (mm\(^2\)), and \( t_{\text{sam}} \) is the thickness of the samples (mm\(^2\)). The sample mass was measured using an analytical balance (Taishi, JF2004, ± 0.001 g). The sample thickness was measured using a caliper, and measurements were made along each of the four sample edges; the average variation between these thickness measurements was ensured to be less than 5% for all samples. The sample volume fractions are sensitive to measurement of the sample cross-sectional area. Therefore, a digital image of each sample cross-section was collected and analyzed in ImageJ Fiji to estimate the sample cross-sectional area as shown in Figure 6.17. The area, thickness, mass, and corresponding volume fractions of the samples are shown in Table 6.3 for the dry-processed and Table 6.4 for the wet-processed PNC samples. In all cases, the sample lengths were at least four
times the thickness to avoid current fringing and stray capacitance during the current measurements of Chapter 7. In most cases, especially at higher original bulk volume fractions (approximately 5%), the measured local PNC sample volume fractions were reduced. Sedimentation of the nanoparticles prior to pouring into the mold (nanoparticle dispersion difficulties at higher volume fractions), sedimentation within the PNC samples (and subsequent removal for the PNC samples with dry-processed nanoparticles), and non-homogeneous assembly due to a field gradient are hypothesized to primarily be responsible.

\[ vf = \left( \frac{n_{sam}}{\rho_{sam} \alpha_{sam} t_{sam}} \right) \left( \frac{\rho_s}{1000} \right) \alpha_{sam} t_{sam} \times 100\% \]  

(6.8)

**Table 6.3**: Geometry, mass, and volume fractions of extracted sections for PNC samples with dry-processed nanoparticles assembled with magnetic fields (300 G DC and 300 G peak 0.05 Hz sinusoidal).

<table>
<thead>
<tr>
<th>Bulk vf (%)</th>
<th>Waveform</th>
<th>Direction</th>
<th>Location</th>
<th>(a_{sam}) (mm(^2))</th>
<th>(t_{sam}) (mm)</th>
<th>(m_{sam}) (g)</th>
<th>(vf) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 DC</td>
<td>Transverse</td>
<td>Center</td>
<td>26.9</td>
<td>1.12</td>
<td>0.0346</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Center</td>
<td>28.9</td>
<td>0.79</td>
<td>0.0261</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Edge</td>
<td>38.5</td>
<td>1.38</td>
<td>0.0616</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>2.0 DC</td>
<td>Transverse</td>
<td>Edge</td>
<td>33.7</td>
<td>1.29</td>
<td>0.0521</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Center</td>
<td>32.4</td>
<td>0.59</td>
<td>0.0231</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Edge</td>
<td>33.8</td>
<td>1.32</td>
<td>0.0538</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>5.0 DC</td>
<td>Transverse</td>
<td>Center</td>
<td>29.6</td>
<td>1.02</td>
<td>0.0391</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Edge</td>
<td>22.2</td>
<td>1.07</td>
<td>0.0308</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>5.0 Sine</td>
<td>Transverse</td>
<td>Center</td>
<td>32.8</td>
<td>0.82</td>
<td>0.0340</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Center</td>
<td>33.1</td>
<td>0.72</td>
<td>0.0326</td>
<td>4.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Edge</td>
<td>33.8</td>
<td>1.34</td>
<td>0.0600</td>
<td>3.7</td>
<td></td>
</tr>
<tr>
<td>3.2</td>
<td>Transverse</td>
<td>Center</td>
<td>26.6</td>
<td>1.31</td>
<td>0.0453</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Center</td>
<td>32.3</td>
<td>1.29</td>
<td>0.0536</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Edge</td>
<td>31.7</td>
<td>1.25</td>
<td>0.0522</td>
<td>3.5</td>
<td></td>
</tr>
</tbody>
</table>
Table 6.4: Geometry, mass, and volume fractions of extracted sections for PNC samples with wet-processed nanoparticles assembled with magnetic fields (300 G DC and 300 G peak 0.05 Hz sinusoidal).

<table>
<thead>
<tr>
<th>Bulk vf (%)</th>
<th>Waveform</th>
<th>Direction</th>
<th>Location</th>
<th>$a_{sam}$ (mm²)</th>
<th>$l_{sam}$ (mm)</th>
<th>$m_{sam}$ (g)</th>
<th>$vf$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>DC</td>
<td>Transverse</td>
<td>Center</td>
<td>100.6</td>
<td>0.99</td>
<td>0.1159</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Axial</td>
<td></td>
<td>80.2</td>
<td>0.88</td>
<td>0.0818</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>Sine</td>
<td>Transverse</td>
<td></td>
<td>106.4</td>
<td>0.98</td>
<td>0.1225</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Axial</td>
<td></td>
<td>91.7</td>
<td>1.03</td>
<td>0.1105</td>
<td>0.6</td>
</tr>
<tr>
<td>1.0</td>
<td>DC</td>
<td>Transverse</td>
<td></td>
<td>84.7</td>
<td>0.86</td>
<td>0.0868</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Axial</td>
<td></td>
<td>82.7</td>
<td>0.57</td>
<td>0.0561</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>Sine</td>
<td>Transverse</td>
<td></td>
<td>95.1</td>
<td>0.93</td>
<td>0.1046</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Axial</td>
<td></td>
<td>84.0</td>
<td>0.97</td>
<td>0.0968</td>
<td>0.9</td>
</tr>
<tr>
<td>2.0</td>
<td>DC</td>
<td>Transverse</td>
<td></td>
<td>98.8</td>
<td>0.90</td>
<td>0.1071</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Axial</td>
<td></td>
<td>83.9</td>
<td>1.04</td>
<td>0.1059</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>Sine</td>
<td>Transverse</td>
<td></td>
<td>99.3</td>
<td>0.92</td>
<td>0.1106</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Axial</td>
<td></td>
<td>79.3</td>
<td>0.80</td>
<td>0.0752</td>
<td>1.0</td>
</tr>
<tr>
<td>3.0</td>
<td>DC</td>
<td>Transverse</td>
<td></td>
<td>106.3</td>
<td>0.88</td>
<td>0.1157</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Axial</td>
<td></td>
<td>81.3</td>
<td>0.77</td>
<td>0.0775</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>Sine</td>
<td>Transverse</td>
<td></td>
<td>86.5</td>
<td>0.75</td>
<td>0.0795</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Axial</td>
<td></td>
<td>83.7</td>
<td>0.77</td>
<td>0.0784</td>
<td>1.7</td>
</tr>
<tr>
<td>5.0</td>
<td>DC</td>
<td>Transverse</td>
<td></td>
<td>84.2</td>
<td>1.15</td>
<td>0.1287</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Axial</td>
<td></td>
<td>96.3</td>
<td>1.01</td>
<td>0.1303</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>Sine</td>
<td>Transverse</td>
<td></td>
<td>92.7</td>
<td>1.32</td>
<td>0.1612</td>
<td>3.6</td>
</tr>
</tbody>
</table>

Figure 6.17: Estimation of the sample surface area through image processing using ImageJ Fiji.
6.3.2 Optical microscope inspection of cross-section surfaces

Inspection of the cross-sectional surfaces was conducted using an optical microscope (Olympus, BX51WI) after polishing. In all cases, the microscope was focused at the mid location of the sample surface, away from the sample edges.

First, the dry-processed samples are discussed (see Figure 6.18 and Figure 6.19). The PNC samples with dry-processed nanoparticles were prepared as discussed above; however, surface polishing was not as well executed as that for the PNC samples with wet-processed nanoparticles. Due to the higher surface roughness (4.5 µm) and smaller assembly sizes, clear observation of the nanoparticle assemblies was not made for the PNC samples with dry-processed nanoparticles at low bulk volume fractions (0.5% and 2.0%). Thus, observations below are made about the PNC samples with bulk volume fractions of 5%. Without magnetic field application, nanoparticle aggregates are randomly orientated and uniformly dispersed, regardless of the sample location (see Figure 6.18A). Once a magnetic field was applied, the nanoparticles were observed to form 1D-aligned assemblies along the field direction, but in a nonhomogeneous manner due to the inhomogeneity of the magnetic field generated by the solenoid coil (stronger field towards the edge location and field curvature) and due to increasing gravitational effect with increasing nanoparticle assembly size. As shown in Figure 6.18B and 6.18C, the assembly lines are denser towards the edge location due to the field gradient. When magnetic field oscillation is introduced, the assembled nanoparticle lines are now more settled towards at the bottom (compare Figure 6.18B and 6.18C). When inspected in the axial direction (see Figure 6.18C), increased cross-sectional area of the nanoparticle assembly lines is confirmed. With field oscillation, transverse assembly is enhanced, resulting in thicker and longer nanoparticle assembly lines and thus increased sedimentation. This trend is compatible with the theoretical study in Chapter 4 and also with that observed with nanoparticle assembly in DI water in Chapter 5.

The inhomogeneity of the nanoparticle structures was further studied by inspecting and comparing the center vs. edge locations (see Figure 6.19). Nanoparticles migrated towards the edge location due to a gradient in the external field caused by the solenoid pair. Curvature of the external field (as will be discussed in Section 6.3.3) produced an upwards force on the nanoparticle assemblies near the edge location leading to a more uniform dispersion as compared to the center location. For both locations, sedimentation was observed due to the size of the nanoparticle aggregates and resulting structures. As previously discussed in Section 6.1.2.2, the size of the nanoparticle aggregates for the dry-processed samples were large and sedimentation was expected.
Thus, structuring with the wet-processed nanoparticles is of interest due to their smaller aggregate size reducing sedimentation and producing homogenous structures.

**Figure 6.18**: Optical microscope images of the PNC samples with dry-processed nanoparticles (bulk volume fraction of 5%) with varying assembly conditions and sample orientations/locations. The nanoparticle assemblies are the lighter regions in the images.
Second, the wet-processed samples are discussed (see Figure 6.20). For these sample, polishing was improved in order to achieve a surface roughness of 0.04 µm and thus the nanoparticle features were observed even for the PNC samples with small nanoparticle volume fractions. Also, as these PNC samples were fabricated using the Helmholtz coil system, without a field gradient, uniformity of the nanoparticle structures was expected (edge vs. center, confirmed by microCT and optical inspection, see Section 6.3.3 and Appendix C, respectively); thus, the PNC samples were only extracted from the center location and inspected below. Unlike the dry-processed nanoparticles, sedimentation was not observed, at least within the resolution of optical microscope images. Structuring of wet-processed nanoparticles was affected by both the nanoparticle volume fraction and the magnetic field conditions (DC vs. sinusoidal), similar to the case of the dry-processed nanoparticles (see Figure 6.20 and Figure 6.21). With increasing volume fraction, the nanoparticle assembly lines were longer and thicker as inter-particle distances become smaller and thus assembly among neighboring nanoparticles is enhanced (zippering). With introduction of field oscillation, the nanoparticle assembly lines again become thicker, but this time through transverse assembly as discussed in Section 5.3.4. This trend is similar to that observed with the SPIONs of Chapter 5. Thus, with field oscillation, when compared with the nanoparticle lines assembled using a DC field, the distance between the nanoparticle assemblies is larger. The lengths of the wet-processed nanoparticle assemblies were observed to be approximately a quarter the size of those found for the dry-processed samples at similar volume fractions (compare Figure 6.18 with Figure 6.20) due to their smaller aggregate size, and therefore reduced magnetic capture radius. In addition, the reduced aggregate size of the wet-processed nanoparticles limited sedimentation as compared to the dry-processed nanoparticles, in agreement with the discussion of Section 6.1.2.2.

![Figure 6.19: Comparison of optical microscope images for PNC samples with dry-processed nanoparticles (bulk volume fraction of 5%, sinusoidal, axial) at center vs. edge locations. The nanoparticle assemblies are the lighter regions in the images.](image-url)
Figure 6.20: Optical microscope images of the PNC samples with wet-processed nanoparticles (center location) with varying assembly conditions and sample orientations. The nanoparticle assemblies are the lighter regions in the images.
Inspection with optical microscopy has been effective to capture the 2D nanoparticle assembly features of different PNC samples. However, inspection of 3D nanoparticle structures can provide further insight, especially in the transverse direction or for PNCs with inhomogeneous nanoparticle structures. Thus, microCT inspection of the 3D nanoparticle structures will be discussed next.

**6.3.3 3D MicroCT inspection of nanoparticle structures**

Inspection of the bulk PNC samples was conducted using microCT (GE Phoenix vtomex L) at the Center for Quantitative Imaging at Pennsylvania State University. MicroCT is a nondestructive technique to visualize density differences in a sample due to the attenuation of x-rays passing through the sample. Attenuation is measured by a detector, and rotation of the sample and remeasurement of the attenuated x-rays allows for a stack of two-dimensional images to be generated, after which segmentation can be used to produce a three-dimensional volume reconstruction. For the present work, microCT allows for inspection of the entire sample cross-

![Figure 6.21](image_url)

**Figure 6.21:** Optical microscope images of the PNC samples with wet-processed nanoparticles (center location, axial direction) with varying assembly condition (DC vs. sinusoidal) and volume fractions. The nanoparticle assemblies are the lighter regions in the images.
section, in addition to through-thickness structures for structure-property correlation, which is not possible with optical inspection. Additional details regarding microCT can be found in literature [241]. Approximately quarter-sized samples (9.6 mm x 9.6 mm x 9.5 mm) were extracted from the original bulk PNC samples using a diamond saw (see Figure 6.20 and Table 6.5). MicroCT was conducted on each sample at a voltage of 100 keV. A voxel resolution of approximately 8 µm x 8 µm x 8 µm was obtained with a 25x magnification. The charge coupled device (CCD) detector area, the focus-to-object distance (FOD), and the focus-to-detector distance (FDD) are summarized in Table 6.5.

![Figure 6.22: Extracted section from bulk PNC sample for microCT evaluation.](image)

**Table 6.5:** List of PNC samples (magnetically assembled with 300 G DC or 300 G peak 0.05 Hz sinusoidal) inspected using microCT and test parameters.

<table>
<thead>
<tr>
<th>Process</th>
<th>Bulk vf (%)</th>
<th>Waveform</th>
<th>FDD (mm)</th>
<th>FOD (mm)</th>
<th>CCD Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry</td>
<td>2.0</td>
<td>DC</td>
<td>600</td>
<td>24</td>
<td>1568 x 1628</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sine</td>
<td></td>
<td></td>
<td>1384 x 1538</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>DC</td>
<td></td>
<td></td>
<td>1389 x 1649</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sine</td>
<td></td>
<td></td>
<td>1341 x 1467</td>
</tr>
<tr>
<td>Wet</td>
<td>3.0</td>
<td>DC</td>
<td>525</td>
<td>21</td>
<td>1756 x 1799</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sine</td>
<td>600</td>
<td>24</td>
<td>1484 x 1511</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>DC</td>
<td>525</td>
<td>21</td>
<td>1199 x 1369</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sine</td>
<td></td>
<td></td>
<td>1427 x 1521</td>
</tr>
</tbody>
</table>

It is emphasized that microCT inspection in this work is limited to be qualitative. The voxel resolution of 8 µm is not enough to capture individual nanoparticle aggregates and small nanoparticle assembly line widths. The voxel resolution can be reduced by decreasing the sample volume size to the limit of detector sensitivity, but the current sample dimension (approximately
9.6 mm) was kept in this work to capture the nonhomogeneous nanoparticle structures across the sample. A common guideline for microCT resolution is the sample dimension divided by 1000 [242]. Below, the tomograms as directly obtained from microCT, without segmentation, will first be discussed in correlation with the nanoparticle structures, and then the microCT data with segmentation will be discussed.

MicroCT tomograms of PNC samples consisting of dry-processed nanoparticles, without segmentation but with some contrast modification, are summarized in Figure 6.23 (axial view) and Figure 6.24 (transverse view). The rectangular regions enclosed by a dashed line in these figures corresponds with the PNC sample sections extracted and tested for characterization, as will be discussed in Chapter 7. It should be noted that the nanoparticle assembly lines are now visible within the PNC samples at a bulk volume fraction of 2%, unlike when inspected with optical microscopy. Through inspection of these microCT tomograms, the same trends were observed for nanoparticle assembly behavior with increasing volume fraction and with introduction of magnetic field oscillation as that observed with optical microscopy. With a smaller volume fraction (2.0%), the distance between nanoparticle aggregates become larger, sometimes larger than the magnetic capture radius, resulting in smaller and individually separated nanoparticle assembly lines. The sample inhomogeneity now can be clearly compared in the axial direction by inspecting multiple cross-sections within the volume; microCT images at the center and edge locations are directly compared in Figure 6.23. More dispersed nanoparticle assembly at the edge location was confirmed, as observed with the axial inspection with optical microscopy (see Figure 6.19). Field oscillation was again confirmed to provide thicker, longer, more separated nanofiller assembly lines that are more prone to sedimentation (see Figure 6.23 and Figure 6.24) due to enhanced transverse assembly. When the sedimentation section of the extracted regions is inspected, the nanoparticles exhibited spatially homogeneous distribution when assembled with a sinusoidal field, while the nanoparticles exhibited rather columnar distribution along the direction of gravity when assembled with a DC field. This difference can be attributed to the assembly behavior difference (zippering vs. transverse assembly).
Figure 6.23: Axial views of microCT tomograms of PNCs with dry-processed nanoparticles at varying volume fractions and different sample locations. The rectangular region enclosed within the dashed lines (--) corresponds to the PNC sections prepared for property characterization. The nanoparticle assemblies are indicated by the lighter regions in the images.
MicroCT tomograms of PNC samples consisting of wet-processed nanoparticles, without segmentation but with some contrast modification, are summarized in Figure 6.25. Due to the fine size of the assemblies, comparable with the microCT resolution, inspection is difficult. Short assembly lines were observed with microCT, similar to that observed with optical microscopy (see Figure 6.20). Differences between the nanofiller assembly by the volume fraction and the magnetic field condition (DC vs. sinusoidal) are not obvious.
Figure 6.25: Transverse and axial views of microCT tomograms of PNCs with wet-processed nanoparticles at varying volume fractions. The nanoparticle assemblies are indicated by the lighter regions in the images.
Segmentation processing was conducted on two representative PNC samples with dry-processed nanoparticles (bulk 5.0 vol%, assembled using a DC and sinusoidal field). Segmentation is a method to correlate attenuation coefficients (or equivalently, greyscale pixel intensity) with specific phases located within the sample. A clustering segmentation methodology using machine learning is incorporated in this work [241]. This technique is performed by first manually selecting representative phases (for example, nanoparticle vs. matrix) which are used as training data for a Fast Random Forest learning algorithm [243]. Classification rules are then applied to the training data based upon the phase identified attenuation coefficients and a set of convolutions (Gaussian, Laplacian, and Sobel). An exemplary segmentation processed image is compared with the original microCT tomogram in Figure 6.26. A set of binary images (white for nanoparticles and black for matrix) were obtained to generate 3D-rendered images. The segmentation process is limited in this work as there is uncertainty regarding boundaries between the nanoparticle assemblies and the matrix, and the packing density of nanoparticles within the assemblies (loosely vs. densely packed). Our preliminary segmentation work provided nanoparticle volume fractions that are almost twice as much as those measured; therefore, the images given below (see Figure 6.27 and 6.28) overexaggerate the volume fraction of nanoparticles within the samples and the assembly size. Thus, in the future, prior to quantitatively analyzing these samples, additional segmentation work needs to be conducted to correlate the volume fractions of the segmented images to the actual volume fraction.

![Output tomogram](image1)
![Segmented tomogram](image2)

**Figure 6.26:** Comparison of pristine vs. segmented tomograms of a PNC sample with dry-processed nanoparticles (bulk 5%) assembled using a sinusoidal field (axial direction). The nanoparticle assemblies are indicated by the lighter regions in the images.
**Figure 6.27:** Binary segmented microCT tomograms of PNCs with dry-processed nanoparticles at varying nanoparticle volume fractions and sample locations. The nanoparticle assemblies are indicated by the lighter regions in the images.
Figure 6.28: A three-dimensional rendering of the microCT tomograms for the PNC samples with dry-processed nanoparticles (5.0 % bulk volume fraction) assembled using DC vs. sinusoidal field.
Chapter 7

Characterization of Anisotropic Transport Properties of 1D Tailored Polymer Nanocomposites

In this chapter, transport properties of 1D tailored PNCs are characterized and correlated with the nanoparticle structures studied in Chapter 6, in order to evaluate the structure-interface-property relationships (Objective II). Maghemite nanoparticles are not necessarily the most effective reinforcement, unlike more conductive (such as carbon or metals) and 1D/2D-shaped reinforcements (such as nanotubes, nanofibers, nanoplatelets). The focus of this work is to understand the structure-interface-property relationships, rather than achieving high property improvements. Due to the strong magnetic response of maghemite, control of the nanoparticle interfaces and interphases using an external magnetic field is effectively achieved as demonstrated in Chapters 4, 5, and 6. In this chapter, the effectiveness of nanoparticle structure tuning in PNCs using novel oscillating magnetic will be evaluated by correlating the measured transport properties with such nanoparticle structures. Local mechanical properties (reduced elastic modulus and hardness) measured using nanoindentation are discussed in Appendix E.

7.1 Bulk DC Volume Electrical Resistivity

7.1.1 Measurement method and set-up

Bulk DC volume electrical resistivities were measured following ASTM D257 for insulating materials (resistivities greater than $10^5 \, \Omega \cdot m$). The experiments were conducted in the Electrical Characterization Lab at the Pennsylvania State University’s Materials Research Institute. The experimental set-up is depicted in Figure 7.1. A DC power source (HP 4140 pA Meter/DC Voltage Source) supplies voltage to a high voltage amplifier (Trek, 10/10B-HS) which then directs the voltage across the test fixture. The current through the test fixture is measured by the same DC power source with a resolution down to $10^{-13} \, A$. Prior to testing, the test fixture electrodes (gold plated, 1.7 mm diameter) were cleaned using sand paper to ensure appropriate contact between the electrode surfaces. The impedance of the test fixture was measured to be $7 \, \Omega$ at a phase angle of
70° for a 1 V input at a frequency of 1 MHz using an LCR meter (Keysight, E4980A). The sample set tested for electrical (and thermal) properties are summarized in Tables 6.3 and 6.4. The cross-sectional length of the samples was prepared to be at least four times the thickness to avoid current fringing and stray capacitance [244] during the current measurements. The polished samples were painted with conductive silver paint (Structures Probe Incorporated, 04998-AB) on both cross-sections. The edges of the samples were scraped with a razor blade and cleaned using isopropyl alcohol (IPA) to remove any excess paint and to avoid a short circuit. The samples were then stored in a container with silica gel (VWR, EM1.01969.1000) for desiccation control. The container was placed within an oven (Shel Lab, 1330GM) for 44 hours at approximately 25 °C and 16% humidity to remove moisture on the samples. After conditioning, a handheld meter (Goldstar, DM-311) was used to ensure that the sample surfaces were conductive and that an open circuit was present across the sample cross-sections. The samples were then placed between the electrodes in the test fixture (see Figure 7.1B); each 1D-aligned PNC sample was measured in two different directions to capture property anisotropy (see Figure 7.1C). Contact of the electrodes with the sample surface was controlled via spring compression. All tests were conducted at room temperature (approximately 22 °C). Voltage was controlled using the GADD measurement program (designed in-house at the Electrical Characterization Lab). The GADD program accepts a script file to direct voltage applied by the voltage source and current measured by the pA meter. GADD script files used here can be found in Appendix D. The current-voltage measurements were conducted twice for the dry-processed samples to verify the observed trends; for each test, the Ag paint was removed with IPA and reapplied to ensure no variation between tests due to the application method of the paint.
7.1.2 Measurement conditions and error range estimation

The current-voltage characteristics of PNC samples can provide insight into electrical percolation. Due to the high resistivities of the samples tested, data scattering is a concern. Therefore, the time to reach steady-state is measured in order to minimize the effects of data scattering. The current-voltage characteristics at the percolation threshold are discussed in terms of the nanoparticle structures in Appendix D. To evaluate the time required to reach the steady-state, the current-voltage characteristics are studied about the most insulating sample, the unmodified matrix (EPON 862 resin with Epikure W cross-linking agent, 100:26.4 mass fraction, following the standard cure cycle: 70 °C for 1 hour, 121 °C for 1 hour, and 171 °C for 2 hours). Three voltages were applied in sequence to evaluate the steady-state response: 100 V, 200 V, and 300 V. At each voltage, the current across the sample was measured each second for 60 s. The steady-state response of the unmodified matrix is shown in Figure 7.2. For all voltages, the current was approximately steady after 5 s, although small variations were present at 200 V until approximately 30 s. Therefore, a step voltage application time of 5 s was selected for the measurements in this work.
As recommended by ASTM D257 for insulating materials, the bulk DC volume resistivities were measured by holding 500 V across the samples for 60 s. The initial voltage across the PNC samples was set as 25 V, with voltage steps of 25 V up to 500 V. For each voltage, the voltage was held for 5 s to achieve a steady-state response. The voltage of 500 V is smaller than the breakdown voltage for bisphenol-F matrices (> 5 kV [245]); nanofillers embedded within a polymer matrix have been shown to further increase the dielectric breakdown voltage of PNCs [246]. The resistance contribution from the experimental set-up is included in the measurement, but is very small (2.4 Ω vs. 10^8 Ω of measured resistance) and thus was negligible. Resistivity (Ω-m) is defined in Equation 7.1, where \( A_{PNC} \) is the electrically conductive cross-sectional area (m^2) and \( t_{PNC} \) is the thickness (m).

\[
\rho_{PNC} = R \left( \frac{A_{PNC}}{t_{PNC}} \right) \quad (7.1)
\]

The error ranges of the measured electrical resistivity values were calculated using the traditional estimation of uncertainty as a sum of the products of the partial derivative and the uncertainty of the respective variables as shown in Equation 7.2. The resistance error range was evaluated by comparing resistance variations measured from 100 V to 500 V with increments of 100 V for two repeated tests on the same sample, but reconditioned (dry-processed samples only). The thickness error range was obtained from repeated measurement of the sample thickness (four points). The cross-sectional area is estimated to have an upper bound error of approximately 1% from repeated area measurements in ImageJ.

\[
\delta \rho_{PNC} = \left| \frac{A_{PNC}}{t_{PNC}} \right| (\delta R) + \left| \frac{R}{t_{PNC}} \right| (\delta A_{PNC}) + \left| \frac{RA_{PNC}}{t_{PNC}^2} \right| (\delta t_{PNC}) \quad (7.2)
\]
7.1.3 Electrical resistivity values and their correlation with the nanoparticle structures

The DC electrical resistivity values of the PNC samples are summarized in Tables 7.1 and 7.2, and in Figure 7.3. The electrical resistivity of the pure thermoset polymer ($\rho_m$) was measured to be between $9.05 \times 10^{13} - 1.48 \times 10^{14} \Omega$-m, in the same range as that previously reported ($10^{14} \Omega$-m [247]). The electrical resistivity of the maghemite nanoparticles was measured as approximately $2.85 \times 10^6 \Omega$-m ($\rho_f$), based on the measured resistance data of the porous cold-sintered maghemite sample [248,249]. This resistivity value is higher than expected (maghemite is an n-type semiconductor [250], < $10^5 \Omega$-m [251]), possibly due to an amorphous interphase layer formed around the nanoparticles during the sintering process. Therefore, both the measured and expected range of maghemite resistivities will be used as the element property to be compared with the PNC properties.

Electrical percolation needs to be achieved in order to effectively reduce electrical resistivities of the insulating polymer with semiconducting or conductive particles. As discussed in Chapter 2, electrical percolation will occur, or electrical resistivity significantly decreases, when nanofillers form continuous conductive pathways, either by carrier tunneling or physical contact of the nanofiller. For randomly orientated, spherical, nanoparticles, a wide variation in the critical volume fraction such that electrical percolation is achieved has been observed. In the past, this percolation threshold was observed to depend on the particle shape, size, and aggregation. For example, randomly orientated spherical magnetite ($\text{Fe}_3\text{O}_4$, 200 nm) has been experimentally shown to have a percolation threshold of approximately 50% volume fraction in epoxy [252], whereas carbon black (prolate aggregates) randomly dispersed within an epoxy matrix achieved percolation at a volume fraction of 10% [253,254]. Below, the effects of PNC sample preparation (nanoparticle preparation and magnetic assembly) and thus nanoparticle structuring on electrical resistivities will be discussed.
Table 7.1: Electrical resistivity values for the PNC samples with dry-processed maghemite nanoparticles. The volume fraction is indicated by \( \text{vf} \).

<table>
<thead>
<tr>
<th>Location</th>
<th>( \text{vf} ) (%)</th>
<th>( \rho_{\text{PNC}} ) (( \Omega )-m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Axial</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Center</td>
<td>0.2</td>
<td>( 2.86 \times 10^{14} \pm 4.56 \times 10^{13} )</td>
</tr>
<tr>
<td>Center</td>
<td>1.4</td>
<td>( 2.76 \times 10^{14} \pm 2.84 \times 10^{13} )</td>
</tr>
<tr>
<td>Center</td>
<td>4.7</td>
<td>( 3.97 \times 10^{6} \pm 6.79 \times 10^{6} )</td>
</tr>
<tr>
<td>Edge</td>
<td>0.4</td>
<td>( 3.55 \times 10^{14} \pm 2.25 \times 10^{13} )</td>
</tr>
<tr>
<td>Edge</td>
<td>1.3</td>
<td>( 3.01 \times 10^{9} \pm 1.52 \times 10^{9} )</td>
</tr>
<tr>
<td>Edge</td>
<td>3.7</td>
<td>( 1.35 \times 10^{7} \pm 1.18 \times 10^{7} )</td>
</tr>
<tr>
<td>Transverse</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Center</td>
<td>0.1</td>
<td>( 5.21 \times 10^{14} \pm 4.56 \times 10^{13} )</td>
</tr>
<tr>
<td>Center</td>
<td>2.6</td>
<td>( 1.56 \times 10^{10} \pm 3.11 \times 10^{10} )</td>
</tr>
<tr>
<td>Edge</td>
<td>1.2</td>
<td>( 2.04 \times 10^{14} \pm 1.87 \times 10^{13} )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Location</th>
<th>( \text{vf} ) (%)</th>
<th>( \rho_{\text{PNC}} ) (( \Omega )-m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Axial</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Center</td>
<td>1.3</td>
<td>( 7.49 \times 10^{13} \pm 7.15 \times 10^{12} )</td>
</tr>
<tr>
<td>Center</td>
<td>3.1</td>
<td>( 7.75 \times 10^{6} \pm 2.16 \times 10^{6} )</td>
</tr>
<tr>
<td>Edge</td>
<td>0.5</td>
<td>( 1.92 \times 10^{10} \pm 1.62 \times 10^{11} )</td>
</tr>
<tr>
<td>Edge</td>
<td>3.5</td>
<td>( 5.07 \times 10^{6} \pm 1.01 \times 10^{7} )</td>
</tr>
<tr>
<td>Transverse</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Center</td>
<td>0.6</td>
<td>( 3.21 \times 10^{14} \pm 3.45 \times 10^{13} )</td>
</tr>
<tr>
<td>Center</td>
<td>3.2</td>
<td>( 2.67 \times 10^{6} \pm 7.75 \times 10^{8} )</td>
</tr>
</tbody>
</table>

Table 7.2: Electrical resistivity values for the PNC samples with wet-processed maghemite nanoparticles. The volume fraction is indicated by \( \text{vf} \).

<table>
<thead>
<tr>
<th>Location</th>
<th>( \text{vf} ) (%)</th>
<th>( \rho_{\text{PNC}} ) (( \Omega )-m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Axial</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Center</td>
<td>0.3</td>
<td>( 1.17 \times 10^{15} )</td>
</tr>
<tr>
<td>Center</td>
<td>1.2</td>
<td>( 3.45 \times 10^{14} )</td>
</tr>
<tr>
<td>Center</td>
<td>1.5</td>
<td>( 1.34 \times 10^{14} )</td>
</tr>
<tr>
<td>Center</td>
<td>1.9</td>
<td>( 1.43 \times 10^{14} )</td>
</tr>
<tr>
<td>Center</td>
<td>4.0</td>
<td>( 2.46 \times 10^{14} )</td>
</tr>
<tr>
<td>Transverse</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Center</td>
<td>0.5</td>
<td>( 1.75 \times 10^{14} )</td>
</tr>
<tr>
<td>Center</td>
<td>1.1</td>
<td>( 1.46 \times 10^{15} )</td>
</tr>
<tr>
<td>Center</td>
<td>1.4</td>
<td>( 3.25 \times 10^{14} )</td>
</tr>
<tr>
<td>Center</td>
<td>1.9</td>
<td>( 3.62 \times 10^{14} )</td>
</tr>
<tr>
<td>Center</td>
<td>3.8</td>
<td>( 3.29 \times 10^{14} )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Location</th>
<th>( \text{vf} ) (%)</th>
<th>( \rho_{\text{PNC}} ) (( \Omega )-m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Axial</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Center</td>
<td>0.6</td>
<td>( 8.59 \times 10^{14} )</td>
</tr>
<tr>
<td>Center</td>
<td>0.9</td>
<td>( 9.09 \times 10^{14} )</td>
</tr>
<tr>
<td>Center</td>
<td>1.0</td>
<td>( 2.61 \times 10^{14} )</td>
</tr>
<tr>
<td>Center</td>
<td>1.7</td>
<td>( 3.52 \times 10^{14} )</td>
</tr>
<tr>
<td>Center</td>
<td>3.6</td>
<td>( 3.00 \times 10^{14} )</td>
</tr>
<tr>
<td>Transverse</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Center</td>
<td>0.6</td>
<td>( 1.81 \times 10^{14} )</td>
</tr>
<tr>
<td>Center</td>
<td>1.0</td>
<td>( 3.87 \times 10^{14} )</td>
</tr>
<tr>
<td>Center</td>
<td>1.4</td>
<td>( 1.69 \times 10^{15} )</td>
</tr>
<tr>
<td>Center</td>
<td>1.9</td>
<td>( 5.81 \times 10^{14} )</td>
</tr>
<tr>
<td>Center</td>
<td>3.6</td>
<td>( 3.64 \times 10^{14} )</td>
</tr>
</tbody>
</table>
To note upfront, the PNCs with randomly-oriented nanoparticles (dry-processed, between 3.1 - 3.2 vol%) and the PNCs with wet-processed nanoparticles (assembled, between 0.3 - 4.0 vol%) did not exhibit electrical percolation. When randomly-oriented, due to their small volume fraction and spherical shape, the nanoparticles were not expected to form a percolated network. With the wet-processed nanoparticles, the assembly lengths were observed to be smaller than sample through-thickness (see Section 6.3). Therefore, even at the highest volume fraction of 4.0 vol%, percolation was not achieved as summarized in Table 7.2. Thus, below, discussion of the structure-interface-property relationships is focused on the measurement results for the PNC samples with dry-processed nanoparticles and three specific observations are made.

First, electrical percolation was evaluated to occur at a smaller volume fraction with the PNCs prepared with a sinusoidal magnetic field than with those prepared with a DC magnetic field as transverse assembly enhanced by the magnetic field oscillation helped elongate nanofiller assembly (see Figure 7.4). The percolation threshold for randomly orientated nanoparticles [255] is commonly evaluated using a power law correlation [256] as shown in Equation 7.3, where \( v_f \) is the volume fraction at percolation onset, and \( t_c \) is the critical exponent. In addition to randomly orientated nanoparticles, this power law has been successfully applied to assembled nanoparticles in recent work [257,258].

![Figure 7.3](image)

**Figure 7.3:** Measured electrical resistivity data, normalized by the unmodified matrix resistivity \( (\rho_{PNC}/\rho_m) \), for the PNC samples with dry-processed maghemite nanoparticles.
Here, the power law curve was evaluated through manual curve fitting as regression techniques with only a few data points (2 - 3) is not recommended. Thus, determined power law parameters are estimations only. The percolation threshold volume fraction ($v_f c$) was estimated to be as low as 0.45% for the PNCs prepared using a DC magnetic field and as 0.15% for the PNCs prepared using a sinusoidal magnetic field. The critical exponent ($t_c$) was also estimated: 2.9 for the PNCs prepared using a DC magnetic field, and 3.8 for the PNCs prepared using a sinusoidal magnetic field. This critical exponent range (between 2-3) indicates a three-dimensional percolated system, instead of one-dimensional [256,259]. The $v_f c$ difference can be attributed to variation in the nanoparticle structures. As illustrated in Figure 7.5A, transverse assembly was enabled with the usage of a sinusoidal magnetic field effectively enhancing contact between neighboring assemblies which connected throughout the PNC sample. This increase in assembly length with field oscillation was also observed with the SPIONs of Chapter 5 and was visually confirmed with microCT inspection in Section 6.3. These observed percolation thresholds are similar to that found for self-assembled tin oxide nanoparticles within an acrylic resin ($v_f c \sim 0.4 \text{ vol}\%$) [260], higher than that observed for assembled CNT/polymer composites ($v_f c < 0.1 \text{ vol}\%$) [261], and much less than that observed for randomly orientated nanofiller as discussed above ($v_f c > 10 \text{ vol}\%$). The estimated percolation threshold for the PNCs prepared with a sinusoidal field ($v_f c \sim 0.15 \text{ vol}\%$) is of interest as this value is just above that found for assembled nanofiller with high aspect ratios (CNTs), demonstrating the importance of controlled contact between the nanoparticles.
Second, anisotropy (axial vs. transverse) of the electrical resistivity data will be discussed. The measured data points were again manually fit to the power law of Equation 7.3 as shown in Figure 7.6. Due to scattered and limited data points, the percolation thresholds are likely higher than that reported here: 1.1 vol% for the PNCs prepared with a DC field, and 0.6 vol% for the PNCs prepared with a sinusoidal field. Regardless, these lower bound percolation threshold estimates are higher in the transverse direction, than that estimated in the axial direction. Even after percolation is achieved, the resulting electrical resistivity values are higher by $10^3 - 10^6$ times in the transverse direction than in the axial direction (see Table 7.1 and Figure 7.3). The measurement data is compatible with the nanoparticle structures observed in Chapter 6. Again, transverse assembly enhanced by a sinusoidal magnetic field enabled interconnected nanoparticles in the transverse direction. Larger nanoparticle volume fractions are required to form percolation in the transverse

![Figure 7.4: Estimated percolation threshold observed with the measured axial electrical resistivity data for PNC samples prepared with dry-processed maghemite particles using A) DC and B) sinusoidal fields, at the edge location. The power law correlation (--) and the parallel model (—) with varying baseline maghemite resistivity values are also plotted.](image)
direction, as the nanoparticle assembly direction is perpendicular to the transverse direction. A continuous network in the transverse direction is only achieved when the nanoparticle assemblies settle, and even then, their network cross-section areas, and thus reduction in electrical resistivity, are much smaller than in the axial direction. The diminished anisotropic response for increasing volume fraction observed here (sinusoidal, anisotropic difference of $\sim 10^4 \ \Omega\cdot\text{m}$ at 0.5 vol% and $\sim 10^2 \ \Omega\cdot\text{m}$ at 3.3 vol%) has also been observed in Monte Carlo simulations where electrical resistivity values in different directions converge for increasing volume fractions even in highly ordered systems [262]. A similar peak anisotropic response based upon volume fraction has also been observed in silicon carbide-CNT-polymer composites [263], with a difference in the percolation threshold based upon the measurement direction (axial vs. transverse) of 0.6 vol%, comparable to an estimated difference of 0.5 vol% found here (sinusoidal).

**Figure 7.5:** Tailoring of nanoparticle interfaces to control charge carrier pathways by modification of the external field waveform: A) DC and B) sinusoidal. A shorter pathway produces reduced resistance. Insert images were captured from microCT of Section 6.3 and are the approximate dimensions of the measured samples.
Third, the effectiveness of nanoparticle implementation to electrical resistivity reduction of polymer nanocomposites will be discussed. The predicted electrical resistivities of PNCs were calculated from the values of the composite elements of the polymer and the maghemite using a simple parallel model (see Equation 7.4).

\[
\rho_{PNC} < vf \rho_f + (1 - vf)\rho_m
\]  

(7.4)

As noted above, the resistivity of the polymer (\(\rho_m\)) was measured as approximately \(10^{14}\) \(\Omega\)-m and the resistivity of the maghemite (\(\rho_f\)) was measured as \(2.85 \times 10^6\) \(\Omega\)-m, higher than that for an n-type semiconductor (< \(10^5\) \(\Omega\)-m). Thus, in this calculation, \(\rho_m\) was set as \(10^{14}\) \(\Omega\)-m and \(\rho_f\) was
varied from $10^5$ Ω-m to $10^7$ Ω-m; the modeled PNC resistivities are plotted in Figures 7.4 and 7.6. The experimentally measured data provides comparable values with the theoretical estimations once a percolated network is effectively formed. Meanwhile, the PNCs assembled using a sinusoidal field exhibited lower resistivities as compared to the model, confirming the effectiveness of conductive pathway formation through transverse assembly. Comparatively, a similar reduction in resistivity after percolation ($10^7$ Ω-m drop in resistivity measured here for the axial samples at approximately 3 vol%, see Figure 7.4) was observed for randomly orientated magnetite particles (approximately $10^7$ Ω-m drop), although at much higher volume fractions (60 vol%) [252]. As the reduction in resistivity is highly dependent upon the element properties, CNT-polymer systems have been shown to reduce resistivity by as much as $10^{12}$ Ω-m after percolation [264].

7.2 Bulk Volume Thermal Conductivity

7.2.1 Measurement method and set-up

Bulk volume thermal conductivities were measured using comparative infrared (IR) thermal microscopy [48]. The experiments were conducted in the Marconnet Thermal and Energy Conversion Lab at Purdue University’s Birck Nanotechnology Center. The experimental set-up is depicted in Figure 7.7 and is described in detail in the literature [265]. An IR microscope (QFI, MWIR-1024) was orientated normal to the edge of the PNC samples located within a test fixture as shown in Figure 7.7C. The IR microscope sensor was cooled prior to testing using liquid nitrogen. The test fixture consists of a cold and hot source. The cold source temperature was regulated at 37 °C through the use of a circulating bath (PolyScience, AD07R-20-A11B). Prior to testing, the cold source was independently circulated to ensure a steady-state temperature was achieved. The hot source temperature was controlled via cylindrical cartridge heaters powered by an AC power source (Powerstat, 3PN116C). Temperature at both sources were monitored using a thermocouple. The same set of samples were measured for thermal conductivities after electrical resistivity testing as summarized in Tables 6.3 and 6.4; the silver paint was gently removed with IPA. The reference material was selected as gum rubber (American Material Supply, 3.12 mm thick) because its known thermal conductivity (0.15 W/m-K [266]) is close to that of the unmodified matrix (0.15 W/m-K). The reference material was cut to the size of the PNC samples using a razor blade. The reference material was attached to the both ends of the PNC samples using a small amount of adhesive (Loctite, Go2Glue), where care was taken to ensure no glue was located
on the sample or reference material edges. The three-layer stack (reference-sample-reference) was then gently squeezed in a vice for 30 minutes to reduce the thermal contact resistance of the interface. Afterwards, the samples were placed at room temperature conditions for 24 hours to cure the adhesive. The edges of the samples were then gently sanded using 400 grit silicon carbide sandpaper until the edges of the reference material and sample were flat, and the edges were gently cleaned using IPA to remove any excess material. Thermal paste was applied to the exposed cross-sectional surfaces of the reference material to ensure good thermal contact between the reference material and the sources. The three-layer stack was then placed within the test fixture between the hot and cold source with a vice.

![Digital images of the A) test fixture and B) experimental set-up for comparative IR microscopy. C) Schematic for the PNC sample orientation within the test fixture to measure anisotropic thermal conductivities.](image)

**Figure 7.7:** Digital images of the A) test fixture and B) experimental set-up for comparative IR microscopy. C) Schematic for the PNC sample orientation within the test fixture to measure anisotropic thermal conductivities.

Comparative IR microscopy correlates measured surface temperature gradients with the material’s thermal conductivity. One-dimensional conduction was assumed and the heat flux ($q_x$, W/m$^2$) through each layer within the stack is described by the one-dimensional form of Fourier’s law as shown in Equation 7.5 where $k$ is the thermal conductivity (W/m-k) and $dT/dx$ is the temperature gradient (K/m).
\[ q_x = k \frac{dT}{dx} \]  
(7.5)

The emissivity and thermal maps (two-dimensional) were analyzed using software (InfraScope) interfaced with the IR microscope. The emissivity was first calibrated at a known temperature to ensure that the IR microscopy temperature measurement is accurate regardless of emissivity variations in the three-layer stack. Both the cold and hot sources were set at 37 °C to provide a uniform temperature throughout the sample stack. The emissivity map across the reference materials and PNC sample was displayed as shown in Figure 7.8A. The emissivity was measured diagonally across both the reference materials and the PNC sample until steady-state values were achieved, after which the emissivity map was stored. After calibration of the emissivity, thermal conductivity measurements were taken at multiple temperatures. The hot source temperature was set at 41 °C, 46 °C, 51 °C, and 57 °C. At each temperature, a steady-state temperature profile was achieved prior to storing the temperature map. An example of the temperature map produced by the IR microscope is shown in Figure 7.8B. Output temperature maps from the IR microscope were analyzed using an in-house code developed at the Marconnet Thermal and Energy Conversion Lab. For each temperature condition, the heat flux was calculated using Equation 7.5 with the measured thermal gradient and the known thermal conductivity \((k_{REF} = 0.15 \text{ W/m-K})\) of the reference materials (see Figure 7.9). The heat flux from the left and right reference material were then averaged to produce an average heat flux \((q_{avg})\) across the PNC sample. The PNC sample thermal conductivity was calculated from the average heat flux and the measured temperature gradient across the PNC sample. The boundary resistances between the PNC and reference samples can be eliminated because the temperature gradient relevant to each section can be easily extracted from the temperature map.

Figure 7.8: Digital images of temperature map across the three-layer stack (reference-sample-reference): during A) emissivity and B) conductivity measurements.
7.2.2 Measurement conditions and error range estimation

As noted above, the temperature gradient was measured at four different hot source temperature: 41 °C, 46 °C, 51 °C, and 57 °C. The temperature gradient of the PNC samples and the heat flux calculate from the temperature gradient of the reference, and its known thermal conductivity, are plotted and compared in Figure 7.10. Each slope is representative of the thermal conductivity of the PNC sample.

The error ranges of the measured thermal conductivities are based upon values in literature for the same experimental set up [265]. An upper bound error for thermal conductivity is estimated as 5% based upon variations in the measured heat flux; additional work will be conducted in the
future to better resolve per sample errors. Also, as observed in Section 6.3, the PNC samples with dry-processed nanoparticles have inhomogeneity and thus the temperature gradients are expected to differ depending on the sample plane. To evaluate the temperature gradient inhomogeneity, two exemplary samples (axial, edge, 3.7 vol% and axial, center, 0.2 vol%) were measured at two different sample planes exhibiting a 10% difference in thermal conductivity; these values are also integrated into the thermal conductivity error.

Figure 7.10: Estimation of the PNC sample thermal conductivity through a linear regression of the four-measurement temperature heat flux and temperature gradients as output from the measurement code. Example linear regression of selected wet-processed PNC samples are shown.

7.2.3 Thermal conductivity values and their correlation with the nanoparticle structures

The thermal conductivity data of the PNC samples \( k_{PNC} \) are summarized in Tables 7.3 and 7.4. The thermal conductivity of the pure polymer \( k_m \) was measured from the two unmodified matrix samples as approximately 0.15 W/m-K. This value is comparable with, but slightly less than, that measured in previous work of 0.20 W/m-K [267], possibly due to a variation in the cure process. Lower thermal transport can be attributed to phonon scattering (voids and defects) and poor intermolecular bonding [268]. The porous cold-sintered maghemite of 56.4% relative density was measured to have thermal conductivity of 0.50 W/m-K. Using two methods, the maghemite element’s thermal conductivity was estimated \( k_e \): the lower bound as 0.86 W/m-K using the parallel model and the upper bound as 1.30 W/m-K using Landauer’s relationship [269] (see [249] for additional details). Comparison of this bulk thermal conductivity value to that found in literature is difficult as no work has been reported on the thermal properties of bulk maghemite, possibly due
to the thermal instabilities of maghemite and a phase change to hematite at relatively low
temperatures (approximately 250 °C) [181]. Considering that the expected value of electrical
resistivity was smaller than the measured electrical resistivity value for the cold-sintered
maghemite sample due to amorphous interfaces, the thermal conductivity measured here can be
potentially mitigated by these interfaces; therefore, the measured thermal conductivity of
maghemite particles is assumed to be at the lower bound.

Thermal conductivity enhancement mechanism is different from electrical transport. While
electrical transport is determined by percolation of conducting pathways, thermal transport is
dominated by thermal boundary resistance [172]. This mechanism difference can be confirmed by
the fact that the PNCs with wet-processed nanoparticles exhibited some thermal conductivity
improvement, while no electrical resistivity reduction was found. Thermal transport is dominated
by phonons (lattice vibrations). At boundaries, the lattice vibration frequency needs to be
modulated in order to transfer from one element to another, and this acoustic mismatch results in
larger thermal resistance at the boundaries between maghemite particles or between maghemite
and polymer [270]. Thus, the hypothesis in this work is that thermal transport can be most enhanced
when maghemite nanoparticles are aligned along the transport direction but with minimum amount
of inter-nanoparticle contacts. Below, the effects of PNC sample preparation (nanoparticle
preparation and magnetic assembly) and thus nanoparticle structuring on thermal conductivities
will be discussed.

**Table 7.3:** Thermal conductivity values for the PNC samples with dry-processed maghemite
nanoparticles. The volume fraction is indicated by $v_f$.

<table>
<thead>
<tr>
<th>DC Waveform</th>
<th>Location</th>
<th>$v_f$ (%)</th>
<th>$k_{PNC}$ (W/m-K)</th>
<th>Sinusoidal Waveform</th>
</tr>
</thead>
<tbody>
<tr>
<td>Axial</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Center</td>
<td>0.2</td>
<td>0.18 ± 0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Center</td>
<td>1.4</td>
<td>0.18 ± 0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Center</td>
<td>4.7</td>
<td>0.27 ± 0.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Edge</td>
<td>0.4</td>
<td>0.19 ± 0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Edge</td>
<td>1.3</td>
<td>0.20 ± 0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Edge</td>
<td>3.7</td>
<td>0.23 ± 0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Transverse</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Center</td>
<td>0.1</td>
<td>0.20 ± 0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Center</td>
<td>2.6</td>
<td>0.20 ± 0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Edge</td>
<td>1.2</td>
<td>0.18 ± 0.03</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Axial |
Center  1.3  0.22 ± 0.03 |
Center  3.1  0.18 ± 0.03 |
Edge    0.5  0.17 ± 0.03 |
Edge    3.5  0.18 ± 0.03 |

Transverse |
Center  0.6  0.18 ± 0.03 |
Center  3.2  0.22 ± 0.03 |
First, the thermal conductivity behaviors of the dry-processed nanoparticles will be discussed (see Figures 7.11 and 7.12). The thermal conductivity is higher in the axial direction than in the transverse direction, as expected. Axial thermal conductivity enhancement is more effective at the edge location than at the center location, with a lower volume fraction. This trend can be attributed to the nanofiller structure difference observed in Section 6.3; nanoparticles are more dispersed in the edge direction than at the center direction, resulting in a reduced effect of thermal boundary resistances. This trend provides contrast between the differences in thermal vs. electrical transport; the center location favored electrical percolation (Figure 7.3). Conversely, thermal transport in the transverse direction was more effective at the center location than at the edge location. This trend is reasonable as thermal transport is not only affected by the boundary resistance between nanoparticles in the transverse direction, but also by the low thermal conductivity of the polymer matrix. Especially at low volume fractions, sedimented nanoparticles are more effective than dispersed nanoparticles to decrease the effect of low resistance of polymer layers between the nanoparticles, rather than the effect of inter-nanofiller boundary resistances.

Second, the effect of the magnetic field (DC vs. sinusoidal), and thus resulting nanofiller structures, on thermal conductivities will be discussed. The PNCs with dry-processed nanoparticles assembled using a sinusoidal field exhibited a very different trend from the those assembled using a DC field (compare Figures 7.11 and 7.12). The most notable trend here is that axial thermal conductivity decreased with the increasing volume fraction (center location). The sinusoidal field enhanced transverse assembly, and thus provided longer and thicker assemblies; axial thermal transport is enhanced with the low volume fraction, but eventually degraded due to an increased number of inter-nanofiller contacts at high volume fraction (observe Figure 6.23). At the high-

Table 7.4: Thermal conductivity values for the PNC samples with wet-processed maghemite nanoparticles. The volume fraction is indicated by $vf$. 

<table>
<thead>
<tr>
<th>Location</th>
<th>$vf$ (%)</th>
<th>$k_{PNC}$ (Ω-m)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Axial</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Center</td>
<td>1.5</td>
<td>0.17 ± 0.03</td>
</tr>
<tr>
<td>Center</td>
<td>1.9</td>
<td>0.16 ± 0.02</td>
</tr>
<tr>
<td>Center</td>
<td>4.0</td>
<td>0.17 ± 0.03</td>
</tr>
<tr>
<td><strong>Transverse</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Center</td>
<td>1.4</td>
<td>0.15 ± 0.02</td>
</tr>
<tr>
<td>Center</td>
<td>3.8</td>
<td>0.17 ± 0.03</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Location</th>
<th>$vf$ (%)</th>
<th>$k_{PNC}$ (Ω-m)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Axial</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Center</td>
<td>1.0</td>
<td>0.15 ± 0.02</td>
</tr>
<tr>
<td>Center</td>
<td>1.7</td>
<td>0.15 ± 0.02</td>
</tr>
<tr>
<td>Center</td>
<td>3.6</td>
<td>0.16 ± 0.02</td>
</tr>
<tr>
<td><strong>Transverse</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Center</td>
<td>1.4</td>
<td>0.14 ± 0.02</td>
</tr>
<tr>
<td>Center</td>
<td>3.6</td>
<td>0.16 ± 0.02</td>
</tr>
</tbody>
</table>
volume fraction, transverse thermal conductivity becomes larger than the axial thermal conductivity.

**Figure 7.11:** Measured thermal conductivity data, normalized by the unmodified matrix conductivity \( (k_{PNC}/k_m) \), of PNC samples with dry-processed nanoparticles assembled using a DC field. The dotted lines (---) are just guidelines. The solid line (—) is the conductivity calculated from the parallel model using three different element conductivities.

**Figure 7.12:** Measured thermal conductivity data, normalized by the unmodified matrix conductivity \( (k_{PNC}/k_m) \), of PNC samples with dry-processed nanoparticles assembled using a sinusoidal field. The dotted lines (---) are just guidelines. The solid line (—) is the conductivity calculated from the parallel model using three different element conductivities.
Third, the effect of the particle preparation (dry vs. wet processing) on thermal conductivity will be discussed. Small but observable thermal conductivity enhancements were observed even with the wet-processed nanoparticles, unlike the case of electrical conductivity (see Figure 7.13). Again, the PNCs assembled with the sinusoidal fields exhibited lower thermal conductivity enhancement than those assembled with the DC fields. This time, the contrast between the axial and transverse was very small, due to the large effect of thermal resistances of the polymer matrix.

![Figure 7.13](image)

**Figure 7.13**: Measured thermal conductivity data, normalized by the unmodified matrix conductivity \( (k_{\text{PNC}}/k_m) \), of PNC samples with wet-processed nanoparticles assembled using a DC field (top) and sinusoidal field (bottom). The dotted lines (---) are just guidelines. The solid line (—) is the conductivity calculated from the element conductivity using the parallel model.

Finally, the effectiveness of nanoparticle implementation to thermal conductivity improvement of polymer nanocomposites will be discussed. The thermal conductivities of PNCs were calculated from the values of the composite elements of the polymer and the maghemite using a simple theoretical parallel model (see Equation 7.6), assuming zero boundary resistances.
\[ k_{PNC} = vf k_f + (1 - vf) k_m \]  

As noted above, the thermal conductivity of the polymer \((k_m)\) was measured as 0.15 W/m-K, and the thermal conductivity of the maghemite \((k_f)\) was measured as 1.3 W/m-K, which is the lower bound. The estimated PNC conductivities are plotted in Figures 7.11, 7.12, and 7.13. In addition, for comparison, element conductivities of 5.0 W/m-K and 15.0 W/m-K are also plotted in Figures 7.11 and 7.12. The experimentally measured data provide better improvement than the theoretical prediction values at 1.3 W/m-K, but mostly because the thermal conductivity values of maghemite are low. While the thermal conductivity of maghemite is small when compared to other nanofillers (for example, 3.9 W/m-K for magnetite [271], 5.0 W/m-K for cobalt oxide [272], and 20 W/m-K for nickel oxide [273]), the PNCs fabricated using dry-processed nanoparticles had measured thermal conductivities up to 25\% of the estimated bulk maghemite thermal conductivity at volume fractions as low as 4.7\%. Comparatively, the maximum effective thermal enhancement observed here \((k_{PNC}/k_m = 1.8, \text{ dry-processing, DC, axial, 4.7\%})\) is approximately 30\% greater than that observed for assembled magnetite at a volume fraction of 7\% [80].
Chapter 8

Conclusions and Recommendations

The potential of an oscillating magnetic field to tailor nanoparticle interfaces, interphases, and structures in the fabrication of scalable polymer nanocomposites has been explored in this work. To obtain an understanding about the magnetic assembly behaviors of nanoparticles within oscillating magnetic fields (Objective I), theoretical and experimental studies were conducted. The theoretical studies about superparamagnetic nanoparticle assembly confirmed that nanoparticle assembly can be tailored by introducing magnetic field oscillation at low frequencies. When an external magnetic field is static, nanoparticles are magnetized and form one-dimensional assemblies aligned along the field direction through head-to-tail attraction. When an external magnetic field oscillates, the induced magnetic moments of nanoparticles rotate, generating temporary field gradients orthogonal to the field direction, enhancing transverse assembly. A low frequency (< 1 Hz) was key to provide enough time for the nanoparticles to respond to these magnetic interaction changes and to complete magnetic assembly. Other factors that affect the magnetic assembly of nanoparticles were also studied: external field (frequency, flux density, and waveform type), nanoparticles (magnetic responsiveness, concentration, and size), and matrices (viscosity). The observed theoretical trends were compared and confirmed with experimental studies about a model system consisting of superparamagnetic iron oxide nanoparticles (SPIONs) in DI water. Their magnetic assembly behaviors were captured in real time, and the parameters of the assemblies were quantitatively evaluated.

The above understanding about the magnetic assembly of model superparamagnetic nanoparticles was then extrapolated to the magnetic assembly of ferrimagnetic nanoparticles (gamma-phase iron oxide, maghemite) in a thermoset polymer matrix to demonstrate the tailorability and scalability of 1D structured PNCs and their properties using oscillating magnetic fields (Objective II). Fabrication methods were established, including nanoparticle surface modification (3-glycidyloxypropyl trimethoxysilane), to ensure nanoparticle dispersion and suspension in the polymer matrix. The nanoparticles’ 1D structures were successfully tailored, but resulted in inhomogeneous nanoparticle dispersion in most PNCs: sedimentation due to increased effect of gravity with increasing nanoparticle assembly size, and spatial inhomogeneity due to a
magnetic field gradient generated by a solenoid pair. These PNCs were sliced and locally inspected for their nanoparticle volume and distribution using optical microscopy and microCT scans. Electrical and thermal properties of these PNCs were measured, and compared with their nanoparticle structures. The accidental inhomogeneity within the PNCs provided insights into the effect and the contrast of inter-nanoparticle contacts on thermal vs. electrical transport. Electrical transport was dominated by the continuity of nanoparticle structures (percolation), while thermal transport was dominated by thermal boundary resistances. The nanoparticle surface modification process was later improved to decrease aggregate size; sizable PNC samples (20 mm × 20 mm × 10 mm) with homogeneously distributed 1D nanoparticle assemblies were achieved.

Based on the obtained understanding about manufacturing and structure-interface-property relationship of magnetically assembled PNCs, in this chapter, I preset a design space and guidelines for tailored PNCs using oscillating magnetic fields (Objective III) to provide guidelines for future manufacturing of PNCs with tailored nanofiller assembly for specific properties, as will be delineated below.

8.1 Contributions of this Work

The major contributions and findings from this thesis work are as follows:

- Provided analysis of magnetic assembly behaviors of nanoparticles in an oscillating magnetic field
  - In contrast with the previous studies about magnetic assembly behaviors of microparticles in static or rotating magnetic fields [41,57], this work focused on that of nanoparticles in oscillating magnetic fields, with the application of polymer nanocomposites with tailored structures and thus properties in mind. The capability to tailor nanoparticle morphology, especially inter-nanoparticle contacts, was expected to largely affect thermal transport effectiveness, and magnetic assembly using oscillating fields was hypothesized to be effective to achieve such nanoparticle structure tailoring.
  - In this analysis, forces that affected nanoparticle assembly were identified, and their effects were evaluated with varying parameters of the external fields (frequency, flux density, and waveform type), nanoparticles (magnetic responsiveness, concentration, and size), and matrices (viscosity). For the limited case of superparamagnetic
nanoparticles, the magnetic force by the locally induced, non-uniform magnetic field between the nanoparticles was identified as dominant.

- Magnetic assembly behaviors of nanoparticles were categorized into head-to-tail attraction, zippering, and transverse assembly, and each behavior is triggered by a different combination of parameters: head-to-tail attraction by flux density and nanoparticle concentration, zippering by nanoparticle size and matrix viscosity, and transverse assembly by frequency and waveform type. Among these assembly behaviors, transverse assembly is the mechanism uniquely triggered by field oscillation; the low frequency range (< 1 Hz) was identified as essential to provide enough time for nanoparticles to respond and to achieve enhanced tailorability of nanoparticle structuring.

- Confirmed the above analysis with experimental studies about a model system consisting of superparamagnetic iron oxide nanoparticles (SPIONs) in DI water
  - Their magnetic assembly behaviors were captured by optical microscopy in real time, and the geometrical parameters of the assemblies were quantitatively evaluated using a code developed in-house. Over 100 magnetic assembly conditions were tested.
  - As expected from the analytical study, most of the geometry changes of the 1D nanoparticle assemblies, from the reference samples produced with a static magnetic field, were observed when assembled using an oscillating field at a low frequency (< 1 Hz). With the frequency as small as 0.1 Hz, separation increased by 139%, length increased by 43%, and width increased by 56% about the PNC sample with 0.02 vol% nanoparticles assembled with a sinusoidal field at a flux density of 100 G.
  - The effects of other critical parameters on magnetic assembly of nanoparticles were measured. More assembly tailorability was observed with a sinusoidal waveform (125% increase in separation over a square waveform) rather than with a static waveform. The lowest external flux density to initiate magnetic assembly was experimentally evaluated; when the flux density is low, the capture radius is smaller than the inter-nanoparticle distances, and thus nanoparticles do not assembly.
  - While analytical studies were limited to superparamagnetic nanoparticles, experimental studies were also conducted about ferrimagnetic (\(M_r = 60 \, \text{emu/g}\)) nanoparticles with increased magnetic responsiveness and remanence. Increased magnetic responsiveness is an advantage for effective assembly, especially to
overcome hydrodynamic drag from polymer matrices, and remanence is expected to help maintain assembly. When assembled with a DC field, the increased capture radius of the ferrimagnetic nanoparticles produced longer (approximately 400% increase) and more separated (approximately 100% increase) assemblies than those achieved with the superparamagnetic nanoparticles. Meanwhile, due to their remanence, when assembled with oscillating fields, higher flux densities are required to balance both lateral and transverse assembly mechanisms.

- Established a method to fabricate and tailor 1D structured polymer nanocomposites using magnetic fields
  - Surface modification was conducted on ferrimagnetic nanoparticles (gamma-phase iron oxide, maghemite) using 3-glycidyloxypropyl trimethoxysilane to ensure nanoparticle dispersion and suspension in a bisphenol-F thermoset polymer matrix with two processes (dry vs. wet). Surface-modified maghemite nanoparticles and their aggregates were characterized (optical microscopy, TEM, FTIR, BET, XRD and VSM) for their surface chemical condition and aggregate size reduction. The effect of surface modification was confirmed to reduce sedimentation layer thickness by approximately 60%.
  - A method was developed to fabricate sizable PNCs (20 mm × 20 mm × 10 mm) with tailored 1D aligned nanoparticle assemblies using an oscillating magnetic field. These PNCs were sliced and locally inspected for their nanoparticle volume fraction and distribution using optical microscopy and microCT scans. First, PNCs were prepared using dry-processed nanoparticles assembled with a nonuniform magnetic field generated by a solenoid pair. With the magnetic field gradient, 1D nanoparticle assembly lines were achieved and tailored, but resulted in inhomogeneous nanoparticle dispersion in most PNCs: sedimentation due to an increased effect of gravity with increasing nanoparticle assembly size, and spatial inhomogeneity due to the magnetic field gradient. Second, PNCs were fabricated using wet-processed nanoparticles, whose aggregate sizes were smaller, assembled using a homogeneous magnetic field generated by a Helmholtz coil (1.91 cm × 1.91 cm × 0.95 cm), this time achieving homogeneously distributed 1D nanoparticles assemblies.
  - Tailorability and scalability were demonstrated about the fabrication of 1D structured PNCs using oscillating magnetic fields. Most importantly, a set of 1D structured PNCs
were fabricated with the same volume fractions but with different line features: short lines vs. long lines that span across the sample thickness, thin lines vs. thick lines that have more inter-nanoparticle contacts, varying inter-line distances, etc. In addition, these samples sizes were large enough to be characterized for their bulk transport properties.

- Conducted structure-interface-property relationship studies to identify and evaluate the effectiveness of oscillating magnetic fields in tailoring nanoparticle structures and thus properties of 1D structured PNCs
  - A comparable data set of properties (electrical resistivity and thermal conductivity) and nanoparticle structures (of 1D structured PNCs) were obtained. While PNC samples prepared with dry-processed nanoparticles exhibited inhomogeneity, their nanoparticle structures were inspected per sample for direct comparison.
  - As for electrical resistivity, continuous nanoparticle structures were critical for effective electrical transport. Field oscillating helped to provide such expansive nanoparticle networks at a smaller volume fraction through enhanced transverse assembly, when compared with those assembled with a static magnetic field. A percolation threshold of 0.15 vol% was estimated with field oscillation, lower than that observed for assembled nanoparticles in literature (tin oxide, 0.4 vol% threshold) [260]. Even in the transverse direction, percolation, but with smaller resistivity reduction, was achieved at a higher volume fraction, due to formation of three-directional networks as the assembly line size increases and sedimentation occurs.
  - As for thermal conductivity, thermal conductivity improvement was most effective with low nanoparticle volume fraction or when assembled with a static magnetic field. Both conditions are associated with a smaller number of inter-nanoparticle contacts, as confirmed with optical microscope/microCT inspection.
  - Contrast between the electrical and thermal transport behaviors was further identified by the transport property data for PNCs with wet-processed nanoparticles. With their small aggregate size, wet-processed nanoparticles did not form assembly lines that expand through the thickness of the PNC samples. Thus, no electrical resistance reduction was observed, while small thermal conductivity improvement was observed with increasing nanoparticle volume fraction. This structure-interface-property
relationship difference can be attributed again to the transport mechanisms explained in the above two points.

8.2 Recommendations for Future Work

8.2.1 Design space and guidelines for magnetic tailoring of polymer nanocomposites

In this thesis, magnetic assembly using oscillating magnetic fields was studied as a novel fabrication method to provide polymer nanocomposites in a tailorable and scalable manner. Thus, below, recommendations, guidelines and corresponding flow chart are given about the parameter conditions to achieve desired nanoparticle assembly using oscillating magnetic fields. The design space is illustrated in Figure 8.1 for nanoparticles undergoing a Brownian magnetic moment reorientation mechanism due to an externally oscillating magnetic field. Assuming enough time is allowed for the nanoparticle assemblies to deplete aggregates and assemblies within their capture radius, three main mechanism control nanoparticle assembly using oscillating magnetic fields: (1) the magnetic field needs to be greater than a threshold such that all free aggregates are captured by the assemblies; (2) the frequency of the field needs to be low enough to ensure complete rotation of the nanoparticles’ magnetic moment to promote transverse assembly and lateral or head-to-tail attraction between the assemblies can occur; (3) increased matrix viscosity requires additional time for nanoparticle rotation and thus reduced field frequencies are required for assembly. For nanoparticles greater than approximately 15 nm in size, the Brownian magnetic moment reorientation mechanism will dominate enabling enhancement of transverse nanoparticle assembly. However, this assembly mechanism requires that the nanoparticles are not constrained. For constrained nanoparticles, where rotation of the magnetic moment occurs by internal reorganization of the magnetic domains through the Néel mechanism, the rotational hydrodynamic effect of the matrix is non-existent. Simulation work in the literature has demonstrated reduced assembly, or magnetic capture rates, between nanoparticles undergoing the Néel mechanism, unlike the Brownian mechanism, due to a reduced torque applied to these nanoparticles [274], leading to a limited transverse assembly mechanism, especially in high viscosity matrices.
In addition to the above design space for tailoring of nanoparticle assemblies, guidelines and a corresponding flow chart (see Figure 8.2) are constructed for fabrication of tailored one-dimensional polymer nanocomposites. Equations specified in previous chapters are duplicated here, and the limitations about the guidelines are also discussed.

A. Magnetic nanoparticle re-orientation:

i. Nanoparticles with a hydrodynamic diameter between approximately 20 nm to 100 nm are desirable. Diameters larger than 20 nm will induce physical rotation of the nanoparticles with oscillation of the external magnetic field and the nanoparticles will undergo a Brownian reorientation mechanism. Diameters below 100 nm will produce a stable single magnetic domain, simplifying control of the nanoparticles.

\[
\frac{3\eta V_H}{k_B T} > \tau_0 e^{\frac{K_V}{k_B T}}
\]
ii. Limitations: Magnetic anisotropic effects from nanofiller shapes other than spherical will alter rotational behaviors of the nanofiller magnetic moments. Comparison of the two mechanisms is only valid if magnetization varies linearly with the external field (thus at low field strengths) and for superparamagnetic nanoparticles.

B. External magnetic field gradient:
   i. A field gradient of less than 0.1% is recommended to produce homogeneous PNCs. While external field gradients have been shown to be useful for localized PNC property enhancement [57], field gradients producing nanoparticle migration limit application specific tailorability. In this work, a field gradient of 3% across the PNC samples produced significant migration of the nanoparticles, leading to inhomogeneous distribution and property enhancement.

\[
\frac{3\mu_0m^2}{2\pi|r|^4} \gg m\frac{\partial B_x}{\partial x}
\]

ii. Limitations: Low field gradients are primarily achievable with Helmholtz coils; however, Helmholtz coils tend to produce a much-reduced field strength as compared to solenoids, leading to a reduction in the magnetic capture radius.

C. Magnetic capture radius:
   i. A magnetic capture radius greater than 10 times the interaggregate distance will significantly improve contact between nanoparticle assemblies, enhancing bulk PNC transport properties. A large magnetic capture radius ensures that magnetic forces, not thermal energy, control nanoparticle motion. In this work, it was observed that a magnetic capture radius greater than 10 times the interaggregate distance produced networked nanoparticle assemblies within the working life (30 minutes).

\[
2c\left(\frac{\pi\mu_0c^3\chi^2H^2}{9k_BT}\right)^{1/3} > 10\delta_a
\]
ii. Limitations: Interactions between magnetic nanoparticles, and the effects of thermal energy, are complex. Here, simplified expressions are shown for far-field approximations between a magnetic dipole pair with aligned magnetic moments. In addition, the translational time due to hydrodynamic effects is not considered, which is important to ensure nanoparticle assemblies are formed prior to cure.

D. Particle sedimentation:

i. A mean Brownian, or thermal, displacement greater than the gravitational displacement is recommended. Thermal diffusion and hydrodynamic drag are effective mechanisms to prevent sedimentation in PNCs. Smaller nanoparticle, or aggregate, sizes and increased matrix viscosity can reduce the effect of sedimentation. In addition, sedimentation can be reduced by approximately 60% with a surface modifier \(0.3 \leq \beta \leq 0.5\) with a surface modifier, \(\beta = 1\) without.

\[
1 - \frac{1}{1 + \frac{36}{(\rho_s - \rho_l) g(2c)^{5/2}} \left( \frac{2k_B T \eta}{3\pi \eta} \right)^{3/5}} > \frac{0.5}{\beta}.
\]

ii. Limitations: Nanoparticle size is correlated with the magnetic capture radius; smaller nanoparticle sizes will reduce the magnetic capture radius. In addition, increased matrix viscosity limits translation and rotation of the magnetic nanoparticles, affecting the required working life and the frequency of the external field. As assembly sizes grow, the effect of sedimentation increases, making it difficult to balance the effects of the magnetic capture radius and sedimentation reduction.

E. Magnetic assembly time:

i. A magnetic moment reorientation frequency greater than 10 times of that of the external field frequency is recommended. While rotation of the induced magnetic field enhances transverse assembly, it is also important that enough time is allowed for the magnetic moment to be orientated parallel to the external field for lateral assembly and zippering to occur.
\[
\frac{mB}{8\pi r_p^3\eta} \gg f
\]

ii. Limitations: The inertia effects are assumed to be small compared to the viscous and magnetic moment interactions. Constrained nanoparticles will reorientate their magnetic moments through reorganization of their internal magnetic domains (if the anisotropic energy barrier is overcome), limiting the effects of transverse assembly.

F. Nanoparticle surface modification:
   i. Mass of the surface modifier to the mass of the nanoparticles should be greater than the ratio between the nanoparticle specific surface area and the specific wetting surface of the surface modifier. Nanoparticles will aggregate due to their high surface energy. Reducing this energy through a surface modifier is important to control the nanoparticle aggregate size and therefore the magnetic capture radius and sedimentation. Ball milling in the presence of the surface modifier and a solvent is an effective technique to reduce the nanoparticle surface energy.

\[
\frac{m_s}{m_m} > \frac{a_s}{sws}
\]

ii. Limitations: Drying the surface modified nanoparticles can lead to reaggregation of the nanoparticles. Storing the surface modified nanoparticles within the milling matrix can prevent reaggregation, but requires that excess milling media be evaporated prior to mixing with the resin, which is difficult for nanoparticle volume fractions above 5%. A high viscosity matrix will limit dispersion of the nanoparticles within the PNC matrix, and additional techniques may need to be incorporated, such as increased temperature, shear mixing with ultrasonication, or filtering after dispersion.
G. Working life and polymer viscosity:

i. The magnetic interaction between two aggregates, or assemblies, should be much greater than the viscous force applied to the aggregates over the working life. Assuming Stokes’ law and that the largest separation between nanoparticle aggregates is the magnetic capture radius ($r_c$), a longer working life ($t_w$) will reduce the effects of hydrodynamic drag, in addition to a reduced viscosity of the matrix, increased magnetic susceptibility of the nanoparticles, or an increased field strength.

$$\frac{3\mu_0(\chi HV)^2}{2\pi c^4} \gg \frac{6\pi \eta c r_c}{t_w}$$

ii. Limitations: Very high viscosity matrices can severely diminish nanoparticle translation and rotation due to an external field, limiting the tailoring of PNCs. High viscosity matrices will produce large nanoparticle assemblies, leading to increased thermal contact resistance (and reduced thermal conductivity) and sedimentation.

8.2.2 Future Work

Based upon the limitations of this work, important research topics that require additional investigation are listed below:

- Additional structure-interface-property relationship studies
  - The wet-processed samples with percolated structures should be fabricated and characterized. Such samples can be achieved by increasing aggregate size and magnetic capture radius, by increasing the particle magnetic susceptibility, and by increasing magnetic field strength and retaining field homogeneity with a Helmholtz coil.
  - The structure-property relationships about PNCs with larger volume fractions needs to be investigated. Tailored nanoparticle contacts to control transport properties at low volume fractions is expected to be much easier. As the nanoparticle concentration grows, control over the nanoparticle contacts becomes difficult as more nanoparticles exist within the capture radius, and tailored property response is expected to be limited.
In addition, improved processing methods for the wet-processed nanoparticles at higher volume fractions is necessary as the current solvent removal process is difficult at high volume fractions.

- Enhanced microCT scanning is desired for more precise structure quantification. Properly prepared samples (cylindrical, small diameter) will provide increased resolutions to quantify nanoparticle structures. In addition, improvement of the segmentation technique to provide volume fractions similar to that measured also needs to be incorporated prior to data analysis.

More data analysis of the current results should be conducted. Extraction of the nanoparticle boundary resistance values would be useful to further quantify the effect of nanoparticle contact control. An improved method to estimate the percolation threshold would also be beneficial to directly correlate external parameters to measured electrical resistivity.

- Integration of field oscillation to tailor PNCs of other types than those investigated in this work
  - Coating specific regions of non-spherical and/or nonmagnetic nanofillers (such as the tips of CNTs, etc) may add another factor for control of the nanofiller structures. For example, attaching a magnetic nanocylinder at the head, and orthogonal to the axis, of a nonmagnetic nanotube would assemble the nanotubes perpendicular to the field direction as the preferred axis for magnetic orientation of a nanocylinder is along its long axis. Field oscillation could control the density of these nanotube forests.
  - Effective control and reorientation of anisotropic magnetic nanofiller is possible with an oscillating field. For example, vibration is generally used to aid in the magnetic alignment of 2D platelets [57] as the platelets tend to get stuck in certain orientations. Field oscillating could remove the need for external vibration as the platelets will rotate (or locally vibrate) due to field oscillation.
  - Field oscillating could also be useful to tailor the deformation of magnetoeLASTomers. Controlled nanofiller organization (thick, thin assembly lines, etc.) can tailor deformation characteristics, and is envisioned to provide application specific control over microfluidic gates (as one example).
Figure 8.2: Flow chart for tailored PNCs using oscillating magnetic fields.
Appendix A

Image Analysis of Nanoparticle Assembly

A.1 Image Processing Algorithm Frontend (Matlab)

% Mychal Spencer
% Pennsylvania State University
% Aerospace Engineering
%
% The purpose of this program is to call the function Mag_Analysis to
% quantitatively analyze the size and distribution of magnetic
% nanoparticles.
%
% Notes: Currently the algorithm is optimized for
% clusters aligned near the horizontal and for clusters that are roughly
% 'cigar' shaped. In addition, the term 'Average' is used to represent
% either the mean or median depending on the skewness of the dataset of
% interest (only applicable if mean_set = 1, if mean_set = 0 only the
% mean is used); if the skewness is greater than 1, the median is used;
% if the skewness is less than one, the mean is used. The confidence
% interval is 95% with respect to the average used.
%
% The function Mag_Analysis has form:
% [outputs] = Mag_Analysis(inputs)
% where,
% [outputs] = [Number of clusters per um^2,
% Average distance between clusters,
% Average length of clusters,
% Average width of clusters,
% Average size of clusters,
% Average angular offset from horizontal
% Grayscale image of analysis region
% Binary image with embedded data
% Width of each cluster
% Length of each cluster
% Size of each cluster
% Average separation of each column
% Matrix containing the cluster of interest]
%
% (inputs) = (RGB image to analyze,
% Sample parameters - maximum of 26 characters
% Sample parameters - maximum of 26 characters
% Magnification - only 5, 10, 20, or 50
% Fraction of image, starting from center, to analyze.
% Standard deviation threshold value
% Threshold fraction to be removed due to artifacts
% Number of image partitions along rows
% Number of image partitions along columns
% Display all images? 1 = yes, 0 = no - faster
% Display a certain cluster? 0 = no, cluster number = yes
% How to evaluate average? 0 = mean only, 1 = mean & median

clc
close all
clear all %#ok<CLALL>

% Inputs:

mod = imread('4.00mg_per_ml at -100G to 100G 5.0 Hz Square-15 mins.bmp'); % Input
param1 = '9/9/15, I7643 4mg/ml in DI '; % Sample parameters
param2 = '5.0 Hz Sq., -100G to 100G, 15min'; % Sample parameters cont.
mag = 20; % Magnification of input image
center = 0.60; % Fraction of image to analyze
eta = -0.15; % Standard deviation threshold
thr_err = 0.10; % Threshold artifact error fraction
num_x = 4; % Partition image prior to threshold for poor images; value
num_y = 6; % of num_x = num_y = 1 is for no partition (1 image)
dis = 0; % Display all images? 1 = yes, 0 = no
cluster = 0; % Display a specific cluster? 0 = no, cluster number = yes
mean_set = 0; % How to evaluate average? 0 = mean only, 1 = mean & median
show_histogram = 1; % Display histograms? 1 = yes, 0 = no

% Outputs:

[Number,Distance,Avg_Length,Avg_Width,Avg_Size,Angle,Grayscale_Image,...
 Binary_Image, Width,Length,Size,Separation,Cluster_Image] = ...
 Mag_Analysis(mod,param1,param2,mag,center,eta,thr_err,num_x,num_y,...
 dis,cluster,mean_set);

% Display:

if dis ~= 1
    figure('Name','Magnetized Grayscale Image - Center Region')
    imshow(Grayscale_Image,'Border','tight','InitialMagnification',60)

    figure('Name','Output Magnetized Black & White Image')
    imshow(Binary_Image,'Border','tight','InitialMagnification',60)

    if cluster ~= 0
        figure('Name','Cluster Image')
        imshow(Cluster_Image,'Border','tight','InitialMagnification',50)
    end
if show_histogram == 1
    figure('Name','Distribution of Cluster Size')
    histogram(Size)
    xlabel('Cluster Size (um^2)')
    ylabel('Frequency')

    figure('Name','Distribution of Cluster Length')
    histogram(Length)
    xlabel('Cluster Length (um)')
    ylabel('Frequency')

    figure('Name','Distribution of Cluster Width')
    histogram(Width)
    xlabel('Cluster Width (um)')
    ylabel('Frequency')

    figure('Name','Distribution of Cluster Separation')
    histogram(Separation)
    xlabel('Cluster Separation (um)')
    ylabel('Frequency')
end
end

A.2 Image Processing Algorithm (Matlab)

function [act_number_norm,avg_cluster_separation,avg_cluster_length, ...
    avg_cluster_width,avg_pixel_size,avg_cluster_angle, ...
    mod_gcenter,mod_bw_output,cluster_width,cluster_length,cluster_size, ...
    cluster_separation,cluster_output] = Mag_Analysis(mod,param1,param2, ...
    mag,center,eta,thr_err,num_x,num_y,dis,cluster,mean_set)

% Mychal Spencer
% Pennsylvania State University
% Aerospace Engineering
%
% The purpose of this program is to quantitatively analyze the size and
% distribution of superparamagnetic Fe particles exposed to constant and
% time-varying magnetic fields.
%
% Notes:
% 1) This algorithm is optimized for elongated
%    clusters aligned along or near the horizontal axis (that is, rows).
%    Erroneous results may occur for clusters not orientated near the
%    horizontal, or for shapes that are not rectangular, 'cigar' shaped,
%    etc.
% 2) It is highly recommended that only between 40-60% of the image center
%    is used for analysis due to reduction of focus near image borders
% (note that a higher fraction leads to better approximations, but poor
% image quality requires a lower fraction).
% 3) Output results improve with increased image contrast between pattern
% features and background (that is, focused images with a clear
% contrast between the pattern and background will produce much
% better results).
% 4) Algorithm does not account for partial sizes of pattern features at
% the edge of the image analysis region (this is most notable for
% pattern features on the left, right, and bottom of the image). Care
% should be taken when analyzing images with pattern features primarily
% aligned along the border of the analysis region - it is recommended in
% such a case that a different region is analyzed.
% 5) This algorithm requires the image processing toolbox and the computer
% vision system toolbox.

% Inputs:
% 1) mod - image to analyze
% 2) param1 - sample parameters - text (26 characters max)
% 3) param2 - sample parameters - text (26 characters max)
% 4) mag - image magnification (5, 10, 20, or 50)
% 5) center - fraction of image, starting from center, to analyze - value
% of 0.5 is recommended (although 0.4 and 0.6 are valid)
% 6) eta - standard deviation threshold value
% 7) thr_err - threshold fraction to be removed due to artifacts
% 8) num_x - number of image partitions along rows
% 9) num_y - number of image partitions along columns
% 10) dis - display all images? 1 = yes, 0 = no - faster
% 11) cluster - display a certain cluster? 0 = no, cluster number = yes
% 12) mean_set - how to calculate average? 0 = mean only, 1 = mean & median
%
% Outputs:
% 1) act_number_norm - number of clusters per um^2
% 2) avg_cluster_separation - average distance between clusters (um)
% 3) avg_cluster_length - average length of clusters (um)
% 4) avg_cluster_width - average width of clusters (um)
% 5) avg_cluster_size - average size of clusters (um^2)
% 6) avg_cluster_angle - average rotation of clusters (wrt x-axis)
% 7) mod_gcenter - grayscale image of analysis region
% 8) mod_bw_output - output image with relevant data
% 9) cluster_width - width for each cluster (um)
% 10) cluster_length - length for each cluster (um)
% 11) cluster_size - size for each cluster (um^2)
% 12) cluster_separation - average separation for each column (um)
% 13) cluster_output - matrix containing the cluster of interest

clc
close all

% 1) Import image file:
if dis == 1
    figure('Name','Magnetized Image')
    imshow(mod,'Border','tight','InitialMagnification',40)
end

% 2) Convert image to grayscale:

mod_g = rgb2gray(mod);
if dis == 1
    figure('Name','Magnetized Grayscale Image')
    imshow(mod_g,'Border','tight','InitialMagnification',40)
end

% 3) Analyze a region in the center of the image:

[n1,m1] = size(mod_g); % Dimensions of the image file
n1 = 2*round(n1/2); % Round to nearest even integer
m1 = 2*round(m1/2); % Round to nearest even integer

if center < 0.40 || center > 0.60
    disp('Warning: Beyond bounds of recommended image fraction')
end

for i = 1:center*n1
    for j = 1:center*m1
        mod_gcenter(i,j) = mod_g(i+n1*(1-center)/2, ...
                        j+m1*(1-center)/2);   %#ok<AGROW>
    end
end

if dis == 1
    figure('Name','Magnetized Grayscale Image - Center Region')
    imshow(mod_gcenter,'Border','tight','InitialMagnification',50)
end

% 4) Convert grayscale image to black and white (binary) via threshold:

[n2,m2] = size(mod_gcenter); % Dimensions of the modified image file
mod_bw = ones(n2,m2);
part_mat = zeros(n2,m2); % Partition matrix containing threshold values
part_x = ones(1,num_x+1);
part_y = ones(1,num_y+1);

for i = 2:num_x+1 % Specify the partition locations for the rows
    if i == 2
        part_x(1,i) = round(n2/num_x);
    elseif i == num_x+1
        part_x(1,i) = n2;
    end
else
    part_x(1,i) = round(part_x(1,i-1) + n2/num_x);
end
end

for j = 2:num_y+1 % Specify the partition locations for the columns
    if j == 2
        part_y(1,j) = round(m2/num_y);
    elseif j == num_y+1
        part_y(1,j) = m2;
    else
        part_y(1,j) = round(part_y(1,j-1) + m2/num_y);
    end
end

for n = 2:length(part_x) % Apply threshold to each partition of the image
    for m = 2:length(part_y)
        temp3 = [];
        ii = 0;
        for i = part_x(1,n-1):part_x(1,n)
            ii = ii + 1;
            jj = 0;
            for j = part_y(1,m-1):part_y(1,m)
                jj = jj + 1;
                temp3(ii,jj) = mod_gcenter(i,j); %#ok<AGROW>
            end
        end
        temp3 = uint8(temp3);
        [counts,binloc] = imhist(temp3);
        temp4 = mean(counts) + eta*std(counts);% Estimate the threshold % using the histogram data
        temp5 = 0;
        for i = 1:length(binloc) % Picks out bin location of threshold
            if temp5 == 0
                if counts(i) > temp4
                    temp5 = i-1; % Threshold
                end
            end
        end
        for i = part_x(1,n-1):part_x(1,n) % Create threshold matrix
            for j = part_y(1,m-1):part_y(1,m)
                part_mat(i,j) = temp5;
            end
        end
    end
end

part_mat_sm = part_mat;
for i = 3:n2-2 % Smooth out the threshold matrix (Gaussian smoothing) 
for j = 3:m2-2 
    part_mat_sm(i,j) = 1/273*(part_mat(i-2,j-2) + 4*part_mat(i-2,j-1) + 7*part_mat(i-2,j) + ... 
                      + 4*part_mat(i-1,j-2) + 16*part_mat(i-1,j-1) + 26*part_mat(i-1,j) + ... 
                      + 16*part_mat(i-1,j+1) + 4*part_mat(i-1,j+2) + ... 
                      + 7*part_mat(i-2,j) + 26*part_mat(i-2,j-1) + 41*part_mat(i-2,j) + ... 
                      + 26*part_mat(i-1,j) + part_mat(i-1,j+1)) + ... 
                      + 4*part_mat(i-1,j+2) + ... 
                      + 4*part_mat(i,j-2) + 16*part_mat(i,j-1) + 26*part_mat(i,j) + ... 
                      + 16*part_mat(i+1,j-1) + 4*part_mat(i+1,j) + ... 
                      + part_mat(i+1,j+1) + 4*part_mat(i+1,j+2) + ... 
                      + 7*part_mat(i,j) + 26*part_mat(i,j-1) + 41*part_mat(i,j) + ... 
                      + 26*part_mat(i,j+1) + part_mat(i,j+2)) + ... 
    end 
end 

for i = 1:n2 % Apply the threshold matrix to the grayscale image 
for j = 1:m2 
    if mod_gcenter(i,j) >= part_mat_sm(i,j) 
        mod_bw(i,j) = 1; 
    else 
        mod_bw(i,j) = 0; 
    end 
end 
end 

if dis == 1 
    figure('Name','Magnetized Black & White Image - Center Region') 
    imshow(mod_bw,'Border','tight','InitialMagnification',50) 
end 

% 5) Remove threshold artifacts and determine size of pattern features 
check = zeros(n2,m2); 
temp1 = 0; 
for i = 2:n2-1 % General idea: find a black pixel which hasn't been 
    % checked, and store surrounding unchecked black pixel 
    % locations. Keep looping over the stored locations until 
    % no new black pixels are found which are connected to the 
    % initial black pixel. The matrix 'check' contains the 
    % patterns and the associated pattern number. This will 
    % allow comparison to a minimum feature size and any pattern 
    % feature below this size will be removed (that is, 
    % threshold artifacts are removed). 
    for j = 2:m2-1 
        temp2 = 0; 
        temp3 = 0; 
        temp4 = 0; 
        if mod_bw(i,j) == 0 & & check(i,j) == 0 
            % If we find a black pixel
temp1 = temp1 + 1; % Number of pattern counter
temp2 = temp2 + 1; % Pixel counter for current pattern
check(i,j) = temp1; % Mark the location as checked
ii = i;
jj = j;
next = [];
while temp4 == 0 && temp3 < 1000000
    temp3 = temp3 + 1; % Loop counter
    if temp3 == 1 % First pass through the loop
        if mod_bw(ii-1,jj) == 0 && check(ii-1,jj) == 0
            temp2 = temp2 + 1;
            check(ii-1,jj) = temp1;
            next(temp2-1,:) = [ii-1 jj]; %#ok<AGROW>
        end
        if mod_bw(ii-1,jj+1) == 0 && check(ii-1,jj+1) == 0
            temp2 = temp2 + 1;
            check(ii-1,jj+1) = temp1;
            next(temp2-1,:) = [ii-1 jj+1]; %#ok<AGROW>
        end
        if mod_bw(ii,jj+1) == 0 && check(ii,jj+1) == 0
            temp2 = temp2 + 1;
            check(ii,jj+1) = temp1;
            next(temp2-1,:) = [ii jj+1]; %#ok<AGROW>
        end
        if mod_bw(ii+1,jj+1) == 0 && check(ii+1,jj+1) == 0
            temp2 = temp2 + 1;
            check(ii+1,jj+1) = temp1;
            next(temp2-1,:) = [ii+1 jj+1]; %#ok<AGROW>
        end
        if mod_bw(ii+1,jj) == 0 && check(ii+1,jj) == 0
            temp2 = temp2 + 1;
            check(ii+1,jj) = temp1;
            next(temp2-1,:) = [ii+1 jj]; %#ok<AGROW>
        end
        if mod_bw(ii+1,jj-1) == 0 && check(ii+1,jj-1) == 0
            temp2 = temp2 + 1;
            check(ii+1,jj-1) = temp1;
            next(temp2-1,:) = [ii+1 jj-1]; %#ok<AGROW>
        end
        if mod_bw(ii,jj-1) == 0 && check(ii,jj-1) == 0
            temp2 = temp2 + 1;
            check(ii,jj-1) = temp1;
            next(temp2-1,:) = [ii jj-1]; %#ok<AGROW>
        end
        if mod_bw(ii-1,jj-1) == 0 && check(ii-1,jj-1) == 0
            temp2 = temp2 + 1;
            check(ii-1,jj-1) = temp1;
    end
end
next(temp2-1,:) = [ii-1 jj-1];  %#ok<AGROW>
end
if isempty(next) == 1
    temp4 = 1;
end
else
    ii = next(temp3-1,1);
    jj = next(temp3-1,2);
    if ii ~= 1
        if mod_bw(ii-1,jj) == 0 && check(ii-1,jj) == 0
            temp2 = temp2 + 1;
            check(ii-1,jj) = temp1;
            next(temp2-1,:) = [ii-1 jj];  %#ok<AGROW>
        end
    end
    if ii ~= 1 && jj ~= m2
        if mod_bw(ii-1,jj+1) == 0 && check(ii-1,jj+1) == 0
            temp2 = temp2 + 1;
            check(ii-1,jj+1) = temp1;
            next(temp2-1,:) = [ii-1 jj+1];  %#ok<AGROW>
        end
    end
    if jj ~= m2
        if mod_bw(ii,jj+1) == 0 && check(ii,jj+1) == 0
            temp2 = temp2 + 1;
            check(ii,jj+1) = temp1;
            next(temp2-1,:) = [ii jj+1];  %#ok<AGROW>
        end
    end
    if ii ~= n2 && jj ~= m2
        if mod_bw(ii+1,jj+1) == 0 && check(ii+1,jj+1) == 0
            temp2 = temp2 + 1;
            check(ii+1,jj+1) = temp1;
            next(temp2-1,:) = [ii+1 jj+1];  %#ok<AGROW>
        end
    end
    if ii ~= n2
        if mod_bw(ii+1,jj) == 0 && check(ii+1,jj) == 0
            temp2 = temp2 + 1;
            check(ii+1,jj) = temp1;
            next(temp2-1,:) = [ii+1 jj];  %#ok<AGROW>
        end
    end
    if ii ~= n2 && jj ~= 1
        if mod_bw(ii+1,jj-1) == 0 && check(ii+1,jj-1) == 0
            temp2 = temp2 + 1;
            check(ii+1,jj-1) = temp1;
            next(temp2-1,:) = [ii+1 jj-1];  %#ok<AGROW>
        end
    end
if jj ~= 1
    if mod_bw(ii,jj-1) == 0 && check(ii,jj-1) == 0
        temp2 = temp2 + 1;
        check(ii,jj-1) = temp1;
        next(temp2-1,:) = [ii jj-1];  %#ok<AGROW>
    end
end
if ii ~= 1 && jj ~= 1
    if mod_bw(ii-1,jj-1) == 0 && check(ii-1,jj-1) == 0
        temp2 = temp2 + 1;
        check(ii-1,jj-1) = temp1;
        next(temp2-1,:) = [ii-1 jj-1];  %#ok<AGROW>
    end
end
if temp3 >= temp2
    temp4 = 1;
end
end
end
end

number = temp1; % Total number of pattern features (over-exaggerated)

pixel_size = zeros(1,number);
check_thr = zeros(n2,m2); % Updated check matrix with threshold applied
% check_rm = zeros(n2,m2); % Updated check matrix with removed components
temp2 = 0;
for i = 1:n2 % Count number of pixels associated with each pattern
    for j = 1:m2
        if check(i,j) ~= 0
            pixel_size(1,check(i,j)) = pixel_size(1,check(i,j)) + 1;
        end
    end
end

for i = 1:n2 % Update the binary image; if the size of the pattern feature
    % is below the threshold artifact error, remove the pattern
    % feature
    for j = 1:m2
        if check(i,j) ~= 0
            if pixel_size(1,check(i,j)) < round(thr_err*mean(pixel_size))
                mod_bw(i,j) = 1;
                %                check_rm(i,j) = check(i,j);
            else
                check_thr(i,j) = check(i,j);
            end
        end
    end
end
for i = 1:number % Remove features with less than threshold error for % accurate count and size (remove threshold artifacts)
    if pixel_size(1,i) >= round(thr_err*mean(pixel_size))
        temp2 = temp2 + 1;
        act_pixel_size(1,temp2) = pixel_size(1,i); %#ok<AGROW>
    end
end

temp3 = 0;
temp4 = 0;
check_thr_reord = zeros(n2,m2);

for i = 1:n2 % Reorder the check matrix to start from 1
    for j = 1:m2
        if check_thr(i,j) ~= 0
            temp4 = temp4 + 1;
            temp5 = 0;
            if temp4 ~= 1
                for ii = 1:length(reord)
                    if check_thr(i,j) == reord(ii)
                        temp5 = ii;
                    end
                end
                if temp5 ~= 0
                    check_thr_reord(i,j) = temp5;
                else
                    temp3 = temp3 + 1;
                    reord(temp3) = check_thr(i,j); %#ok<AGROW>
                    check_thr_reord(i,j) = temp3;
                end
            end
        end
    end
end

cluster_number = temp3;
avg_pixel_size = round(mean(act_pixel_size)); % Average pattern size
act_number = length(act_pixel_size); % Actual number of patterns

if dis == 1
    figure('Name','Black & White Image of Quantitative Matrix')
    imshow(check_thr_reord,'Border','tight','InitialMagnification',50)
    figure('Name','Color Image of Quantitative Matrix')

% 6) Quantitative analysis of cluster features (length, width, separation)

north = zeros(2,cluster_number); % North index location for each cluster
south = zeros(2,cluster_number); % South index location for each cluster
east = zeros(2,cluster_number); % East index location for each cluster
west = zeros(2,cluster_number); % West index location for each cluster

for i = 1:n2 % Find the index location for each cluster
  for j = 1:m2
    if check_thr_reord(i,j) ~= 0
      temp1 = check_thr_reord(i,j);
      if west(2,temp1) == 0
        west(1,temp1) = i;
        west(2,temp1) = j;
      else
        if west(2,temp1) > j
          west(1,temp1) = i;
          west(2,temp1) = j;
        end
      end
      if east(2,temp1) == 0
        east(1,temp1) = i;
        east(2,temp1) = j;
      else
        if east(2,temp1) < j
          east(1,temp1) = i;
          east(2,temp1) = j;
        end
      end
      if north(1,temp1) == 0
        north(1,temp1) = i;
        north(2,temp1) = j;
      else
        if north(1,temp1) > i
          north(1,temp1) = i;
          north(2,temp1) = j;
        end
      end
      if south(1,temp1) == 0
        south(1,temp1) = i;
        south(2,temp1) = j;
      else
        if south(1,temp1) < i
          south(1,temp1) = i;
          south(2,temp1) = j;
        end
      end
    end
  end
end
min_i = zeros(2, cluster_number); % Minimum row position for each cluster
max_i = zeros(2, cluster_number); % Maximum row position for each cluster
min_j = zeros(2, cluster_number); % Minimum column position for each cluster
max_j = zeros(2, cluster_number); % Maximum column position for each cluster
cluster_angle = zeros(1, cluster_number); % Angle of each cluster

for ii = 1:cluster_number % Determine the min and max row and column locations
    if north(1, ii) <= south(1, ii)
        min_i(1, ii) = north(1, ii);
        min_i(2, ii) = north(2, ii);
        max_i(1, ii) = south(1, ii);
        max_i(2, ii) = south(2, ii);
    else
        min_i(1, ii) = south(1, ii);
        min_i(2, ii) = south(2, ii);
        max_i(1, ii) = north(1, ii);
        max_i(2, ii) = north(2, ii);
    end
    if west(2, ii) <= east(2, ii)
        min_j(1, ii) = west(1, ii);
        min_j(2, ii) = west(2, ii);
        max_j(1, ii) = east(1, ii);
        max_j(2, ii) = east(2, ii);
    else
        min_j(1, ii) = east(1, ii);
        min_j(2, ii) = east(2, ii);
        max_j(1, ii) = west(1, ii);
        max_j(2, ii) = west(2, ii);
    end
    cluster_angle(ii) = atan((max_j(1, ii) - min_j(1, ii))/(min_j(2, ii) - max_j(2, ii)));
    if isnan(cluster_angle(ii)) == 1
        cluster_angle(ii) = 0;
        disp('Error: Line angle not calculated - zero degrees used')
    end
    for i = min_i(1, ii):max_i(1, ii) % Store clusters in an array
        for j = min_j(2, ii):max_j(2, ii)
            cluster_info(ii, i-min_i(1, ii)+1, j-min_j(2, ii)+1) = check_thr_reord(i, j);
        end
    end
end

avg_cluster_angle = mean(cluster_angle); % Average angle of each cluster
cluster_length = zeros(1, cluster_number);
cluster_width = zeros(1,cluster_number);

for ii = 1:cluster_number % Determine cluster length and width
    cluster_length(ii) = (max_j(2,ii)-min_j(2,ii))/(cos(avg_cluster_angle));
    temp1 = 0;
    for j = min_j(2,ii):max_j(2,ii)
        for i = min_i(1,ii):max_i(1,ii)
            if check_thr_reord(i,j) == ii
                temp1 = temp1 + 1;
            end
        end
    end
    cluster_width(ii) = cos(avg_cluster_angle)*temp1/(max_j(2,ii)-min_j(2,ii));
end

cluster_separation_temp = zeros(1,m2);

for j = 1:m2 % The separation between clusters (vertical separation)
    temp1 = 0;
    temp2 = 0;
    temp3 = 0;
    temp4 = 0;
    temp5 = 0;
    for i = 1:n2
        if i == 1 % If on the first loop store the value
            temp1 = check_thr_reord(i,j);
        else % Not on the first loop move until opposite is found
            if check_thr_reord(i,j) == temp1
                temp1 = check_thr_reord(i,j);
            end
                if temp5 == 0 & & temp2 == 1
                    temp2 = 0;
                    temp4 = temp4 + 1;
                end
                if check_thr_reord(i,j) == 0
                    temp2 = 1;
                    temp5 = 0;
                end
            end
        end
        if temp2 == 1
            temp3 = temp3 + 1;
            temp5 = temp5 + 1;
        end
    end
    if check_thr_reord(i,j) == 0 % We only want separation between clusters
        temp3 = temp3 - temp5;
    end
    cluster_separation_temp(j) = temp3/temp4;
end
temp1 = 0;
temp2 = 0;
for j = 1:m2 % If an entire column has white space we'll have NaN in vector
    if isnan(cluster_separation_temp(j)) == 0
        temp1 = temp1 + 1;
        cluster_separation(temp1) = cluster_separation_temp(j); %#ok<AGROW>
    else
        temp2 = temp2 + 1;
    end
end

if temp2 ~= 0
    disp('Warning: Columns with no spacing between clusters found');
end

cluster_separation = cos(avg_cluster_angle)*cluster_separation;

% 7) Statistical analysis of data

cluster_size = act_pixel_size;

for i = 1:4
    if i == 1 % Cluster size
        skewness_cluster_size = skewness(cluster_size(isfinite(cluster_size))); % Determine
        the skewness
        if skewness_cluster_size > 1 && mean_set == 1 % If the data is skewed
            avg_cluster_size = median(cluster_size);
            ci_cluster_size = bootci(2000,@median,cluster_size);
        else
            avg_cluster_size = mean(cluster_size(isfinite(cluster_size)));
            ci_cluster_size = bootci(2000,@mean,cluster_size(isfinite(cluster_size))); % 95%
        end
    elseif i == 2 % Cluster length
        skewness_cluster_length = skewness(cluster_length(isfinite(cluster_length)));
        if skewness_cluster_length > 1 && mean_set == 1
            avg_cluster_length = median(cluster_length);
            ci_cluster_length = bootci(2000,@median,cluster_length);
        else
            avg_cluster_length = mean(cluster_length(isfinite(cluster_length)));
            ci_cluster_length = bootci(2000,@mean,cluster_length(isfinite(cluster_length)));
        end
    elseif i == 3 % Cluster width
        skewness_cluster_width = skewness(cluster_width(isfinite(cluster_width)));
        if skewness_cluster_width > 1 && mean_set == 1
            avg_cluster_width = median(cluster_width);
            ci_cluster_width = bootci(2000,@median,cluster_width);
        else
            avg_cluster_width = mean(cluster_width(isfinite(cluster_width)));
            ci_cluster_width = bootci(2000,@mean,cluster_width);
        end
    end
end
avg_cluster_width = mean(cluster_width(isfinite(cluster_width)));  
ci_cluster_width = bootci(2000,@mean,cluster_width(isfinite(cluster_width)));  
end  
else % Cluster separation  
skewness_cluster_separation=  
    skewness(cluster_separation(isfinite(cluster_separation))));  
if skewness_cluster_separation > 1 & & mean_set == 1  
    avg_cluster_separation = median(cluster_separation));  
ci_cluster_separation = bootci(2000,@median,cluster_separation));  
else  
    avg_cluster_separation = mean(cluster_separation(isfinite(cluster_separation))));  
ci_cluster_separation=  
    bootci(2000,@mean,cluster_separation(isfinite(cluster_separation))));  
end  
end  
end  

% Alternate method to calculate confidence interval (using t test)  
%SEM=  
    std(cluster_width(isfinite(cluster_width)))/sqrt(length(cluster_width(isfinite(cluster_width))));  
% standard error  
% ts = tinv([0.05 0.95],length(cluster_width(isfinite(cluster_width)))-1);  
% t score  
% CI = mean(cluster_width(isfinite(cluster_width))) + ts*SEM;  
% 95% CI

% 8) Convert pixel values to metric distance via calibration data

% mag = 10;  

if mag == 5 % All magnification data from calibration on 4/2/15  
mag_mult = 1.343;  
elseif mag == 10  
mag_mult = 0.6791;  
elseif mag == 20  
mag_mult = 0.3387;  
elseif mag == 50  
mag_mult = 0.1353;  
else  
disp('Error: Incorrect magnification value used')  
end  

avg_cluster_size = (mag_mult)^2*avg_cluster_size;  
avg_cluster_length = mag_mult*avg_cluster_length;  
avg_cluster_width = mag_mult*avg_cluster_width;  
avg_cluster_separation = mag_mult*avg_cluster_separation;  
act_number_norm = act_number/(n2*m2*(mag_mult)^2);  

ci_cluster_size = (mag_mult)^2*ci_cluster_size;  


ci_cluster_separation = mag_mult*ci_cluster_separation;

% 9) Output

if cluster ~= 0
    [t1,t2,t3] = size(cluster_info);
    cluster_output_temp = cluster_info(cluster,:,:);
    cluster_output = reshape(cluster_output_temp,t2,t3);
else
    cluster_output = 0;
end

% param1 = '4/14/15, 1to7 I7643'; % INPUT
% param2 = 'Sq. 1.0Hz, 0to82G, 10min'; % INPUT
x = round(0.60*n2);
y = round(0.02*m2);
mod_bw_output = mod_bw;

for i = x:n2
    for j = 1:round(0.45*m2)
        mod_bw_output(i,j) = 1;
    end
end

text1 = sprintf('Sample Info:
\n%ix Mag.',param1,param2,mag);
text2 = sprintf('Patterns: %0.2e/um^2',act_number_norm);
text3 = sprintf('Average:');
text4 = sprintf('%0.1f (skew = %0.1f) (CI [%0.1f %0.1f])',avg_cluster_size,skewness_cluster_size,ci_cluster_size(1),ci_cluster_size(2));
text5 = sprintf('%0.1f (skew = %0.1f) (CI [%0.1f %0.1f])',avg_cluster_length,skewness_cluster_length,ci_cluster_length(1),ci_cluster_length(2));
text6 = sprintf('%0.1f (skew = %0.1f) (CI [%0.1f %0.1f])',avg_cluster_width,skewness_cluster_width,ci_cluster_width(1),ci_cluster_width(2));
text7 = sprintf('%0.1f (skew = %0.1f) (CI [%0.1f %0.1f])',avg_cluster_separation,skewness_cluster_separation,ci_cluster_separation(1),ci_cluster_separation(2));
text8 = sprintf('Angle (rad) = %2.2d',avg_cluster_angle);
text9 = sprintf('%0.2f, eta = %0.2f, thr_err = %0.2f',center,eta,thr_err);
text10 = sprintf('num_x = %i, num_y = %i',num_x,num_y);
text11 = sprintf('mean_set = %i',mean_set);
text = strcat(text1,text2,text3,text4,text5,text6,text7,text8,text9,text10,text11);
H = vision.TextInserter(text);
H.Color = [0, 0, 0];
H.Location = [y x];
H.FontSize = round((center-0.6)*70+25);
mod_bw_output = step(H,mod_bw_output);

if dis == 1
    figure('Name','Output Magnetized Black & White Image')
imshow(mod_bw_output,'Border','tight','InitialMagnification',50)
end

if dis == 1
    figure('Name','Distribution of Cluster Size')
    histogram(cluster_size)
    xlabel('Cluster Size (um^2)')
    ylabel('Frequency')

    figure('Name','Distribution of Cluster Length')
    histogram(cluster_length)
    xlabel('Cluster Length (um)')
    ylabel('Frequency')

    figure('Name','Distribution of Cluster Width')
    histogram(cluster_width)
    xlabel('Cluster Width (um)')
    ylabel('Frequency')

    figure('Name','Distribution of Cluster Separation')
    histogram(cluster_separation)
    xlabel('Cluster Separation (um)')
    ylabel('Frequency')
end
Appendix B

Confidence Interval of the Characteristic Dimensions

B.1 Histograms

The optical microscope images collected in Chapter 5 after 15 minutes of field application were processed using a Matlab code as detailed in Section 5.1.2 and Appendix A. For each image, or condition, a histogram was generated for each characteristic dimension. Example histograms are shown in Figure B.1 though Figure B.3. Based upon these histograms, a 95% confidence interval was established based upon the mean characteristic dimension. Here, the confidence interval was estimated using bootstrapping [275] via the Matlab function bootci.

Figure B.1: A) Optical microscope image of SPION assembly after 15 minutes of field application for a volume fraction of 0.04% and a field condition of ±100 G, 0.1 Hz square waveform. Corresponding histograms for the characteristic dimensions: B) length, C) separation, and D) width.
Figure B.2: A) Optical microscope image of SPION assembly after 15 minutes of field application for a volume fraction of 0.06% and a field condition of 100 G DC. Corresponding histograms for the characteristic dimensions: B) length, C) separation, and D) width.
Figure B.3: A) Optical microscope image of SPION assembly after 15 minutes of field application for a volume fraction of 0.08% and a field condition of ±50 G, 1.0 Hz square waveform. Corresponding histograms for the characteristic dimensions: B) length, C) separation, and D) width.
Appendix C

Optical Images of PNCs with Wet-Processed Nanoparticles at the Edge Location

C.1 Optical Images

The PNC samples with wet-processed nanoparticles were optically inspected at the edge location to verify uniformity of the nanoparticle structures. Similar to that discussed in Section 6.3.2, the samples with wet-processed nanoparticles at the edge location were polished to 0.05 µm to enable observation with an optical microscope. First, as shown in Figure C.1, a uniform distribution of the nanoparticle structures was observed in the axial direction at the bottom, middle, and top of the PNC samples (edge location) for bulk volume fractions of 2.0% and 3.0%. Thus, the smaller aggregate size of the wet-processed nanoparticles, along with the uniform field generated by the Helmholtz coil, produced a homogenous nanoparticle dispersion. Second, the wet-processed nanoparticle structures were observed to be smaller at the edge location, as compared to the center location, as shown in Figure C.2. Since the magnetic field generated by the Helmholtz coil was verified to be uniform with a gaussmeter, the size differences between the nanoparticle structures at the edge and center location may be due to nonuniform heating of the mold. The mold was heated using a heat pad applied to the bottom surface of the mold. Due to this, it is hypothesized that a thermal gradient was present within the polymer during cure, leading to variations in the viscosity and therefore larger nanoparticle structures at the sample center location due to a higher viscosity. In the future, uniform heating of the polymer during cure can be achieved by placing the sample, along with the coils, within an oven.
Figure C.1: Optical microscope images of the PNC samples with wet-processed nanoparticles (edge location, axial direction) with varying volume fractions at a DC field (300 G). The inspection regions (bottom, middle, and top of the sample) are indicated. The nanoparticle assemblies are the lighter regions in the images.
Figure C.2: Optical microscope images of the PNC samples with wet-processed nanoparticles (center and edge location, axial direction) with varying volume fractions and DC field (300 G). The nanoparticle assemblies are the lighter regions in the images.
Appendix D

Current/Voltage Measurements of PNCs

D.1 GADD Script Files

Steady-state measurement:

```
set parameter=HP4140, dcsource=HP4140, amp=EXTERNAL_TREK1010BHS
sweep dc, start=100, stop=300, step=100, yaxis
    sweep time, start=0, stop=60, step=1, xaxis
    measure pa, plot
endsweep
endsweep
```

Current/voltage measurement per ASTM D257:

```
set parameter=HP4140, dcsource=HP4140, amp=EXTERNAL_TREK1010BHS
sweep dc, start=25, stop=500, step=25, xaxis
    wait s=5
    measure pa, plot
endsweep
sweep dc, start=500, stop=500, step=0, xaxis
    wait s=60
    measure pa1, plot
endsweep
```

D.2 Current/Voltage Plots

D.2.1 Data scattering

The current-voltage plots were observed to have more data scattering with the samples of high resistivity due to limitation of the pA meter resolution (approximately $10^{13}$ A). The current-voltage plots of the two samples of unmodified matrix, which is expected to have the largest resistivities, are shown in Figure D.1A. Due to their large band gap, both of the unmodified matrix samples demonstrated low current values (approximately $10^{13}$ A) over the voltage range. In addition, due to the currents being near the resolution of the pA meter, a large variation in the trends were observed due to system noise. Data scattering of current-voltage plots was also observed with some PNC samples where continuous nanoparticle networks were not present. As shown in Figure
D.2, PNCs with randomly-oriented maghemite nanoparticles exhibited data scattering, even with their relatively high-volume fraction of approximately 3.1 vol%. Even when the maghemite nanoparticles were magnetically aligned, the PNC samples with dry-processed nanoparticles extracted from the center location (axial direction, see Figure D.3A and C) exhibited similar data scattering. As evaluated in Section 6.3, the nanofiller network at the center location is different from that at the edge location, due to the field inhomogeneity. It should be noted that that PNCs assembled with the sinusoidal magnetic fields reduced data scattering at smaller nanofiller volume fraction (percolation). The current-voltage plot of a PNC sample assembled using the DC magnetic field (DC, axial, edge location, 0.4 vol%) exhibited data scattering, while a PC sample assembled using the sinusoidal field with a similar condition (sinusoidal, axial, edge location, 0.4 vol%, see Figure D.3D) exhibited minimum data scattering. In other words, a higher volume fraction was necessary in order to achieve a continuous nanoparticle pathway when assembled using a DC magnetic field. As discussed in Chapter 5 and 6, a sinusoidal magnetic field enhances transverse assembly and thus is effective in increasing the nanofiller assembly length; such trend was also confirmed with the microCT observation (see Section 6.3).

Above, discussion was focused on the measurements for PNC samples with dry-processed nanoparticles in the axial direction. Here, current-voltage characteristics in the transverse direction are discussed, and also of PNC samples with wet-processed nanoparticles. Data scattering was observed in the transverse direction until a higher volume fraction when compared to that observed in the axial direction: 2.6 vol% for DC field and 3.2 vol% for sinusoidal field. Unlike the PNC samples with dry-processed nanoparticles, the PNC samples with wet-processed nanoparticles always exhibited data scattering, even with a high-volume fraction (see Figure D.4). As inspected in Section 6.3, improved homogenous dispersion and structuring can produce a larger gap between maghemite assemblies that block charge carrier tunneling.

D.2.2 Non-linear trend

Once continuous nanofiller networks are formed, the current-voltage plots exhibit nonlinear trends (see Figure D.1B, D.3B and D.3D). A nonlinear, or non-ohmic, current-voltage response can be attributed to the intrinsic nature of semiconductors [276]. Ignoring the effects of temperature (as these tests were conducted at room temperature), charge carriers in semiconducting materials (either electrons or electron holes) will drift due to application of an electrical field, or external voltage. Within PNCs or pure maghemite, few of these charge carriers are available for transport as the band gap of maghemite is estimated to be approximately 2 eV [220,277] leading to
a high resistance. In addition, scattering of the charge carriers due to impurities, such as voids, boundaries, etc, and lattice vibrations [278,279] will also increase the resistance. When two conducting or semiconducting nanoparticles are in close proximity, but not physically contacting due to a thin insulating layer or interphase (less than 2 nm thick [280]), charge carrier tunneling [281] will occur due to a quantum confinement effect [282]; this effect dominates semiconductors and their composites, producing a complex electrical transport phenomenon [283] and nonlinear current-voltage behavior [276]. In semiconductors, the nonlinear current ($i$) – voltage ($V$) behavior is typically represented by a power law [284]: $i = V_0 V_i^{n_i}$, where $V_0$ is correlated to the grain structure of the material and $n_i$ is an independent parameter. As the nanofiller volume fraction approaches percolation, the nonlinear exponent will decrease as charge carrier tunneling becomes less favorable than drift through conductive nanoparticle contacts, although tunneling will still be the dominant mechanism. The power law exponent value for the 1D-assembled PNC sample at 0.5 vol% (sinusoidal field, axial, edge location) in Figure D.3D is 3.60, the 1D-assembled PNC sample at 1.3 vol% (DC field, axial, edge location) in Figure D.3B is 3.21, the 1D-assembled PNC samples at 3.5 vol% (DC and sinusoidal field, axial, edge location) is approximately 2.7, and finally the pure maghemite sample at 56.4% relative density in Figure D.1B is 1.54.
Figure D.1: Current-voltage trends of A) two unmodified matrix samples and B) one pure (cold-sintered) maghemite sample.

Figure D.2: Current-voltage trends for a PNC sample with randomly orientated (no magnetic field) nanofiller.
Figure D.3: Current-voltage trends for selected dry-processed PNCs. A) DC, axial, center location at 1.4 vol%, B) DC, axial, edge location at 1.3 vol%, C) sinusoidal, axial, center location at 1.3 vol%, and D) sinusoidal, axial, edge location at 0.5 vol%. Onset of the nonlinear current-voltage trends are shown in B) and D) for a DC and sinusoidal waveform, respectively. Corresponding microCT tomograms are also indicated in the figure (approximately 5 mm x 5 mm).
Figure D.4: Current-voltage trends for selected wet-processed PNCs. A) DC, axial, center location at 1.5 vol%, B) DC, axial, center location at 1.9 vol%, C) DC, axial, center location at 4.0 vol%, and D) sinusoidal, axial, center location at 3.6 vol%.
Appendix E

Local (Surface) Mechanical Properties

E.1 Measurement Method and Set-up

Stiffness and hardness data of the PNCs were measured using nanoindentation [285]. The experiments were performed at the Materials Characterization Lab at Pennsylvania State Universities’ Material Research Institute. The experimental set-up is depicted in Figure E.1. A separate sample set from the ones used for electrical and thermal conductivity measurement was prepared (10 mm x 10 mm x 1 mm); the sample conditions, including the corresponding volume fractions, are listed in Table E.1. These samples were embedded in an epoxy matrix and polished to a surface roughness of 0.04 µm (see Figure E.1B). The backside of the epoxy was polished using 240 grit sandpaper until a level surface was obtained so that the sample could be laid level. The front side of the sample, where nanoindentation was conducted, was polished using an automatic polishing machine (Allied High-Tech Products, Multiprep) at 150 RPM and 13.3 N: 600 grit silicon carbide sandpaper for 2 minutes, 1200 grit silicon carbide sandpaper for 2 minutes, 3 µm polycrystalline diamond suspension for 5 minutes, 1 µm polycrystalline diamond suspension for 5 minutes, and 0.04 µm colloidal silica suspension for 5 minutes. The embedded PNC samples were then placed within an automated nanoindentation machine (Hysitron, TI 980). The microscope, as shown in Figure E.1A, was used to locate and focus on the sample surfaces. A geometry was defined around each sample and several quick approaches of the indentation tip (Berkovich, approximately 7 µm) to the sample surface were conducted to establish a safe working distance for the indenter tip. Indentations of 9000 µN were conducted over a 3x3 grid (50 µm apart from each other) and this indentation grid was repeated at multiple locations (top, middle, and bottom) on the sample surface to capture the nanostructure inhomogeneity of the sample (see Figure E.2). Load-displacement curves of each test were recorded.
The reduced elastic modulus and hardness were automatically calculated from the load-displacement curves by the nanoindentation machine software using the Oliver and Pharr method [286]. The reduced elastic modulus \(E_r\) is correlated to the indentation load \(P\) and depth \(h\) through Equation E.1, where \(A_p\) is the projected area of the elastic contact based upon the indenter tip. The hardness of the PNC samples \(H_p\) was determined from the maximum indentation load \(P_{\text{max}}\) as shown in Equation E.2. An example load-displacement curve is shown in Figure E.3 for

<table>
<thead>
<tr>
<th>vf (%)</th>
<th>Waveform</th>
<th>Direction</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5</td>
<td>DC</td>
<td>Transverse</td>
<td>Center</td>
</tr>
<tr>
<td>3.5</td>
<td>DC</td>
<td>Axial</td>
<td></td>
</tr>
<tr>
<td>3.3</td>
<td>Sine</td>
<td>Transverse</td>
<td></td>
</tr>
<tr>
<td>3.3</td>
<td>Sine</td>
<td>Axial</td>
<td></td>
</tr>
<tr>
<td>4.0</td>
<td>None</td>
<td>(Randomly Orientated)</td>
<td></td>
</tr>
</tbody>
</table>
a PNC sample with wet-processed nanoparticles (DC, axial, 1.9 vol%, center location). At each indentation location (top, middle, bottom), the mean and standard deviation of the reduced elastic modulus and hardness was calculated based upon the nine indentations (3x3 grid).

\[
\frac{dp}{dh} = \frac{2}{\sqrt{\pi}} E_r \sqrt{A_p}
\]

(E.1)

\[
H_p = \frac{P_{\text{max}}}{A_p}
\]

(E.2)

**Figure E.2:** Nanoindentation grid locations on a sample cross-section: A) schematic showing nanoindentation locations at the top, middle, and bottom, and B) SEM image of an exemplary 9x9 indentation grid.

**Figure E.3:** Example load-displacement curve measured about a PNC sample with wet-processed nanoparticles (DC, axial, 1.9 vol%, center location).
E.2 Reduced Elastic Modulus and Hardness

The measured reduced elastic modulus ($E_{PNC}$) and hardness ($H_{PNC}$) values are summarized in Table E.2, and in Figures E.4 and E.5. Nanoindentation is sensitive to the elastic contact area ($A_p$) and properties of the indenter head (diamond, 1100 GPa elastic modulus, and 0.07 Poisson’s ratio). Comparison of the measured unmodified matrix elastic modulus ($E_m$) and hardness ($H_m$) values to literature are important to verify the measurement methodology. Here, a reduced elastic modulus of 3.62 GPa was measured for the unmodified matrix. Assuming a Poisson ratio of 0.35 for the unmodified matrix [287], the elastic modulus of the unmodified matrix is calculated [286] to be 3.19 GPa. This value is comparable to previous work which demonstrated an elastic modulus of EPON 862 and an Epikure W cross-linker as approximately 2.8 GPa using tensile testing [288]. The hardness of the unmodified matrix was measured as 242 MPa, which is in good agreement with tests conducted in literature using nanoindentation (255 MPa [289]).

The reduced modulus data of PNCs consisting of dry-processed nanoparticles (see Figure E.4) indicate that the nanoparticle volume fraction is dominant in improving the reduced elastic modulus. The reduced modulus values are consistently larger at the bottom location, where local nanoparticle volume fractions are higher; the modulus value changes were negligible at the top and middle locations where local nanoparticle volume fractions are low. Similarly, the PNCs assembled with a sinusoidal field exhibited larger modulus improvement at the bottom locations than those assembled with static fields at the bottom locations. Again, this trend can be attributed to the higher local nanoparticle volume fraction; the nanoparticle assemblies produced increased sedimentation (see Figure 6.23) with a sinusoidal field due to enhanced transverse assembly. In addition, PNCs with dry-processed and randomly oriented nanoparticles also exhibited the largest modulus at the bottom location due to sedimentation; while surface modification reduced sedimentation by approximately 60% (see Figure 6.10), without milling (such as for wet-processed nanoparticles) sedimentation was still observed. No significant differences were observed about modulus data in the axial vs. transverse directions. Meanwhile, the reduced modulus data for PNCs consisting of wet-processed nanoparticles (see Figure E.5) were comparable regardless of the measurement locations (top, middle, or bottom), indicating a homogeneous nanoparticle distribution. The trends of hardness followed those observed with the reduced modulus.

The elastic modulus of the unmodified matrix is expected to improve with nanoparticle addition due to the larger stiffness of the nanoparticles and also due to the interface strength between the nanoparticles and matrix. The addition of nanoparticles to the matrix is also expected
to enhance the hardness of the samples as the nanoparticles themselves act as barriers to dislocation motion. For effective stress transfer between the nanoparticles and the matrix, strong interfacial bonding is essential, and thus surface modification of the nanoparticle surfaces has the added benefit (in addition to sedimentation reduction) of improving this interfacial bonding. Meanwhile, mechanical reinforcement with 0D nanoparticles is not as effective as other 1D/2D nanoparticles with high aspect ratio (random [290] and assembled CNTs [291]).

Table E.2: Elastic modulus and hardness averaged over the 3x3 indentations. The error indicated is represented by the standard deviation of the 9 measurements.

<table>
<thead>
<tr>
<th>Process</th>
<th>vf (%)</th>
<th>Field</th>
<th>Direction</th>
<th>Test Location</th>
<th>$E_r$ (GPa)</th>
<th>%</th>
<th>$H_p$ (MPa)</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry</td>
<td>3.5</td>
<td>DC</td>
<td>Transverse</td>
<td>Top</td>
<td>3.83 ± 0.06</td>
<td>5.8</td>
<td>270 ± 6.9</td>
<td>11.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Middle</td>
<td>4.30 ± 0.9</td>
<td>18.9</td>
<td>300 ± 68.9</td>
<td>24.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Bottom</td>
<td>5.85 ± 1.8</td>
<td>61.5</td>
<td>349 ± 105</td>
<td>44.4</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>DC</td>
<td>Axial</td>
<td>Top</td>
<td>3.94 ± 0.03</td>
<td>8.9</td>
<td>273 ± 2.1</td>
<td>12.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Middle</td>
<td>3.80 ± 0.06</td>
<td>5.1</td>
<td>273 ± 3.4</td>
<td>12.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Bottom</td>
<td>7.78 ± 2.6</td>
<td>115.0</td>
<td>470 ± 168</td>
<td>94.2</td>
</tr>
<tr>
<td></td>
<td>3.3</td>
<td>Sine</td>
<td>Transverse</td>
<td>Top</td>
<td>3.97 ± 0.01</td>
<td>9.7</td>
<td>274 ± 1.0</td>
<td>13.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Middle</td>
<td>3.87 ± 0.02</td>
<td>7.0</td>
<td>271 ± 1.2</td>
<td>12.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Bottom</td>
<td>7.61 ± 3.9</td>
<td>110.3</td>
<td>527 ± 273</td>
<td>117.6</td>
</tr>
<tr>
<td></td>
<td>3.3</td>
<td>Sine</td>
<td>Axial</td>
<td>Top</td>
<td>3.86 ± 0.03</td>
<td>6.7</td>
<td>274 ± 2.9</td>
<td>13.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Middle</td>
<td>3.84 ± 0.01</td>
<td>6.0</td>
<td>274 ± 1.0</td>
<td>13.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Bottom</td>
<td>8.32 ± 4.3</td>
<td>129.9</td>
<td>504 ± 281</td>
<td>108.2</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td></td>
<td>Randomly orientated</td>
<td>Top</td>
<td>4.16 ± 0.11</td>
<td>14.9</td>
<td>278 ± 7.1</td>
<td>14.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Middle</td>
<td>5.13 ± 2.0</td>
<td>41.8</td>
<td>360 ± 227</td>
<td>48.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Bottom</td>
<td>9.51 ± 3.9</td>
<td>162.7</td>
<td>582 ± 323</td>
<td>140.3</td>
</tr>
<tr>
<td>Wet</td>
<td>1.9</td>
<td>DC</td>
<td>Transverse</td>
<td>Top</td>
<td>4.05 ± 0.09</td>
<td>11.9</td>
<td>271 ± 6.4</td>
<td>11.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Middle</td>
<td>4.31 ± 0.9</td>
<td>19.2</td>
<td>296 ± 91.7</td>
<td>22.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Bottom</td>
<td>4.07 ± 0.09</td>
<td>12.4</td>
<td>269 ± 11.8</td>
<td>11.1</td>
</tr>
<tr>
<td></td>
<td>1.9</td>
<td>DC</td>
<td>Axial</td>
<td>Top</td>
<td>4.06 ± 0.2</td>
<td>12.1</td>
<td>261 ± 7.5</td>
<td>7.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Middle</td>
<td>3.92 ± 0.09</td>
<td>8.4</td>
<td>267 ± 5.5</td>
<td>10.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Bottom</td>
<td>3.97 ± 0.2</td>
<td>9.7</td>
<td>275 ± 9.2</td>
<td>13.5</td>
</tr>
<tr>
<td></td>
<td>1.9</td>
<td>Sine</td>
<td>Transverse</td>
<td>Top</td>
<td>4.14 ± 0.03</td>
<td>14.3</td>
<td>270 ± 4.1</td>
<td>11.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Middle</td>
<td>4.09 ± 0.1</td>
<td>12.9</td>
<td>269 ± 5.4</td>
<td>11.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Bottom</td>
<td>4.06 ± 0.2</td>
<td>12.1</td>
<td>264 ± 14.9</td>
<td>9.3</td>
</tr>
<tr>
<td></td>
<td>1.7</td>
<td>Sine</td>
<td>Axial</td>
<td>Top</td>
<td>4.05 ± 0.04</td>
<td>11.9</td>
<td>272 ± 2.9</td>
<td>12.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Middle</td>
<td>4.22 ± 0.7</td>
<td>16.6</td>
<td>292 ± 72</td>
<td>20.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Bottom</td>
<td>3.99 ± 0.1</td>
<td>10.3</td>
<td>266 ± 7.7</td>
<td>9.9</td>
</tr>
</tbody>
</table>
Figure E.4: Measured reduced elastic modulus for A) dry- and B) wet-processed PNC samples. The standard deviation is indicated.
Figure E.5: Measured hardness for A) dry- and B) wet-processed PNC samples. The standard deviation is indicated.
Bibliography

[16] Ruschau, Yoshikawa, Newnham, Resistivities of conductive composites, J. Appl. Phys. 3


[32] Vaia, Maguire, Polymer nanocomposites with prescribed morphology: Going beyond


[148] Périgo, Hemery, Sandre, Ortega, Garaio, Plazaola, Teran, Fundamentals and advances in


[181] Liu, Shaw, Jiang, Bloemendal, Hesse, Rolph, Mao, Analysis on variety and characteristics


Gelest, Gelest Silane Coupling Agents, n.d.


Pecharromán, Gonzalez-Carreno, T., Iglesias, The Infrared Dielectric Properties of


[239] Fu, Ding, Ren, Li, Wu, Yang, Preparation of magnetic porous NiFe2O4/SiO2 composite xerogels for potential application in adsorption of Ce(iv) ions from aqueous solution, RSC Adv. 27 (2017) 16513–16523.


Dai, Mechanical Properties and Deformation Behaviors of Nanoporous Anodic Aluminum Oxide Membrane, Pennslyvania State University, 2017.


Tack, Thermodynamic and mechanical properties of EPON 862 with curing agent DETDA by molecular simulation, Texas A&M University, 2006.


VITA

Mychal Spencer

Education


Master of Science in Mechanical Engineering at Purdue University, August 2007. Thesis title: "Indirect determination of the strain and stress in physical models of the vocal folds using digital image correlation."

Bachelor of Science in Mechanical Engineering at Washington State University, August 2005.

Research and Professional Experience

Graduate Research Assistant, Department of Aerospace Engineering, Penn. State University.

Lead Engineer, General Electric.

Recent Publications


