MUILTI-FUNCTIONAL PAN-BASED COMPOSITE FIBERS

A Dissertation
Presented to
The Academic Faculty

by

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In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy in the
School of Materials Science and Engineering

Georgia Institute of Technology
December 2014

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MULTI-FUNCTIONAL PAN-BASED COMPOSITE FIBERS

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Date Approved: November 14, 2014
To My Family
ACKNOWLEDGEMENTS

I would like to express my deepest appreciation to my advisor Professor Kumar. The completion of my thesis would not have been possible without his encouragement and guidance. I would like to extend my sincere thanks to Professor Anselm Griffin, Professor Donggang Yao, Professor Chuck Zhang, and Dr. Han Gi Chae for spending their time serving on my thesis committee and providing their critical opinions and suggestions.

I would like to thank Professor G. P. Bud Peterson, Dr. Bo Feng, Mr. Aniruddha Joshi, and Mr. Jaeyun Moon for substantial and invaluable discussion on the study of thermal conductivity. I want to acknowledge Professor Yogendra K. Joshi and Mr. Sangbeom Cho for sharing the infrared camera for their heating study. I am also thankful to Professor Z. John Zhang, Dr. Daniel Sabo, and Ms. J. Robbins for their help with magnetic property measurement and decisive opinions on magnetic fibers. I am grateful to Professor James M. Tour and Dr. Changsheng Xiang for providing GONR samples and experimental suggestions for GONR reinforced composite fibers.

Special thanks to Dr. Prabhakar V. Gulgunje for his meticulous help and substantial knowledge of fiber spinning technology during the initial experiments of bi-component fibers. I am thankful to Dr. Young Ho Choi, Dr. Yaodong Liu, and Dr. Ericka J. Ford for providing training and personal instructions for various equipment and experimental methods. In addition, I am thankful to Mr. Bradley A. Newcomb for the TEM work and for valuable discussions on my research. I would also like to recognize the effort that I received from Mr. Clive Liu for the study of carbon fibers.
I would like to express my gratitude to my group members including, Dr. Kishor Gupta, Dr. M.G. Kamath, Dr. Ashok Singh, Dr. Sushanta Ghoshal, Dr. Chandrani Pramanik, Mr. Amir Davijani, Mr. Huibin Chang, and Mr. Po-Hsiang Wang, who always provided assistance to overcome challenges in the laboratory. I am also thankful to previous group members including, Dr. Marilyn Minus, Dr. Xiangyang Hao, Dr. Hongming Dong, Dr. Vijay Raghavan, Mr. Kevin Lyons, Mr. Dawei Gao, and Mr. Ken McDonald, who supported me considerably during this study.

I am grateful to the National Textile Center and the Air Force Office of Scientific Research for funding this study.

Finally, thanks to my great parents and my lovely wife, Jewel (Yen-Chu). Only their endless support and abundant love can encourage me to complete my dream.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>iv</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>x</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xiii</td>
</tr>
<tr>
<td>SUMMARY</td>
<td>xx</td>
</tr>
<tr>
<td><strong>CHAPTER</strong></td>
<td></td>
</tr>
<tr>
<td><strong>1 INTRODUCTION</strong></td>
<td>1</td>
</tr>
<tr>
<td>1.1 Overview</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Carbon Nanotubes</td>
<td>2</td>
</tr>
<tr>
<td>1.2.1 Properties of Carbon Nanotubes</td>
<td>2</td>
</tr>
<tr>
<td>1.2.2 Polymer/Carbon Nanotube Nanocomposites</td>
<td>4</td>
</tr>
<tr>
<td>1.3 Iron Oxide Nanoparticles</td>
<td>7</td>
</tr>
<tr>
<td>1.3.1 Properties of Iron Oxide Nanoparticles</td>
<td>7</td>
</tr>
<tr>
<td>1.3.2 Iron Oxide/Polymer Nanocomposites</td>
<td>11</td>
</tr>
<tr>
<td>1.4 Graphene Nanoribbons</td>
<td>13</td>
</tr>
<tr>
<td>1.4.1 Properties of Graphene Nanoribbon</td>
<td>13</td>
</tr>
<tr>
<td>1.4.2 Fabrication of GNR by Un-zipping Carbon Nanotube</td>
<td>14</td>
</tr>
<tr>
<td>1.4.3 Polymer/GNR and Polymer/GONR Nanocomposites</td>
<td>15</td>
</tr>
<tr>
<td>1.5 Functional Fibers</td>
<td>17</td>
</tr>
<tr>
<td>1.5.1 Smart Fibers</td>
<td>17</td>
</tr>
<tr>
<td>1.5.2 Heating Fibers</td>
<td>18</td>
</tr>
<tr>
<td>1.5.3 Magnetic Fibers</td>
<td>19</td>
</tr>
<tr>
<td>1.6 Polyacrylonitrile (PAN) Fibers</td>
<td>20</td>
</tr>
</tbody>
</table>
1.7 Bi-component Fibers 21
1.8 Objectives 22
1.9 References 23

2 FUNCTIONAL POLYMER - POLYMER/CARBON NANOTUBE BI-COMPONENT FIBERS 48

2.1 Introduction 48

2.2 Experimental Procedure 49

2.2.1 PAN/MWNT Composite Solution 49
2.2.2 Gel Spinning PAN – PAN/MWNT Bi-component Fibers 51
2.2.3 Characterization 52

2.3 Results and Discussion 54

2.3.1 Processing of PAN and PAN/MWNT Bi-component fibers 54
2.3.2 Morphology of PAN and PAN/MWNT Bi-component fibers 55
2.3.3 Mechanical Properties 61
2.3.4 Electrical Conductivity 63
2.3.5 Effect of Annealing Process on Structure and Mechanical Properties 65
2.3.6 Thermal Conductivity 68

2.4 Conclusions 71

2.5 References 72

3 ELECTRICAL CONDUCTIVITY AND JOULE HEATING OF PAN/CNT COMPOSITE FIBERS 75

3.1 Introduction 75

3.2 Experimental Procedure 76

3.3 Results and Discussion 79

3.3.1 Effect of Annealing Process 79
3.3.2 Effect of Stretching 82
3.3.3 Effect of Joule Heating 83
3.3.4 Estimation of Thermal Conductivity 91
3.3.5 Estimation of Joule Heating Effect 93
3.3.6 Measurement of Joule Heating Effect by IR camera 96
3.3.7 Influence of Fiber Length on Joule Heating Effect 100
3.4 Conclusions 103
3.5 References 104

4  HIGH STRENGTH SUPERPARAMAGNETIC COMPOSITE FIBERS 111

4.1 Introduction 111
4.2 Experimental Procedures 114
  4.2.1 Fe$_3$O$_4$/PAN Composite Solution 114
  4.2.2 Gel-Spinning of Fe$_3$O$_4$/PAN Composite Solution 114
  4.2.3 Characterization 116
4.3 Results and Discussion 117
  4.3.1 Morphology of Fe$_3$O$_4$/PAN Magnetic Fibers 117
  4.3.2 Structure of Fe$_3$O$_4$/PAN Magnetic Fibers by WAXD 120
  4.3.3 Mechanical Properties of Fe$_3$O$_4$/PAN Magnetic Fibers 124
  4.3.4 Morphology of Magnetic Fe$_3$O$_4$/PAN (10/90) Core and PAN Sheath Bi-component Fibers 127
  4.3.5 Structure and Mechanical Properties of Magnetic Fe$_3$O$_4$/PAN (10/90) Core and PAN Sheath Bi-component Fibers 129
  4.3.6 TGA Test of Fe$_3$O$_4$/PAN Magnetic Fibers 131
  4.3.7 Magnetic Properties of Fe$_3$O$_4$/PAN Magnetic Fibers 135
4.4 Conclusions 140
4.5 References 141
5 GRAPHENE OXIDE NANORIBBON REINFORCED PAN-BASED COMPOSITE FIBERS

5.1 Introduction 144

5.2 Experimental Procedure 145
  5.2.1 PAN/GONR Composite Solution 145
  5.2.2 Gel Spinning PAN/GONR Composite Fibers 146
  5.2.3 Stabilization and Carbonization of Composite Fibers 147
  5.2.4 Characterization 147

5.3 Results and Discussion 149
  5.3.1 Dispersion of GONR 149
  5.3.2 Morphology of Gel-Spun PAN/GONR Composite Fibers 151
  5.3.3 Dissolution of PAN/GONR Composite Fibers 154
  5.3.4 Structure of PAN/GONR Composite Fibers 158
  5.3.5 Mechanical Properties of PAN/GONR Composite Fibers 161
  5.3.6 PAN/GONR Composite Carbon Fibers 165

5.4 Conclusions 170

2.5 References 171

6 CONCLUSIONS AND RECOMMENDATIONS 176

6.1 Conclusions 176

6.2 Recommendations for Future Study 178

APPENDIX A: DISSOLUTION OF PAN CORE AND PAN/CNT SHEATH BI-COMPONENT FIBERS 182

APPENDIX B: ESTIMATION OF TEMPERATURE PROFILE OF COMPOSITE FIBERS AS A RESULT OF JOULE HEATING 187

APPENDIX C: PMMA CORE AND PAN/CNT SHEATH BI-COMPONENT FIBERS 192
LIST OF TABLES

Table 1.1: Properties of Carbon Nanotubes 4
Table 1.2: Properties of Graphene and Graphene Nanoribbon 14
Table 2.1: Processing parameters of PAN/MWNT (90/10) core and PAN sheath bi-component fibers. 49
Table 2.2: Processing parameters of PAN core and PAN/MWNT (90/10) sheath bi-component fibers. 50
Table 2.3: Processing parameters of PAN/MWNT (90/20) core and PAN sheath bi-component fibers. 50
Table 2.4: Processing parameters of PAN core and PAN/MWNT (90/20) sheath bi-component fibers. 51
Table 2.5: Structure and properties of PAN/MWNT (90/10) core and PAN sheath bi-component fibers before annealing. 61
Table 2.6: Structure and properties of PAN core and PAN/MWNT (90/10) sheath bi-component fibers before annealing. 62
Table 2.7: Structure and properties of PAN/MWNT (90/20) core and PAN sheath bi-component fibers before annealing. 62
Table 2.8: Structure and properties of PAN core and PAN/MWNT (90/20) sheath bi-component fibers before annealing. 63
Table 2.9: Electrical conductivity of selected PAN core and PAN/MWNT (90/10) sheath Bi-component fibers before and after annealing. 64
Table 2.10: Structure and properties of selected PAN/MWNT (90/10) core and PAN sheath bi-component fibers after annealing. 67
Table 2.11: Structure and properties of selected PAN core and PAN/MWNT (90/10) sheath bi-component fibers after annealing. 67
Table 3.1: Listing of compositions, draw ratios, diameters, and linear density for the fibers investigated in this study. 77
Table 3.2: Electrical conductivities of PAN/CNT composite fibers with various annealing temperatures. 79
Table 3.3: Structural parameters of PAN/CNT composite fibers with 20 wt% MWNT before and after annealing at 180 °C for 2 hours. 82

Table 3.4: Structural parameters of PAN polymer crystal of composite fibers with 20 wt% CNT content at different applied current. 88

Table 3.5: Structural parameters of stabilized composite fibers at different applied currents. 91

Table 3.6: Summary of electrical conductivity and maximal temperature difference of composite fibers with 20 wt% CNT content with various input currents and voltages. 98

Table 4.1: Summary of recent research on electro-spun Fe₃O₄/PAN composite fibers. 113

Table 4.2: Processing parameters of Fe₃O₄/PAN composite fibers and control PAN fibers. 115

Table 4.3: Processing parameters of Fe₃O₄/PAN (10/90) core and PAN sheath bi-component fibers. 115

Table 4.4: Structural parameters of Fe₃O₄/PAN composite and control PAN fibers. 123

Table 4.5: Properties of Fe₃O₄/PAN composite and control PAN fibers. 125

Table 4.6: Structural parameters of Fe₃O₄/PAN (10/90) core and PAN sheath bi-component fibers. 130

Table 4.7: Mechanical properties of Fe₃O₄/PAN (10/90) core and PAN sheath bi-component fibers. 131

Table 5.1: Processing parameters of PAN/GONR fibers and PAN fibers. 146

Table 5.2: Structural parameters of PAN/GONR composite and control PAN fibers. 160

Table 5.3: Mechanical Properties of PAN/GONR composite and control PAN fibers. 162

Table 5.4: Dynamic mechanical analysis results of PAN/GONR and PAN fibers. 165

Table 5.5: Structural parameters of stabilized and carbonized PAN/GONR and PAN fibers. 168

Table 5.6: Mechanical properties of carbonized PAN/GONR composite fibers. 169

Table 6.1: Possible nanoparticles or polymer candidates for different properties and applications. 181
Table C.1: Processing parameters of PMMA core and PAN/CNT (90/10) sheath bi-component fibers.

Table C.2: Mechanical properties and structural parameters of PMMA core and PAN/MWNT (90/10) sheath bi-component fibers.
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Illustrations of C\textsuperscript{60}, graphene, SWNT, and MWNT.</td>
<td>3</td>
</tr>
<tr>
<td>1.2</td>
<td>Toughening mechanism of polymer/CNT composites</td>
<td>5</td>
</tr>
<tr>
<td>1.3</td>
<td>Illustrations of (a) percolation concentration and (b) the effect of the</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>alignment of CNTs on intersection probability.</td>
<td></td>
</tr>
<tr>
<td>1.4</td>
<td>Illustration of Fe\textsubscript{3}O\textsubscript{4} inverse spinel crystal</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>structure.</td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>Illustration of ferrimagnetism, paramagnetism, and superparamagnetism.</td>
<td>9</td>
</tr>
<tr>
<td>1.6</td>
<td>Illustration of size effect on coercivity.</td>
<td>10</td>
</tr>
<tr>
<td>1.7</td>
<td>Illustration of different methods for unzipping carbon nanotubes.</td>
<td>15</td>
</tr>
<tr>
<td>1.8</td>
<td>Typical cross sections of bi-component fibers.</td>
<td>21</td>
</tr>
<tr>
<td>2.1</td>
<td>Illustration of DCTBM thermal conductivity measurement system.</td>
<td>53</td>
</tr>
<tr>
<td>2.2</td>
<td>(a) The illustration of sheath-core bi-component fiber with overall fiber</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>radius (r_2) and core radius (r_1). Optical micrographs of PAN sheath</td>
<td></td>
</tr>
<tr>
<td></td>
<td>and PAN/MWNT (with 10 wt% MWNT) core bi-component fibers – (b) sample A1,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>and (c) sample A4. (d) PAN/MWNT (10 wt% MWNT) sheath and PAN core – sample</td>
<td></td>
</tr>
<tr>
<td></td>
<td>A7.</td>
<td></td>
</tr>
<tr>
<td>2.3</td>
<td>Optical micrographs of (a) PAN sheath and PAN/MWNT (with 20 wt% MWNT) core</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>bi-component fibers – sample B1, and (b) PAN/MWNT (20 wt% MWNT) sheath and</td>
<td></td>
</tr>
<tr>
<td>2.4</td>
<td>SEM images and cross-sectional schematics of the PAN and PAN/CNT (with</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td>10 wt% MWNT) bi-component fibers (a) and (b) for sample A3, (c) and (d) for</td>
<td></td>
</tr>
<tr>
<td></td>
<td>sample A6, and (e) and (f) for sample A8.</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>SEM images and cross-sectional schematics of the PAN and PAN/CNT (with</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>20 wt% MWNT) bi-component fibers (a) and (b) for sample B6, (c) and (d) for</td>
<td></td>
</tr>
<tr>
<td></td>
<td>sample B12, and (e) and (f) for sample B18.</td>
<td></td>
</tr>
<tr>
<td>2.6</td>
<td>SEM images of (a) pristine CNTs, (b) fractured section of A8 fiber in sheath</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>component, and (c) the magnification image of denoted region in (b).</td>
<td></td>
</tr>
<tr>
<td>2.7</td>
<td>WAXD diffraction patterns and equatorial intensity plots of (a) sample A7</td>
<td>66</td>
</tr>
<tr>
<td></td>
<td>and (b) sample A8 fibers before and after annealing.</td>
<td></td>
</tr>
</tbody>
</table>
Figure 2.8: Schematics of the PAN/CNT structures for the as-spun and drawn fibers before and after annealing.

Figure 2.9: Thermal conductivity of the (a) as-spun and (b) fully drawn A1, A2, A7, and A8 fibers measured by DCTBM method.

Figure 3.1: Illustration of real time measurement of electrical conductivity and wide angle x-ray diffraction of PAN/CNT fiber.

Figure 3.2: Voltage of PAN/CNT composite fibers with 20 wt% CNT content during annealing process at 180 °C with 10 μA applied current at a constant length of 25.4 mm.

Figure 3.3: Electrical conductivity of PAN/CNT composite fibers with 20 wt% CNT content during the annealing process at 180 °C with 10 μA applied current at a constant length of 25.4 mm.

Figure 3.4: WAXD diffraction patterns and integrated radial scans of PAN/CNT composite fibers with 20 wt% MWNT before and after annealing at 180 °C for 2 hours.

Figure 3.5: Electrical conductivity and tensile stress of PAN/CNT fibers as a function of tensile elongations during stretching test.

Figure 3.6: Electrical conductivity of PAN/CNT fibers under various applied current.

Figure 3.7: Photographs of (a) original and (b) electrically broken down PAN/CNT composite fibers. A bundle of PAN/CNT filaments was used for this experiment.

Figure 3.8: FT-IR spectra of PAN/CNT composite fibers with 20 wt% CNT content (a) before and (b) after Joule heating treatment, (c) stabilized PAN fibers and carbonized PAN fibers with carbonization temperature at (d) 700, (e) 1000, and (f) 1450 °C, respectively.

Figure 3.9: Two dimensional WAXD diffraction patterns of PAN/CNT fibers at various electrical currents.

Figure 3.10: Integrated radial scans of WAXD diffraction patterns of PAN/CNT fibers at various electrical currents.

Figure 3.11: Deconvoluted profile of WAXD integrated radial scans of PAN/CNT fibers at electrical currents of 1.6 mA per filament.

Figure 3.12: Schematic diagram of Joule heating around CNTs.

Figure 3.13: Estimated thermal conductivity of composite fibers with various CNT contents and CNT orientation factors from 0.1 to 0.5.
Figure 3.14: Schematic diagram of the Joule heating phenomenon.

Figure 3.15: Temperature profile of a composite fiber along the fiber length with 20 wt% CNT content at various electrical currents (L = 0.005 m, h = 200 W/m²K, K = 30 W/mK, d = 44 μm, and σ obtained from Figure 3.6).

Figure 3.16: (a) Temperature profile of single composite fiber with 20 wt% CNT content (fiber length L= 5mm) measured by an infra-red camera and (b) temperature distribution along the trace-line from X to Y.

Figure 3.17: Experimental and estimated maximal temperature differences (ΔT_max) at various input electrical current and voltage of composite fibers with 20 wt% CNT content.

Figure 3.18: Voltage of PAN/CNT composite fibers with 20 wt% CNT at different lengths and at various applied currents.

Figure 3.19: Electrical conductivity of PAN/CNT composite fibers with 20 wt% CNT at different lengths and at various applied currents.

Figure 3.20: Maximal Temperature (calculated from heat transfer equation) of PAN/CNT composite fibers with 20 wt% CNT at different lengths and at various applied currents.

Figure 4.1: (a) Spools of Fe₃O₄/PAN composite fibers and (b) a bundle of Fe₃O₄/PAN composite fibers attracted by a magnet bar.

Figure 4.2: (a) SEM images of Fₘ composite fiber and (b) fiber lateral surface under higher magnification.

Figure 4.3: Optical micrographs of cross sections of composite fibers (a) F₀ and (b) Fₘ.

Figure 4.4: SEM images of (a) Fₘ fiber cross section and (b) corresponding SEM image under higher magnification.

Figure 4.5: TEM images of (a) Fe₃O₄ nanoparticles in PAN matrix from Fₘ fibers and (b) as-received Fe₃O₄ nanoparticles.

Figure 4.6: Wide angle x-ray diffraction patterns and integrated radial scans of (a) as-received Fe₃O₄ nanoparticles with PDF reference (#00-019-0629), and (b) S₁ PAN fibers.

Figure 4.7: Wide angle x-ray diffraction patterns and integrated radial scans of (a) F₁ composite fibers with corresponding equatorial (b) and meridional (c) scans.
Figure 4.8: Dynamic mechanical storage modulus (a and b) and tan δ (c and d) plots for Fe₃O₄/PAN composite and PAN control fibers as a function of temperature at a frequency of 0.1 Hz.

Figure 4.9: Optical micrographs of cross sections of (a) FA₀, (b) FB₀, (c) FC₀, and (d) FC₁ composite bi-component fibers.

Figure 4.10: (a) SEM image and (b) cross-sectional schematic of FB₃ bi-component fibers.

Figure 4.11: TGA plots of Fe₃O₄ nanoparticles in air and in nitrogen at a heating rate of 5 °C/min up to 900 °C.

Figure 4.12: WAXD patterns and integrated scans of as-received Fe₃O₄ nanoparticles and corresponding particles after TGA test in N₂ and in air (TGA was done at a heating rate of 5 °C/min up to 900 °C). PDF reference of Fe₃O₄ (PDF#00-019-0629) and α-Fe₂O₃ (PDF#00-001-1053) are also included.

Figure 4.13: TGA plots of PAN (S₁ fiber) and Fe₃O₄/PAN (F₁ fiber) at a heating rate 5 °C/min.

Figure 4.14: SEM images of heat-treated F₁ fibers after TGA test (a) in air and (b) in nitrogen.

Figure 4.15: WAXD patterns and integrated scans of Fe₃O₄/PAN (F₁ fiber) after TGA tests.

Figure 4.16: Fe₃O₄ nanoparticles in DMF with an arrow indicating the aggregation of Fe₃O₄ particles attracted by a magnetic bar.

Figure 4.17: (a) Zero-field-cooling magnetization under 100 G magnetic field and (b) Field-dependent magnetization of as-received Fe₃O₄ nanoparticles at 300K with inserted image showing enlarged partial hysteresis curves.

Figure 4.18: (a) Number fraction and (b) volume fraction of as-received Fe₃O₄ nanoparticles (calculated from Figure 4.4 (d)).

Figure 4.19: (a) Zero-field-cooling magnetization under 100 G magnetic field and (b) Field-dependent magnetization of F₀ fibers at 300K with inserted image showing enlarged partial hysteresis curves.

Figure 5.1: (a) SEM images of as-received GONR and (b) the number fraction of GONR width distribution.

Figure 5.2: TEM image of partial un-zipped CNT.
Figure 5.3: UV-Visible absorption spectra of the GONR dispersion in DMF with various sonication times. The inset figure shows the maximal absorption at 270 ~290 nm with various sonication times.

Figure 5.4: (a) A spool of PAN/GONR composite fibers and (b) micrograph of GB03 fiber cross sections.

Figure 5.5: SEM images of (a) fiber lateral surface of a GB03 fibers and (b) fractured surface with GONRs protruding from the surface indicated by arrows. The image of fractured surface is taken from the broken fiber in the inset image.

Figure 5.6: SEM images of GB30 fiber cross-sections.

Figure 5.7: (a) TEM images of GB30 fiber with an arrow indicating the fibril axial direction and (b) a schematic illustrating the GONR strip in the TEM image.

Figure 5.8: GA02 composite fibers after being placed in DMF for various lengths of time.

Figure 5.9: SEM images of GA02 PAN/GONR composite fibers after being placed in DMF for 15 minutes.

Figure 5.10: Number fraction of (a) strip width distribution and (b) void size distribution analyzed from Figure 5.9 (b).

Figure 5.11: (a) GA20 PAN/GONR composite fibers and (b) A20 control PAN fibers after being placed in DMF for one week.

Figure 5.12: SEM images of (a) GA20 PAN/GONR composite fibers and (b) the fiber lateral surface after being placed in DMF for one week.

Figure 5.13: Raman spectra of GB30 composite fibers parallel (0°) and perpendicular (90°) to the polarization direction.

Figure 5.14: (a) Tensile strength and (b) tensile modulus of PAN/GONR (GA series) and PAN (A series) fibers at various draw ratios.

Figure 5.15: Dynamic mechanical storage modulus (a and b) and tan δ (c and d) plots for PAN/GONR composite and PAN control fibers as a function of temperature at a frequency of 10 Hz.

Figure 5.16: (a) SEM images of GC1 composite carbon fiber. (b) ~ (d) high magnification images of selected regions in (a).
Figure 5.17: Two dimensional WAXD diffraction patterns of (a) GC1 carbonized, (b) GS1 stabilized, and (c) GB30 original PAN/GONR composite fibers, and (d) the corresponding radial integrated scans.

Figure A.1: SEM images of A7 fibers before dissolution process. (b) is higher magnification image of denoted region in (a).

Figure A.2: SEM images of partially dissolved A7 fibers after being placed in DMAc for 5 minutes. (b) is higher magnification image of denoted region in (a).

Figure A.3: SEM images of partially dissolved A7 fibers after being placed in DMAc for 30 minutes. (b) is higher magnification image of denoted region in (a).

Figure A.4: SEM images of A8 fibers after being placed in DMAc for three days. (b) is lower magnification image of A8 fibers, and (c) is higher magnification image of denoted region in (a).

Figure A.5: SEM images of recovered CNTs from boiling DMAc with dissolved A7 fibers.

Figure A.6: SEM images of recovered CNTs from naturally cooled down DMAc with dissolved A7 fibers at room temperature.

Figure B.1: Temperature profile of a composite fiber along the fiber length with 20 wt% CNT content at various electrical currents (L = 0.005 m, h = 200 W/m²K, K = 30 W/mK, d = 44 μm, and σ is obtained from Figure 3.6).

Figure B.2: Temperature profile of a composite fiber along the fiber length with 20 wt% CNT content at various fiber lengths (I = 1 mA, h = 200 W/m²K, K = 30 W/mK, d = 44 μm, and σ = 45 S/m).

Figure B.3: Temperature profile of a composite fiber along the fiber length with 20 wt% CNT content at various fiber diameters (L = 0.005 m, I = 1 mA, h = 200 W/m²K, K = 30 W/mK, and σ = 45 S/m).

Figure B.4: Temperature profile of a composite fiber along the fiber length with 20 wt% CNT content at various electrical conductivities (L = 0.005 m, I = 1 mA, h = 200 W/m²K, d = 44 μm, and K = 30 W/mK).

Figure B.5: Temperature profile of a composite fiber along the fiber length with 20 wt% CNT content at various thermal conductivities (L = 0.005 m, I = 1 mA, h = 200 W/m²K, d = 44 μm, and σ = 45 S/m).

Figure B.6: Temperature profile of a composite fiber along the fiber length with 20 wt% CNT content at various convection coefficients (L = 0.005 m, I = 1 mA, K = 30 W/mK, d = 44 μm, and σ = 45 S/m).
Figure C.1: Optical micrographs of M₀ PMMA core and PAN/CNT sheath bi-component fibers.

Figure C.2: (a) SEM image and (b) cross-sectional schematic of M₀ PMMA core and PAN/CNT sheath bi-component fibers.

Figure C.3: SEM images of fractured surface of M₀ PMMA core and PAN/CNT (90/10) sheath bi-component fibers. (b) is lower magnification image of M₀ fibers, and (c) is higher magnification image of denoted region in (a).

Figure C.4: Wide angle x-ray diffraction patterns of PMMA powder and PMMA core and PAN/CNT sheath bi-component fibers with different draw ratios.

Figure C.5: (a) Integrated radial scans and (b) equatorial scans of wide angle x-ray diffraction patterns of PMMA powder and bi-component fibers with different draw ratios.
SUMMARY

Various nano-fillers can introduce specific functions into polymers and expand their application areas. Myriad properties, such as mechanical, electrical, thermal, or magnetic properties can be combined with original polymer characteristics, including flexibility, light weight, and ease of use. These composites can be used to produce multi-functional fibers for the next generation of textiles or fabrics. This research adopts polyacrylonitrile (PAN) as the matrix polymer with different nano-fillers, such as carbon nanotubes (CNT), iron oxide nanoparticles (Fe₃O₄), and graphene oxide nanoribbons (GONR). Gel-spinning technology is used to fabricate PAN-based composite fibers as single- or bi-component fibers. These fibers are characterized for their structure, morphology, and mechanical properties, as well as for their electrical, thermal, and magnetic properties.

Chapter 1 introduces different nano-fillers (CNT, Fe₃O₄, and GNR), including their properties as well as corresponding composite materials. This chapter also summarizes various functional fibers (smart fibers, heating fibers, and magnetic fibers) PAN fibers, bi-component spinning technology, and presents the objectives of this thesis. Chapter 2 focuses on PAN – PAN/CNT core-sheath bi-component fibers fabricated by gel-spinning technology. Bi-component fibers with a PAN sheath and a PAN/CNT core as well as a PAN/CNT sheath and a PAN core can exhibit good mechanical properties with CNT concentration as high as 20 wt% CNT in the PAN/CNT component. Such bi-component fibers can be used for wearable electronics or for thermal management. Chapter 3 investigates the response of PAN/CNT composite fibers to the surrounding temperature (annealing process) and external force. The chapter also discusses the joule
heating effect, which occurs when external current is applied on the composite fibers. The results show that PAN/CNT composite fibers can be used as active heating fibers, and the electric current can increase the temperature of the PAN/CNT fibers high enough to stabilize and carbonize PAN. This joule heating effect can provide an alternative method for the manufacturing process of carbon fibers to save considerable energy and space. Chapter 4 investigates magnetic fibers by fabricating single-component and bi-component composite fibers with well-dispersed 10 wt% Fe₃O₄ nanoparticles. These novel magnetic fibers with high strength and superparamagnetic properties at room temperature can be used for actuators, inductors, EMI shielding, or microwave absorption. Chapter 5 discusses GONR reinforced PAN-based composite fibers. 1 wt% GONR in fibers can improve the PAN polymer structure and therefore enhance its mechanical properties. Chapter 6 presents the conclusions and recommendations for future work.
CHAPTER 1

INTRODUCTION

1.1 Overview

By fabricating polymer nanocomposites with different fillers [1, 2], including nano-plates (nano-sheets), nanotubes (nano-fibers), and nano-particles [3], we can introduce specific properties from the fillers and expand their applications areas. Myriad functions, such as the mechanical, electrical, thermal, optical, or magnetic properties from various fillers can be combined with original polymer characteristics, including flexibility, light weight, and ease of use. These composites can be used as new materials to produce multi-functional fibers as the next generation of textiles or fabrics [4]. For example, fibers can be mixed with fillers or pigments that can respond to light or temperature [5], and these photo-chromic [6-10] and thermo-chromic [11-14] fibers can be used as switches or sensors. Other possible uses can be developed based on shape memory [15-17], light-emitting [18, 19], energy-harvesting [12, 20, 21], and energy-storage behavior [22, 23].

Instead of focusing on the above functional materials, more interesting research recently has been investigating active functional fibers, including wearable electronics and temperature regulation fibers. Another useful functional fiber is a magnetic fiber, which can be used for actuators, inductors, EMI shielding, and microwave absorption, etc. This chapter will focus on these properties and introduce different nano-fillers (carbon nanotubes, iron oxide nano-particles, and carbon nano ribbons) used in this research. The fillers will first be introduced in sections 1.2 ~ section 1.4, and then their properties and applications will be discussed in section 1.5. In addition, since
polyacrylonitrile (PAN) is one of the most common polymers used to fabricate fibers, PAN-based composite fibers were adopted as the main polymer in this research. Therefore, PAN-based fibers as well as bi-component fiber technology will be introduced toward the end of this chapter.

1.2 Carbon Nanotubes

1.2.1 Properties of Carbon Nanotubes

After Harry Kroto, Jim Heath, Sean O’Brien, Robert Curl, and Rick Smalley discovered buckminsterfullerene [24] in 1985, various carbon-based nanomaterials were synthesized and/or investigated [25], including multi-walled carbon nanotubes[26] by Iijima in 1991, single-walled carbon nanotubes[27, 28] by Iijima and Ichihashi at NEC and Bethune et al. at IBM in 1993, and graphene [29] by Geim and Novoselov in 2004. Because of their specific sp² structure, this new carbon family (Figure 1.1) possesses specific physical and chemical properties and has led to great deal of research.

The carbon nanotube (CNT) is a significant member in the carbon family [30]. According to the number of layers, CNT can be a single-walled carbon nanotube (SWNT), a double-walled carbon nanotube (DWNT), a few-walled carbon nanotube (FWNT), or a multi-walled carbon nanotube (MWNT). Various carbon nanotubes can be fabricated by several developed methods[31, 32], including arc discharge, chemical vapor deposition, laser ablation, and HiPCO. Different manufacturing techniques provide different yields and purity, resulting in significant price difference among them. Their properties are influenced by the wrapping direction (chirality)[33-36] and the size of carbon nanotubes (diameter and length)[37]. Even though modification may impair their
original physical properties, carbon nanotubes can also be modified by covalent or non-covalent functionalization[38] to incorporate different properties.

With the natural 1D tube conformation and sp² carbon structure, CNT can provide specific longitudinal physical properties: mechanical properties, electrical conductivity, and thermal conductivity, which are summarized in Table 1.1. In general, CNTs present lower density than metals and ceramics [41]. Because of the unpaired electrons of the sp² structure [41, 42] and the intrinsic tube conformation, CNTs can exhibit electrical conductivity as high as 10⁶ S/m along the tube axis [43]. For thermal conductivity, the 1D tube structure also implies less Umklapp scattering of phonons, and a longer average mean free path of phonons in the axial direction [44-46]. Since the heat is transported by phonons through CNT, CNT can exhibit high thermal conductivity in the range of 2000 ~6000 W/m·K [47].
Table 1.1 Properties of Carbon Nanotubes

<table>
<thead>
<tr>
<th>Properties</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modulus</td>
<td>0.2 ~ 1 TPa*</td>
</tr>
<tr>
<td></td>
<td>[37, 48-51]</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>10 ~ 150 GPa*</td>
</tr>
<tr>
<td></td>
<td>[49, 50, 52-54]</td>
</tr>
<tr>
<td>Electrical Conductivity</td>
<td>$10^2$ ~ $10^6$ S/m</td>
</tr>
<tr>
<td></td>
<td>[43]</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>2000 ~ 6000 Wm$^{-1}$K$^{-1}$</td>
</tr>
</tbody>
</table>

*Modulus and strength values depend on the CNT diameter and on the presence of defects.

1.2.2 Polymer/Carbon Nanotube Nanocomposites

By fabricating polymer composites with different fillers [1, 2], such as metal nanoparticles, clay nanosheets, or carbon nanotubes, we can introduce specific properties from the fillers and expand their application areas. Since CNTs can show specific mechanical, electrical, and thermal properties, we can reinforce a polymer or enhance the electrical and thermal conductivity by dispersing CNTs in a polymer matrix. Extensive research in polymer/CNT nanocomposites [31, 57] has been conducted using a variety of polymers, including poly(propylene) (PP) [58-61], poly(ethylene terephthalate) (PET) [62-64], poly(ethylene) (PE) [65-67], polyacrylonitrile (PAN) [68-72], poly(vinyl alcohol) (PVA)[73-76], poly(methyl methacrylate) (PMMA) [77, 78] , poly(ethylene oxide) (PEO) [79, 80], poly(ether ketone) (PEK) [81], and PBO (Zylon™) [82]

In general, CNTs can improve the mechanical properties of a polymer significantly. Since nanoscale CNTs exhibit high strength and modulus, a small amount of CNTs can reinforce polymer. For example, if a crack grows inside the composites, the growing crack has to overcome the block of carbon nanotubes through pulling out, deforming, or breaking carbon nanotubes (Figure 1.2). This so-called sword and sheath
mechanism [83-85] increases the dissipation energy, restrains the cracking, and toughens
the whole material. The dispersion and alignment [83] of CNT can also affect their
mechanical properties. Polymer/CNT composites exhibit higher mechanical properties
along the CNT direction for stretched films or fibers. Moreover, because of the
interaction between CNT and the polymer [71, 73, 86-92], the interphase (a boundary
layer or a interfacial region between CNTs and polymer) induced by CNTs exhibit
different physical properties such as molecular density and polymer chain orientation,
which also results in different mechanical properties [93] in polymer/CNT composites.

Figure 1.2 Toughening mechanism of polymer/CNT composites [85].

By mixing CNTs into a polymer matrix, electrical conductivity can be introduced
into polymer. When the content of CNT is higher than a specific value, an effective CNT
network is established as continuous paths to transfer electrons (Figure 1.3). This so-
called percolation concentration [67, 83, 94, 95] is the threshold and requirement to
substantially increase electrical conductivity of polymer/CNT composites. However, not
only the concentration but also the orientation [75, 96-101] of CNTs can affect electrical
conductivity. According to Figure 1.3, neither random nor perfect parallel CNTs can achieve the maximum probability of intersection. Since more inter-tube intersection means more effective CNT network, the highest electrical conductivity can be achieved only when CNTs exhibit an appropriate orientation.

Figure 1.3 Illustrations of (a) percolation concentration and (b) the effect of the alignment of CNTs on intersection probability [96, 98].

Since the thermal conductivity of carbon nanotubes (2000–6000 Wm\(^{-1}\)K\(^{-1}\)) [47, 55, 56] is much higher than that of the conventional polymers (0.2 ~ 0.5 Wm\(^{-1}\)K\(^{-1}\))[102], the improvement of thermal conductivity is the other promising benefit. However, the increase of thermal conductivity of polymers with the addition of CNTs is usually not as high as that of electrical conductivity. The first reason is that the difference in thermal conductivity between carbon nanotubes and polymers is not as large as the difference in electrical conductivity. The second and more important reason is a huge interfacial thermal resistance between polymers and CNTs [103-106]. From previous research, interfacial thermal resistance between carbon nanotubes and polymers can be estimated
to be $10^{-8}$ m$^2$K/W, which is equal to the thermal resistance of a 20 nm-thick layer of polymer[107].

This interfacial resistance for a filler-matrix system, so-called Kapitza resistance[104], results from the acoustic mismatch between CNT and the polymer. According to the diffusive mismatch model[108], the difference in thermal density of states between two materials reduces the coupling and induces significant Umklapp scattering, finally impairing thermal conductivity. Furthermore, even when the concentration of CNT is high enough to establish the CNT network, high geometrical overlapping[109] between the tubes is required to successfully transfer phonons. This is because un-parallel CNTs cause high inter-tube thermal resistance [110-112], results in a significant decrease in thermal conductivity. Therefore, high alignment of CNTs is necessary to induce more geometrical overlapping between tubes and therefore increase thermal conductivity.

1.3 Iron Oxide Nanoparticles

1.3.1 Properties of Iron Oxide Nanoparticles

Nanoparticles of the spinel and garnet families, rare earth elements, specific metals (Fe, Co, and Ni) and their alloys, and other metal oxides can exhibit magnetic properties[113]. Iron oxide magnetic material can be found in the nature. Various iron oxide particles, such as magnetite (Fe$_3$O$_4$), hematite ($\alpha$-Fe$_2$O$_3$), and maghemite ($\gamma$-Fe$_2$O$_3$) have been investigated over decades [114]. Fe$_3$O$_4$ is different from other iron oxide materials, and this dark-brown material is classified as a ferrite (a magnetic ceramic
family, MO·Fe₂O₃, where M = Fe, Ni, Co, Mn, or Cu [114]) with an inverse spinel crystal structure (Figure 1.4).

Magnetite has a face-centered cubic lattice and eight formula units (with total eight Fe²⁺ and sixteen Fe³⁺) per unit cell. Because of this inverse spinel crystal structure, eight Fe²⁺ and eight Fe³⁺ (half number) reside in the octahedral sites, and residual eight Fe³⁺ with the opposite spin direction reside in the octahedral sites, leading to a net magnetic moment. Therefore, magnetite is a ferrimagnetic material, which can undergo a transition to paramagnetism at a Curie temperature of 850 K [114]. Because Fe³⁺ exists in both octahedral and tetrahedral sites, bulk magnetite can also show electrical conductivity around 10⁴ S/m at room temperature [115].

Figure 1.4 Illustration of Fe₃O₄ inverse spinel crystal structure [116].

Figure 1.5 illustrates ferromagnetic, paramagnetic, and superparamagnetic behavior. Saturation magnetization (Mₛ) presents the maximal magnetization induced by
an external magnetic field. When the external field is removed, the existing residual magnetization is called remanent magnetization ($M_R$). Remanent magnetization can be suppressed to zero when coercive force ($H_c$), an external field in a direction opposite to that of the original field, is applied. For ferrimagnetic magnetite, the saturation magnetization ($M_s$) is $92 \sim 100$ emu/g for a bulk material [114], while its remanent magnetization ($M_R$) and coercive force ($H_c$) vary depending on the size of particles and the surrounding temperature.

Figure 1.5 Illustration of ferrimagnetism, paramagnetism, and superparamagnetism [114].

Figure 1.6 demonstrates the influence of size on the coercivity of particles. A micro- or large-scale particle has multiple domains. When the particle size decreases, the number of domains can also decrease, leading to a decrease of spin compensation.
between the different domains. Therefore, the coercivity increases with decreasing particle size. However, when the particle size decreases to only a single-grain domain [117], the decrease in particle size reduces the coercivity. Because the atoms in the outer boundary (shell) of the particle lack translational symmetry, resulting in the reduction of coordination number and the alignment of the spins, the magnetic property in the surface is disordered [118]. In other words, the contribution of magnetization from the shell portion of particles is lower than that from the inner portion of particles. As a result, a decrease in particle size actually increases the portion of the shell region of particles, and therefore the value of effective coercivity in one particle is decreased.

For a single domain magnetic nanoparticle, the other important factor is blocking temperature ($T_B$), determined by the Néel -Brown relaxation law [119] and expressed by the equation below:

\[
T_B = \frac{k_B T}{J} \quad \text{(Néel -Brown Relaxation Law)}
\]
\[ T_B = \frac{KV}{k_B \ln(\tau_m/\tau_o)} \]  

(1.1)

where \( K \) is magnetic anisotropic energy, \( V \) is volume, \( k_B \) is the Boltzmann constant, \( \tau_o \) is the relaxation time (a material characteristic), and \( \tau_m \) is the measurement time. Because of the nanoparticle’s magnetic anisotropy, there are usually two stable orientations of magnetic momentum antiparallel to each other along the magnetic anisotropy in one single domain. The rotation of spin needs to overcome an energy barrier \((KV)\), and this energy barrier depends on the crystal structure, the size and shape of the particle, the internal tension, and the particle interaction. For a certain nanoparticle with \( V \) and \( \tau_o \) under a measurement time-scale \( \tau_m \), the blocking temperature determines whether the magnetic dipole moment can be freely rotated. In other words, at a temperature lower than the blocking temperature, the magnetic moment of a nanoparticle is blocked by barrier energy and magnetic moment of this particle is in a stable state. In contrast, at a temperature higher than the blocking temperature, nanoparticles can show the so-called superparamagnetic \([119, 120]\) properties with no typical hysterical magnetic behavior.

1.3.2 Iron Oxide/Polymer Nanocomposites

Iron oxides and their applications perhaps are the most widely studied magnetic nanoparticles. For large scale applications, \( \text{Fe}_3\text{O}_4 \) nanoparticles have an advantage of being relatively inexpensive and various synthesis methods \([118, 121-123]\) of \( \text{Fe}_3\text{O}_4 \) nanoparticles have been proposed. \( \text{Fe}_3\text{O}_4 \) nanoparticles with different sizes \([124-127]\), shapes \([128-135]\) or modifications \([136-140]\) have been produced. These nanoparticles can exhibit different physical properties and various functionalities for easy adoption to various applications. \( \text{Fe}_3\text{O}_4 \) nanoparticles have been harnessed for bio-application\([121]\) in
magnetic resonance imaging (MRI) [125], drug delivery[140-142], real-time separation[143-145] of protein or metals, and labeling[146-148] of materials or cells. Magnetic nanoparticles can be also suspended in an organic solvent or water to form a magnetic colloidal liquid. This so-called Ferrofluid [149-151] can be applied for liquid seal and thermal dissipation. Another important application of Fe₃O₄ nanoparticles is microwave absorption [133, 134, 139, 152-154]. Fe₃O₄ nanoparticles can absorb X band microwave with the frequency range at 8 ~ 12 GHz. An object coated or covered with Fe₃O₄ nanoparticles or Fe₃O₄/polymer composites can attenuate both the absorption and reflection of microwave. As a result, Fe₃O₄ nanoparticles can be used as EMI shielding materials or applied for invisible technology.

Various methods have been proposed to fabricate Fe₃O₄ nanoparticle/organic material composites [155]. Examples include the sol-gel method, dispersion with surfactants, particle surface modification, rapid solvent evaporation and spray drying, and in-situ polymerization, etc. Studies have been carried out using Fe₃O₄ nanoparticles in different polymer matrices, including epoxy [156, 157], poly (urethane) (PU) [158, 159], poly (methyl methacrylate) (PMMA) [125, 160], and vinyl-ester resin [161]. In addition, various Fe₃O₄/polymer fibers have also been fabricated by wet spinning cellulose [162] and alginate [163], and by electro-spinning poly (ethylene oxide) (PEO) [164], poly (ethylene terephthalate) (PET) [165, 166], poly (vinylpyrrolidone) (PVP) [167], and poly (acrylonitrile) (PAN) [168-173]. In general, continuous large-scale production of polymer/nanoparticle composite fibers with high mechanical properties is still a challenge. However, this research successfully proposes a method to fabricate high-strength composite fibers with Fe₃O₄ nanoparticles, which will be discussed in Chapter 3.
1.4 Graphene Nanoribbons

1.4.1 Properties of Graphene Nanoribbon

Graphene, as illustrated in Figure 1.1, is a flat monolayer packed by carbon atoms with a two dimensional honeycomb structure [174]. It can be stacked into layers as graphite or rolled up to form a tube structure as CNTs [175]. Geim and Novoselov [29] proposed a Scotch-Tape method to produce single layer graphene from graphite in 2004, and the first United State Patent about graphene was issued in 2006[176]. Numerous research efforts have focused on graphene and its nanocomposite [175, 177]. Among various graphene research, strip-like graphene nanoribbon (GRN) was introduced[174], and the fabrication methods of GNR were developed recently [178-181].

GNR has the same flat sp² carbon honeycomb layered structure as graphene. Most physical properties of GNR are similar to those of graphene [174, 175, 177, 182], including the mechanical properties, electrical current density, thermal conductivity, and surface area (Table 1.2). However, its specific structure gives GNR some different benefits over other carbon materials. Because of its ribbon-like structure, GNR’s one-dimensional shape is more suitable for applications requiring nano-fillers with high aspect ratios. Furthermore, both sides of GNR can interact with other materials.

GNR is metallic or semi-conducting, depending on the form of the GNR edge (zigzag or arm-chair) [174, 183]. However, when the width of GNR is less than 10 nm, GNR becomes a semiconductor with a tunable band gap and shows spintronic properties in the presence of an electric field [184, 185]. This so-called half metal has controllable electron spin in one direction, which can be used for smaller and faster devices or magnetoelectronics.
Table 1.2 Properties of Graphene and Graphene Nanoribbon

<table>
<thead>
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<th>Properties</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modulus</td>
<td>~ 1 TPa</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>130 GPa</td>
</tr>
<tr>
<td>Electrical Conductivity*</td>
<td>~ 6000 S/cm</td>
</tr>
<tr>
<td>Max current density</td>
<td>&gt; 10^8 A/cm^2</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>3000 ~ 5000 Wm^{-1}K^{-1}</td>
</tr>
<tr>
<td>Surface Area</td>
<td>2630 m^2/g</td>
</tr>
</tbody>
</table>

*Electrical properties of GNR depend on the form of its edge and the width

1.4.2 Fabrication of GNR by Un-zipping Carbon Nanotube

Several methods have been proposed to fabricate graphene nanoribbons. In the beginning, a bottom-up synthesis method was suggested [195, 196], but the yield was low and the shape was not uniformed. Others started to use CNTs as the raw material to fabricate GNR, as illustrated in Figure 1.7. Since CNTs have the same carbon structure as GNR, GNR can be produced by unzipping or opening CNTs [181]. The shape and uniformity can also be controlled by the selection of CNTs. Initially, metal atoms with acid [178] or nanoparticles (Co and Ni) with nitrogen gas [197] were used to open CNT. However, the efficiency was still lower than 50% and the final size of the GNRs have broad distribution.

The challenge to fabricating uniform GNR was overcome after better methods were proposed by Dai [179] and Tour groups [180, 198] in 2009. In Dai’s method, CNTs were placed on a substrate and coated with PMMA. After the substrate was removed, the CNTs, which were embedded in PMMA, were etched by Ar plasma. In this way, CNT opened up and GNR were retrieved by removing the PMMA. In Tour’s method, CNTs were oxidized by using a KMnO_4/H_2SO_4 solution to produce graphene oxide nanoribbon
(GONR). The unzipping direction was able to be controlled along the tubes, and these graphene oxide nanoribbon (GONR) can be used directly or further reduced to GNR for different applications. If these two results are compared, the GNR from Dai’s method is more uniform and appears to be more suitable for electronics or semiconductor applications. In contrast, the GNR from Tour’s method can be produced faster and in larger quantities, and the quality appears to be more suitable for nanocomposite applications.

Figure 1.7 Illustration of different methods for unzipping carbon nanotubes [181].

1.4.3 Polymer/GNR and Polymer/GONR Nanocomposites

GNR and GONR have been used in different polymer/GNR composite research. The first research is mixing 0.3 wt% GNRs in epoxy-based polymer [199], and the composites showed a 22% increase in strength and a 30% increase in modulus. Later,
various polymers were selected to fabricate polymer/GONR composites, including PVA [200], chitosan [201], and PMMA [202]. In these reports, GONRs can also improve mechanical properties with a 50 ~ 100 % increase in strength and a 50 ~ 150 % increase in modulus. Other research also include hybridizing GNRs with CNTs first and then incorporating these mixtures into polymer, such as PVA [203] and polyurethane [204]. GNRs can assist the dispersion of CNTs and the mixture of GNR/CNT exhibits similar ability to reinforce those polymer composites.

GNRs can be sprayed on Kevlar fibers, and the electrical conductivity can be enhanced [205] to 20 S/cm. However, the enhancement by GNR was less than that by SWNT, while the SWNT-coated Kevlar fibers showed electrical conductivity of 65 S/cm. The other application of GNR is EMI shielding, and only 1 wt% GNRs in PVA film with a thickness of 0.6 mm can cause at least EMI shielding effect of 30 dB in X band. This means the microwave was attenuated 99.9% by only 1 wt% GNRs [206]. In addition, GONR/PAN composite nanofibers [207] were fabricated by electrospinning method recently, and these fibers can be twisted and carbonized to obtain carbon composite yarns. According to the report, GONRs improved the mechanical properties of both PAN/GONR composite fibers and the corresponding carbon fibers. PAN/GONR exhibited a tensile strength of approximately 180 MPa and a tensile modulus of approximately 5.5 GPa. The corresponding carbon nanofibers exhibited a tensile strength of approximately 380 MPa and a tensile modulus of approximately 50 GPa. GONR can reinforce both the precursor nanofibers and their carbon nanofibers.
1.5 Functional Fibers

1.5.1 Smart Fibers

One idea for next generation fibers is smart fibers [208-211] and wearable electronics that combine traditional fibers with conductivity and the ability to interact with the surroundings. Sometimes referred to as textronics, wearable electronics include three different areas of science: textile science, electronics, and computer science. This new material can provide the original function of fibers. It can be soft, light weight, and easy to use but adds electronic properties and sensitivities. One criterion for smart fibers is electrical conductivity, which can also transfer information and responds to the environment (e.g. temperature, humidity, force, etc.). This allows for the creation of new devices and applications, such as soft switches, light-emitting textiles, and flexible sensors for health care devices and security systems.

The idea of smart fibers is promising, but the technology to fabricate smart fibers is still in the initial stages. Previous studies have included wet spinning conductive polyaniline [212], dry spinning poly(p-phenylene vinylene) [213], incorporating metal particles on fibers by coating[214], in-situ synthesis [215], and bridging [216]. Another approach is fabricating spiraling polyethylene-based multilayers [217], which comprise layered conductive and isolated films. In addition, carbon nanotubes also show the potential to be used to fabricate smart fibers. However, only a few studies used a dip-and-dry process to coat carbon nanotubes on the surface of fibers [218-220], and few studies have tried to fabricate bi-component fibers with CNTs [221-224].
1.5.2 Heating Fibers

The electricity usage of commercial and residential buildings accounts for more than 70% of all electricity used in the United States [225]. If the building set temperature can be decreased in winter by 4 °C, then the consumption of building heating energy can be decreased at least by 10% [226]. Therefore, it is crucial to produce heating fibers since these flexible and light-weight fibers can not only maintain the temperature (prevent heat dissipation) but also heat human bodies or residential buildings. For example, when people wear heating fibers, we can set a lower building temperature, which will decrease the building’s heating energy consumption considerably [226]. In addition, heating fibers can be used for people who need to stay in extreme weather, such as on the mountains or deep in the sea. By wearing heating fibers, one can maintain a comfortable temperature while working at relatively low temperatures.

Textile fabrics with active heating capability can not only prevent heat loss, but also provide thermal energy to the body. A traditional method for textile heat-regulation is to improve heat insulation by trapping warm air between the body and its surroundings. Examples of such fibers are micro-fibers (Thinsulate™) [227], fleece structures (POLARTEC®) [228], or hollow fibers (ThermoTech®) [229]. In addition to insulation, other heat regulating technology includes moisture absorption to trap energy dissipation from sweating (MOISCARE® and HEATTECH) [230, 231], absorption and reflection of radiation from the skin (Celliant® and OMNI-HEAT™) [153, 232], and the use of phase change materials in the fiber (Outlast®) [233]. However, if one wants to provide continuous heating for the human body, an important pathway is electrical heating. Traditionally, active heating methods have been utilized for heating garments and textiles,
by applying electrical current to fine metal heating wires embedded in textiles or electrically conductive metal particles blended in polymers. One example is MobileWarming®, which uses steel alloy fibers to generate heat[234]. Another example is heating rubbers mixed with metal materials (Top-Bound Enterprise) [235]. The other method is to fabricate textiles with carbon fibers. When electrical current is passed through the carbon fibers, far-infrared wave is also generated for heating. Examples of this technology are LinkWin and RapidFIRE™ [236, 237].

1.5.3 Magnetic Fibers

Fabrication of magnetic nanoparticle/polymer composites can introduce specific physical properties into the conventional polymer matrix. When magnetic nanoparticles are incorporated into the polymer matrix, magnetic nanoparticle/polymer composites [155] can exhibit both magnetic properties and conventional polymer properties, such as a light weight, ease of use, and flexibility. Their magnetic properties can be harnessed for the applications of hyperthermia behavior (ferromagnetic resonance heating) [163, 230, 238-240], microwave absorption [133, 134, 139, 152-154], data-storage [125, 129, 241], magneto-chromatic behavior [242], magneto-optical effect [243, 244], sensors [125, 159], and electromagnetic interference (EMI) shielding [125, 158, 160, 162, 245-247]. For example, an Fe₃O₄/polymer composite fabricated by mixing Fe₃O₄ nanoparticles into an elastic or rubber-like polymer matrix (e.g. polysiloxane [231] or hydrogel [229]) can respond to a magnetic field and act as an actuator (transducer) [248, 249] or shape memory material [250]. The so-called morphing soft magnetic composites can show remote contactless magnetic actuation with a high actuation rate and quick response and
can be utilized as switches and artificial muscles. Incorporating the magnetic field and the spin arrangement of Fe$_3$O$_4$ particles can lead to other applications of magnetic polymer composite, including recording paper [251], security yarns (tags, paper, or textile) [252, 253], and transparent labeling. More recent interesting applications have been magneto-optical response devices [254] and motors [255]. These light-weight soft magnetic composites can potentially replace heavy permanent (hard) magnets in motors.

1.6 Polyacrylonitrile (PAN) Fibers

PAN fibers are lightweight and soft, and they provide good warm protection and sunlight resistance [256, 257]. Since the first commercial PAN fiber, Orlon, introduced by DuPont in the 1940s, PAN fibers have become a good substitute for wool fibers. PAN fibers are not only utilized as textiles for clothes or carpets, but also employed as a precursor to fabricate carbon fibers. Generally, PAN fibers are fabricated by wet or dry spinning processes [256-258]. Owing to the gel structure that results from the dipole-dipole interaction between nitrile groups on the PAN polymer chains [259-262], PAN fibers can also be fabricated by gel spinning technology.

Since carbon nanotubes can reinforce polymers, PAN/CNT fibers have been fabricated by wet-spinning and dry-jet-wet spinning previously [68-71, 221]. Various CNTs, including MWNT, SWNT, DWNT, and VGCNF have been used to fabricate composite fibers, and CNT can be well-dispersed in fibers. The studies suggest that the drawing process helps exfoliate carbon nanotubes and CNTs can induce a PAN interphase on the surface of CNTs. The interaction between CNTs and polymer chains can improve fiber structure to fabricate stronger fibers.
1.7 Bi-component Fibers

Bi-component fibers have been one important component in the field of polymer science and engineering for over 70 years [4, 263-265]. From their original purpose of mimicking natural wool fibers with a side-by-side structure for a self-crimping effect in the 1940s [264, 265], through the first commercial bi-component fibers introduced by DuPont in the 1960s, various cross-sectional shapes and combinations of polymers have been fabricated into bi-component fibers. In general, bi-component fibers consist of two different parts divided into two distinct regions, with both materials in the two parts able to perform according to their own properties. The geometry of the two regions on the cross section can be sheath-core, side-by-side, layer-by-layer, islands-in-the-sea, and segmented pie, as illustrated in Figure 1.8. Therefore, with specific geometry and processing methods, micro-scale fibers can be fabricated to obtain more surface area and give the fibers greater comfort. In addition, triple- or multi-component fibers with more complicated geometry have also become available recently [266-268].

![Figure 1.8 Typical cross sections of bi-component fibers](image)

Most conventional bi-component fibers have consisted of two different polymers, but a new approach recently is to modify, coat, or mix one component with other materials, such as fillers or specific compounds, as a new kind of nanocomposite.
Therefore, other functions can be introduced from these extra fillers to utilize their specific characteristics [269-274] to enhance aesthetic, mechanical, electrical, or thermal properties. For example, one can introduce pigments, fragrances, metal particles, or other chemical compounds such as drugs or sensors in one component. Thus, we can enhance color, aroma, unique physical properties, or specific sensitivities in bi-component fibers.

1.8 Objectives

This thesis focuses on PAN-based composite fibers with different nano-fillers, including CNT, Fe$_3$O$_4$ nanoparticles, and GONR. It also discusses different physical properties, including mechanical, electrical, thermal, and magnetic properties of these composite fibers. The overall objectives of this study are listed below:

- To fabricate PAN – PAN/CNT core-sheath bi-component fibers with as high as 20 wt% CNTs and investigate the mechanical, electrical, and thermal properties of bi-component fibers.
- To study the effect of annealing temperature, annealing time, and the stretching process on the electrical conductivity of PAN/CNT composite fibers.
- To study Joule heating effect on PAN/CNT composite fibers by applying an external electrical current.
- To fabricate Fe$_3$O$_4$/PAN single-component fibers and PAN – Fe$_3$O$_4$/PAN sheath-core bi-component fibers, and investigate the influence of Fe$_3$O$_4$ nanoparticles on the mechanical properties and superparamagnetic properties of these composite fibers.
- To fabricate PAN/GONR composite fibers and investigate the influence of GONR on their mechanical properties and on the corresponding composite carbon fibers.
1.9 References


[12] Y. M. Li, S. D. Ji, Y. F. Gao, H. J. Luo, and M. Kanehira, "Core-shell VO2@TiO2 nanorods that combine thermochromic and photocatalytic properties for


CHAPTER 2
FUNCTIONAL POLYMER - POLYMER/CARBON NANOTUBE BI-COMPONENT FIBERS

2.1 Introduction

Carbon nanotubes with outstanding properties can be introduced to polymer matrix to manufacture polymer and carbon nanotube (polymer/CNT) nanocomposites. Few studies have been conducted on bi-component fibers utilizing carbon nanotubes [1-6]. For examples, PAN sheath - SWNT core [6], PMMA sheath – SWNT core [5, 6], PEO/MWNT sheath – PEO core [3], and cellulose sheath – CNT core [2] fibers have been reported by electrospinning, while polyamide sheath – PE/CNT core fibers have been processed by melt spinning [4]. Gel spinning can provide high polymer chain alignment and improved mechanical properties, and as previously reported [1, 7-16], successful gel spinning of PAN/CNT and PVA/CNT composite fibers [7, 8]. In this chapter, PAN sheath and PAN/CNT core as well as PAN/CNT sheath and PAN core bi-component fibers were processed by gel spinning. These fibers exhibit good mechanical properties, as well as significantly enhanced electrical and thermal conductivities when compared to the fibers without CNTs. These new fibers can be used as functional wearable textiles that can transmit electrical signal [17, 18] or can be used for thermal management [19].
2.2 Experimental Procedure

2.2.1 PAN/MWNT Composite Solution

PAN (homopolymer, molecular weight: $2.5 \times 10^5$ g/mol) was obtained from Japan Exlan Co. and dried in an oven at 100 °C for two days. Multi-wall carbon nanotubes (MWNT), with an average diameter of 21.0 ± 3.1 nm were obtained from Cheap Tubes Inc. MWNT powder was dispersed in dimethylacetamide (DMAc from Sigma-Aldrich Co.) at a concentration of 0.5 g/300 ml via homogenization (T18, IKA Works Inc.) followed by bath sonication (Bransonic, 3510-MT) for 24 h. PAN powder was separately dissolved in DMAc at a concentration of 14 g/100 ml at 90 °C and MWNT/DMAc dispersion was added to this PAN solution. The excess solvent was evaporated using a vacuum distillation process. The addition of MWNT dispersion and solvent removal processes were repeated to obtain the desired MWNT concentration (10 wt% and 20 wt%) with respect to the weight of the polymer. The final concentrations utilized in the investigation of the PAN/CNT solutions are listed in Tables 2.1 ~ 2.4.

Table 2.1 Processing parameters of PAN/MWNT (90/10) core and PAN sheath bicomponent fibers.

<table>
<thead>
<tr>
<th>Sample a</th>
<th>Core component PAN/MWNT (90/10)</th>
<th>Sheath component PAN</th>
<th>Draw ratio&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Diameter&lt;sup&gt;d&lt;/sup&gt; (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(r&lt;sub&gt;2&lt;/sub&gt;/r&lt;sub&gt;1&lt;/sub&gt;)&lt;sup&gt;b&lt;/sup&gt;: 2.5 - 2.6</td>
<td></td>
<td>CDR        HDR  TD R</td>
<td></td>
</tr>
<tr>
<td>A1</td>
<td>Solution Conc.: 8.3 g/dL</td>
<td>Solution Conc.: 14 g/dL</td>
<td>2 -- 2</td>
<td>45.7 ± 1.1</td>
</tr>
<tr>
<td>A2</td>
<td>g/dL</td>
<td>g/dL</td>
<td>2 9 18</td>
<td>16.0 ± 0.6</td>
</tr>
<tr>
<td>A3</td>
<td>Flow rate: 0.4 cc/min</td>
<td>Flow rate: 1.2 cc/min</td>
<td>2 11 22</td>
<td>14.4 ± 0.5</td>
</tr>
<tr>
<td>A4</td>
<td>Solution Conc.: 9.5 g/dL</td>
<td>Solution Conc.: 14 g/dL</td>
<td>2 -- 2</td>
<td>51.8 ± 3.2</td>
</tr>
<tr>
<td>A5</td>
<td>g/dL</td>
<td>g/dL</td>
<td>2 10 20</td>
<td>17.4 ± 1.1</td>
</tr>
<tr>
<td>A6</td>
<td>Flow rate: 0.3 cc/min</td>
<td>Flow rate: 2 cc/min</td>
<td>2 10.5 21</td>
<td>15.9 ± 0.9</td>
</tr>
</tbody>
</table>

<sup>a</sup> A1, A4 were as-spun fibers, and A2, A3, A5, and A6 were drawn fiber from A1 and A4 fibers.
<sup>b</sup> r<sub>2</sub>/r<sub>1</sub> is the ratio of overall fiber radius (r<sub>2</sub>) to core radius (r<sub>1</sub>).
<sup>c</sup> CDR – cold draw ratio, HDR – hot draw ratio, TDR – total draw ratio (Spin draw ratio is equal to 1).
Table 2.2 Processing parameters of PAN core and PAN/MWNT (90/10) sheath bi-component fibers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Core component</th>
<th>Sheath component PAN/MWNT (90/10)</th>
<th>Draw ratio</th>
<th>Diameter (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Core component</td>
<td>Sheath component</td>
<td>CDR</td>
<td>HDR</td>
</tr>
<tr>
<td></td>
<td>PAN</td>
<td>PAN/MWNT (90/10)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A7</td>
<td>Solution Conc.: 14 g/dL</td>
<td>Solution Conc.: 11.6 g/dL</td>
<td>1.6</td>
<td>--</td>
</tr>
<tr>
<td>A8</td>
<td>Flow rate: 0.4 cc/min</td>
<td>Flow rate: 0.6 cc/min</td>
<td>1.6</td>
<td>6.9</td>
</tr>
</tbody>
</table>

a A7 was as-spun fiber and A8 was fiber drawn from A7 as-spun fiber.
b $r_2/r_1$ is the ratio of overall fiber radius ($r_2$) to core radius ($r_1$).
c CDR – cold draw ratio, HDR – hot draw ratio, TDR – total draw ratio (Spin draw ratio is equal to 1).

Table 2.3 Processing parameters of PAN/MWNT (90/20) core and PAN sheath bi-component fibers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Core component</th>
<th>Sheath component PAN</th>
<th>Draw ratio</th>
<th>Diameter (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Core component</td>
<td>Sheath component PAN</td>
<td>CDR</td>
<td>HDR</td>
</tr>
<tr>
<td></td>
<td>PAN/MWNT (90/20)</td>
<td>PAN</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B1</td>
<td>Solution Conc.: 11.2 g/dL</td>
<td>Solution Conc.: 13.5 g/dL</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>B2</td>
<td>Flow rate: 0.4 cc/min</td>
<td>Flow rate: 1.5 cc/min</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>B3</td>
<td>Solution Conc.: 11.2 g/dL</td>
<td>Solution Conc.: 13.5 g/dL</td>
<td>2</td>
<td>7.5</td>
</tr>
<tr>
<td>B4</td>
<td>Flow rate: 0.4 cc/min</td>
<td>Flow rate: 1.6 cc/min</td>
<td>2</td>
<td>9</td>
</tr>
<tr>
<td>B5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B9</td>
<td>Solution Conc.: 11.2 g/dL</td>
<td>Solution Conc.: 13.5 g/dL</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>B10</td>
<td>Flow rate: 0.3 cc/min</td>
<td>Flow rate: 1.6 cc/min</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>B11</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B12</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a B1, B7 were as-spun fibers, and others were drawn fiber from the corresponding as-spun fibers.
b $r_2/r_1$ is the ratio of overall fiber radius ($r_2$) to core radius ($r_1$).
c CDR – cold draw ratio, HDR – hot draw ratio, TDR – total draw ratio (Spin draw ratio is equal to 1).
Table 2.4 Processing parameters of PAN core and PAN/MWNT (90/20) sheath bi-component fibers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Core component</th>
<th>Sheath component</th>
<th>Draw ratio</th>
<th>Diameter (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PAN</td>
<td>PAN/MWNT (90/20)</td>
<td>CDR</td>
<td>HDR</td>
</tr>
<tr>
<td>B13</td>
<td>1.8</td>
<td>1.8</td>
<td>52.4±2.0</td>
<td></td>
</tr>
<tr>
<td>B14</td>
<td>1.8</td>
<td>1.8</td>
<td>28.6±1.9</td>
<td></td>
</tr>
<tr>
<td>B15</td>
<td>1.8</td>
<td>5.6</td>
<td>10</td>
<td>25.7±2.0</td>
</tr>
<tr>
<td>B16</td>
<td>1.8</td>
<td>6.7</td>
<td>12</td>
<td>21.6±1.2</td>
</tr>
<tr>
<td>B17</td>
<td>1.8</td>
<td>8.3</td>
<td>15</td>
<td>18.8±1.1</td>
</tr>
<tr>
<td>B18</td>
<td>1.8</td>
<td>10</td>
<td>18</td>
<td>18.1±0.9</td>
</tr>
</tbody>
</table>

a B13 was as-spun fiber and others was fiber drawn from B13 as-spun fiber.
b \( r_2/r_1 \) is the ratio of overall fiber radius \( (r_2) \) to core radius \( (r_1) \).
c CDR – cold draw ratio, HDR – hot draw ratio, TDR – total draw ratio (Spin draw ratio is equal to 1).

2.2.2 Gel Spinning PAN – PAN/MWNT Bi-component Fibers

PAN/CNT composite fibers were spun using bi-component fiber spinning unit manufactured by Hills, Inc (Melbourne FL). This is a two piston driven unit containing two reservoirs for the sheath and the core components. This unit can be used for solution spinning or melt spinning and the temperatures and flow rates of the two solutions or melts can be controlled independently. As mentioned earlier, PAN/CNT solution was used either for the sheath or for the core component. When the PAN/CNT solution was used as the core component, the control PAN solution was used as the sheath component, and vice-versa. Both solutions were maintained at 70 °C in the reservoir and subsequently co-extruded through a single-hole spinneret with a diameter of 200 mm maintained at 100 °C. The extrudate was passed through a 25 mm air gap and then through a methanol gelation bath maintained at −50 °C. The sheath/core radii ratio was controlled by changing the flow rates of the two components. The as-spun fiber was then stored to enhance gelation in a methanol bath at −50 °C overnight, and was subsequently drawn at
room temperature followed by drawing at 165 °C in a glycerol bath. The information of flow rate and draw ratio for the fiber spinning process are also listed in Tables 2.1 ~ 2.4.

2.2.3 Characterization

Fiber cross-sections were observed using an optical microscope and scanning electron microscope (SEM, Zeiss Ultraplus60). For sample preparation, the fibers were rewound as a bundle, embedded in epoxy (UltraBed), and cured overnight at 60 °C. The embedded samples were sectioned in 10 – 15 µm thickness using a microtome (Leica RM 2255). The sliced samples were observed first by optical microscopy, and then stuck on SEM stage by carbon tape and coated with Au by Hummer 5 Gold Sputterer for SEM investigation. The obtained images were analyzed using image analysis software (ImageJ, NIH). Fiber tensile properties were measured at a gauge length of 25.4 mm and at a cross-head speed of 0.127 mm/s, using RSA III solids analyzer (Rheometric Scientific Co.). Wide angle X-ray diffraction (WAXD) using CuKα (λ = 0.1542 nm) manufactured by Rigaku Micromax- 002 (operating voltage and current 45 KV and 0.65 mA) was conducted on a fiber bundle. Diffraction patterns were recorded by a detection system (Rigaku R-axis IV++) and analyzed by AreaMax (version 1.00), and MDI Jade (version 9.0). From the WAXD data, PAN crystallinity, PAN crystal size, and the Herman’s orientation factors of the polymer and of carbon nanotubes were calculated following previously described methods [8, 10].

Electrical conductivity along the fiber axis was measured using the 4-point probe method. Fibers were fixed by colloidal silver paste (EMS) on glass slides. The voltage was measured under different current by a four-point probe head (Signatone) and a
sourcemeter (Keithley 2400). The final conductivity was calculated according to the slope of V-I curve and the geometry of fibers. Thermal conductivity was measured by steady-state DC thermal bridge method (DCTBM) [20], as illustrated in Figure 2.1. Bicomponent fibers were coated with a thin layer Pt, and then suspended over two heat sinks. The system is in a closed chamber with vacuum under $10^{-6}$ torr. According to the one-dimensional heat conducting model [20], the temperature distribution $T = T(x)$ and the average increase in temperature $\Delta T$ owing to the heating current are given in equations (1) and (2).

$$T = T_0 + \frac{VI}{2\lambda A} x - \frac{VI}{2\lambda A} x^2$$ (2.1)

$$\Delta T = \frac{VI}{2\lambda A}$$ (2.2)

where $\lambda$ is thermal conductivity, $I$ is the current, $V$ is the voltage, and $A$ is the cross section area of fibers. By measuring electric resistance under various temperatures and different electrical powers, the relationship between electric resistance and temperature can be obtained and used to calculate thermal conductivity of fibers via above equations.

Figure 2.1 Illustration of DCTBM thermal conductivity measurement system [20].
2.3 Results and Discussion

2.3.1 Processing of PAN and PAN/MWNT Bi-component fibers

The various fiber processing parameters utilized in the current investigation are listed in Tables 2.1 ~ 2.4. The ratio of the effective outer fiber radius to that of the core radius was determined by the concentrations of the two solutions and their flow rates. This ratio was comparable to the actual ratio observed in the fiber cross-section. In the current gel-spinning process, when CNT content in the composite layer was approximately 10 wt% with respect to the weight of the polymer, the maximal draw ratio for the bi-component fibers of approximately 22 with PAN/CNT composite as the core and approximately 11 with the PAN/CNT composite as the sheath was achieved. When the CNT content was 20 wt%, the maximal draw ratio for the bi-component fibers was approximately 19 with PAN/CNT composite as the core and approximately 18 with the PAN/CNT composite as the sheath. The outer diameter to the core diameter ratio varied between 1.2 and 3.8, and this ratio as well as CNT content influence the maximal draw ratios. In the previous study of single-component fibers with 5 wt% CNTs, a draw ratio of approximately 10 was achieved [8], while at CNT contents higher than 10 wt%, the draw ratio was below 5 [9]. Thus, in the current investigation at a given MWNT concentration, PAN – PAN/MWNT bi-component fibers exhibited significantly higher draw ratios than the corresponding single component PAN/MWNT fibers. This higher draw ratio in the current bi-component fiber is attributed to the component that does not contain carbon nanotubes. For example, Fiber C13 had 20 wt% CNT content as the sheath, which was higher than 10 wt% CNT content for Fiber A8. However, Fiber C13 had more pure PAN portion in fibers (lower $r_2/r_1$) and therefore showed higher maximal
draw ratio than Fiber A8. This is consistent with the previous reports on layered bi-component polypropylene tapes containing fillers such as CNTs [21, 22]. With high draw ratios, improved mechanical properties can be obtained in the bi-component system.

### 2.3.2 Morphology of PAN and PAN/MWNT Bi-component fibers

Optical micrographs of the bi-component fibers (Figures 2.2 and 2.3) exhibited a kidney-bean cross-sectional shape for most cold drawn PAN and PAN/CNT bi-component fibers but somewhat irregular cross-sections for the PAN/CNT (90/10) sheath and PAN core fibers (sample A7). This is related to variations in coagulation rate of different fibers. The coagulation rate depends on solution concentration, and the temperatures of the extrudate and that of the methanol coagulation/gelation bath. Take PAN and PAN/MWNT (90/10) bi-component fibers as examples, extrudate and coagulation bath temperatures were the same in all trials. However, the solid content of the control PAN solution that formed the sheath in samples A1 and A4 (14 g/dL) was higher than that of the PAN/CNT solution that formed sheath in sample A7 (<11.6 g/dL). This difference in solution concentration is attributed to the differences in the cross-sectional shape in the two cases in the current investigation and is consistent with previous literature reports [23, 24]. However, it was also noted that solvent and non-solvent diffusion rate will also play a role in governing the fiber cross-sectional shape.
Figure 2.2 (a) The illustration of sheath-core bi-component fiber with overall fiber radius $r_2$ and core radius $r_1$. Optical micrographs of PAN sheath and PAN/MWNT (with 10 wt% MWNT) core bi-component fibers – (b) sample A1, and (c) sample A4. (d) PAN/MWNT (10 wt% MWNT) sheath and PAN core – sample A7.

Figure 2.3 Optical micrographs of (a) PAN sheath and PAN/MWNT (with 20 wt% MWNT) core bi-component fibers – sample B1, and (b) PAN/MWNT (20 wt% MWNT) sheath and PAN core – sample B13.
Figures 2.4 and 2.5 show SEM cross-sectional images and the schematics of the drawn PAN sheath - PAN/MWNT core as well as the PAN/MWNT sheath and PAN core bi-component fibers. The sheath and core components appear to adhere well to each other in both cases. The effective diameters (summarized in Tables 2.1 ~ 2.4) were in the range of 44 ~ 52 μm for the cold drawn fibers and in the range of 14 ~ 19 μm for the hot drawn fibers. Magnified SEM images of the fractured area for the PAN/MWNT sheath cross-section region revealed large number of fibril type entities which appear to be carbon nanotubes (Figure 2.6). Average diameter of these fibrillar entities is approximately 79.1 ± 6.7 nm, and is much larger than the average diameter of the MWNTs used in this work, which is 21.0 ± 3.1 nm. The difference in the two diameters is attributed to the PAN coating on the CNTs as well as the coating of the sputtered gold used for SEM sample preparation. The sputtered gold coating thickness of approximately 10 nm was used. Therefore, the PAN coating thickness on the CNT in the current investigation is estimated to be approximately 19 nm, and is comparable to the coating thickness reported previously [9]. PAN core and PAN/MWNT sheath bi-component fibers with 10 wt% MWNT were also placed in DMAc at room temperature in different lengths of time to investigate the interior structure of CNTs. After the composite fibers were dissolved in the solvent, MWNT can also be recovered through filtration process. These corresponding results were given in Appendix A for further discussion.
Figure 2.4 SEM images and cross-sectional schematics of the PAN and PAN/CNT (with 10 wt% MWNT) bi-component fibers (a) and (b) for sample A3, (c) and (d) for sample A6, and (e) and (f) for sample A8.
Figure 2.5 SEM images and cross-sectional schematics of the PAN and PAN/CNT (with 20 wt% MWNT) bi-component fibers (a) and (b) for sample B6, (c) and (d) for sample B12, and (e) and (f) for sample B18.
Figure 2.6 SEM images of (a) pristine CNTs, (b) fractured section of A8 fiber in sheath component, and (c) the magnification image of denoted region in (b).
2.3.3 Mechanical Properties

Tensile properties and structural analysis results for various fibers are listed in Tables 2.5 ~ 2.8. Tensile strength and modulus of fully drawn fibers (e.g. sample A6) were as high as 720 MPa and 20 GPa, respectively. This strength is much higher than that for the electrospun nonwoven bi-component PEO/MWNT sheath – PEO core and cellulose sheath – CNT core fibers (strength < 10 MPa) [53, 54] and also higher than the melt spun bi-component polyamide sheath – PE/CNT core fibers fibers (strength < 500 MPa) [55]. Typical tensile properties of textile fibers such as poly (ethylene terephthalate) (PET) are on the order of 0.5 GPa (strength) and 10 GPa (modulus). Thus tensile properties of the gel spun bi-component PAN – PAN/MWNT carbon fibers are better than the other typical fibers used in textile applications. As expected, the fiber drawing process resulted in increased PAN crystallinity ($X_c$), crystal size ($L_c$), PAN molecular alignment ($f_{PAN}$), and increased MWNT orientation ($f_{CNT}$) (Table 2.5 ~ Table 2.8).

Table 2.5 Structure and properties of PAN/MWNT (90/10) core and PAN sheath bi-component fibers before annealing.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Draw Ratio</th>
<th>Tensile Strength (MPa)</th>
<th>Tensile Modulus (GPa)</th>
<th>Elongation at break (%)</th>
<th>Structural parameters $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$X_c$ (%)</td>
</tr>
<tr>
<td>A1</td>
<td>2</td>
<td>172 ± 13</td>
<td>7.8 ± 0.7</td>
<td>44.8 ± 4.7</td>
<td>45.0</td>
</tr>
<tr>
<td>A2</td>
<td>18</td>
<td>599 ± 55</td>
<td>18.5 ± 1.2</td>
<td>5.1 ± 6.9</td>
<td>53.1</td>
</tr>
<tr>
<td>A3</td>
<td>22</td>
<td>639 ± 55</td>
<td>20.3 ± 1.5</td>
<td>5.0 ± 0.4</td>
<td>56.2</td>
</tr>
<tr>
<td>A4</td>
<td>2</td>
<td>149 ± 10</td>
<td>5.7 ± 0.6</td>
<td>60.7 ± 8.3</td>
<td>45.4</td>
</tr>
<tr>
<td>A5</td>
<td>20</td>
<td>618 ± 93</td>
<td>16.1 ± 1.6</td>
<td>5.7 ± 0.5</td>
<td>56.1</td>
</tr>
<tr>
<td>A6</td>
<td>21</td>
<td>720 ± 77</td>
<td>20.0 ± 1.5</td>
<td>5.8 ± 0.3</td>
<td>54.7</td>
</tr>
</tbody>
</table>

$^a$ $X_c$ and $L_c$ ($2\theta \approx 17^o$) represents crystallinity and crystal size, respectively. $f_{PAN}$ ($2\theta \approx 17^o$) and $f_{CNT}$ ($2\theta \approx 26^o$) are Herman’s orientation factors for PAN crystal and CNT.
Table 2.6 Structure and properties of PAN core and PAN/MWNT (90/10) sheath bi-component fibers before annealing.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Draw Ratio</th>
<th>Tensile Strength (MPa)</th>
<th>Tensile Modulus (GPa)</th>
<th>Elongation at break (%)</th>
<th>Structural parameters a</th>
</tr>
</thead>
<tbody>
<tr>
<td>A7</td>
<td>1.6</td>
<td>155 ± 10</td>
<td>9.2 ± 0.7</td>
<td>17.1 ± 2.5</td>
<td>Xc: 44.8, Lc: 3, fPAN: 0.23, fCNT: 0.77</td>
</tr>
<tr>
<td>A8</td>
<td>11</td>
<td>419 ± 33</td>
<td>16.1 ± 1.1</td>
<td>4.9 ± 0.3</td>
<td>Xc: 51.1, Lc: 9.1, fPAN: 0.77, fCNT: 0.88</td>
</tr>
</tbody>
</table>

a Xc and Lc (θ ≈ 17°) represents crystallinity and crystal size, respectively. fPAN (θ ≈ 17°) and fCNT (θ ≈ 26°) are Herman’s orientation factors for PAN crystal and CNT.

Table 2.7 Structure and properties of PAN/MWNT (90/20) core and PAN sheath bi-component fibers before annealing.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Draw Ratio</th>
<th>Tensile Strength (MPa)</th>
<th>Tensile Modulus (GPa)</th>
<th>Elongation at break (%)</th>
<th>Structural parameters a</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>2</td>
<td>166 ± 16</td>
<td>7.1 ± 0.9</td>
<td>21.1 ± 4.38</td>
<td>Xc: 46.7, Lc: 3.4, fPAN: 0.34, fCNT: 0.57</td>
</tr>
<tr>
<td>B2</td>
<td>8</td>
<td>369 ± 28</td>
<td>10.1 ± 0.6</td>
<td>8.6 ± 2.08</td>
<td>Xc: 49.5, Lc: 9.0, fPAN: 0.78, fCNT: 0.77</td>
</tr>
<tr>
<td>B3</td>
<td>10</td>
<td>424 ± 53</td>
<td>12.2 ± 1.0</td>
<td>8.2 ± 0.75</td>
<td>Xc: 50.7, Lc: 9.5, fPAN: 0.80, fCNT: 0.80</td>
</tr>
<tr>
<td>B4</td>
<td>12</td>
<td>429 ± 61</td>
<td>13.5 ± 1.2</td>
<td>6.6 ± 0.92</td>
<td>Xc: 53.0, Lc: 9.7, fPAN: 0.80, fCNT: 0.82</td>
</tr>
<tr>
<td>B5</td>
<td>15</td>
<td>457 ± 74</td>
<td>16.2 ± 1.7</td>
<td>5.2 ± 0.74</td>
<td>Xc: 54.6, Lc: 10.7, fPAN: 0.83, fCNT: 0.82</td>
</tr>
<tr>
<td>B6</td>
<td>18</td>
<td>450 ± 53</td>
<td>16.9 ± 1.5</td>
<td>4.0 ± 0.44</td>
<td>Xc: 55.7, Lc: 10.6, fPAN: 0.83, fCNT: 0.84</td>
</tr>
<tr>
<td>B7</td>
<td>2</td>
<td>170 ± 13</td>
<td>7.7 ± 0.6</td>
<td>43.8 ± 14.7</td>
<td>Xc: 45.3, Lc: 3.3, fPAN: 0.32, fCNT: 0.55</td>
</tr>
<tr>
<td>B8</td>
<td>8</td>
<td>269 ± 26</td>
<td>7.1 ± 0.6</td>
<td>9.3 ± 0.75</td>
<td>Xc: 47.3, Lc: 8.6, fPAN: 0.78, fCNT: 0.79</td>
</tr>
<tr>
<td>B9</td>
<td>10</td>
<td>456 ± 34</td>
<td>12.9 ± 1.3</td>
<td>8.4 ± 0.70</td>
<td>Xc: 48.9, Lc: 8.9, fPAN: 0.81, fCNT: 0.77</td>
</tr>
<tr>
<td>B10</td>
<td>12</td>
<td>535 ± 38</td>
<td>15.7 ± 1.1</td>
<td>7.5 ± 0.78</td>
<td>Xc: 50.2, Lc: 9.9, fPAN: 0.82, fCNT: 0.82</td>
</tr>
<tr>
<td>B11</td>
<td>15</td>
<td>559 ± 65</td>
<td>17.5 ± 1.4</td>
<td>6.1 ± 0.49</td>
<td>Xc: 52.2, Lc: 10.5, fPAN: 0.82, fCNT: 0.83</td>
</tr>
<tr>
<td>B12</td>
<td>19</td>
<td>552 ± 42</td>
<td>17.7 ± 1.1</td>
<td>4.8 ± 0.65</td>
<td>Xc: 53.9, Lc: 10.6, fPAN: 0.83, fCNT: 0.85</td>
</tr>
</tbody>
</table>

a Xc and Lc (θ ≈ 17°) represents crystallinity and crystal size, respectively. fPAN (θ ≈ 17°) and fCNT (θ ≈ 26°) are Herman’s orientation factors for PAN crystal and CNT.
Table 2.8 Structure and properties of PAN core and PAN/MWNT (90/20) sheath bicomponent fibers before annealing.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Draw Ratio</th>
<th>Tensile Strength (MPa)</th>
<th>Tensile Modulus (GPa)</th>
<th>Elongation at break (%)</th>
<th>Xc (%)</th>
<th>Lc (nm)</th>
<th>f_{PAN}</th>
<th>f_{CNT}</th>
</tr>
</thead>
<tbody>
<tr>
<td>B13</td>
<td>1.8</td>
<td>118 ± 16</td>
<td>6.7 ± 0.35</td>
<td>6.0 ± 1.6</td>
<td>43.3</td>
<td>3.1</td>
<td>0.23</td>
<td>0.66</td>
</tr>
<tr>
<td>B14</td>
<td>8</td>
<td>228 ± 15</td>
<td>7.8 ± 0.58</td>
<td>7.6 ± 0.4</td>
<td>48.9</td>
<td>8.3</td>
<td>0.69</td>
<td>0.78</td>
</tr>
<tr>
<td>B15</td>
<td>10</td>
<td>262 ± 21</td>
<td>9.1 ± 0.7</td>
<td>6.9 ± 0.5</td>
<td>50.9</td>
<td>9.3</td>
<td>0.78</td>
<td>0.80</td>
</tr>
<tr>
<td>B16</td>
<td>12</td>
<td>374 ± 29</td>
<td>12.7 ± 1.4</td>
<td>6.5 ± 0.5</td>
<td>52.4</td>
<td>9.7</td>
<td>0.80</td>
<td>0.82</td>
</tr>
<tr>
<td>B17</td>
<td>15</td>
<td>466 ± 27</td>
<td>13.8 ± 0.5</td>
<td>6.3 ± 0.3</td>
<td>54.6</td>
<td>10.2</td>
<td>0.82</td>
<td>0.83</td>
</tr>
<tr>
<td>B18</td>
<td>18</td>
<td>485 ± 44</td>
<td>14.1 ± 0.8</td>
<td>5.9 ± 0.8</td>
<td>55.7</td>
<td>10.3</td>
<td>0.81</td>
<td>0.86</td>
</tr>
</tbody>
</table>

*a Xc and Lc (2θ ≈ 17°) represents crystallinity and crystal size, respectively. f_{PAN} (2θ ≈ 17°) and f_{CNT} (2θ ≈ 26°) are Herman’s orientation factors for PAN crystal and CNT.

### 2.3.4 Electrical Conductivity

The electrical conductivity of both the as spun and drawn bicomponent fibers with PAN/CNT sheath was on the order of $10^{-5}$ S/m (Table 2.9), which is in the lower range of the electrical conductivity of the polymer/carbon nanotube composite fibers [36, 55, 66-68] ($10^{-5} \sim 10^{0}$ S/m), while the range for bulk polymer/CNT composites electrical conductivity is typically as high as $10^3$ S/m. Electron transfer can take place by electron tunneling or hopping [69-71]. Large Schottky barrier [69, 72] between junction tubes reduces electrical conductivity during inter-tube electron transfer. Tube-tube contact resistance as well as distance between carbon nanotubes is responsible for the moderate electrical conductivity in the current investigation. The second reason for moderate electrical conductivity is the high carbon nanotube orientation in these gel spun fibers. In general, not only concentration but also orientation [44, 66, 73-76] of carbon nanotubes affect electrical conductivity of the composite. Due to carbon nanotube alignment [73-76], electrical conductivity of the polymer/CNT composites decreased when these
composite materials were drawn/stretched extensively [44, 66, 76, 77]. Neither the random nor perfectly oriented carbon nanotubes result in high conductivity in the composite, and the best conductivity was obtained at the intermediate CNT orientation [73-75].

Table 2.9 Electrical conductivity of selected PAN core and PAN/MWNT sheath Bi-component fibers before and after annealing.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Draw Ratio</th>
<th>Diameter [μm]</th>
<th>Conductivity [S/m]</th>
<th>Pre-Annealed</th>
<th>Post-Annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A7</td>
<td>1.6</td>
<td>44.1 ± 1.6</td>
<td>1.49 x 10^{-5}</td>
<td>0.366</td>
<td></td>
</tr>
<tr>
<td>A8</td>
<td>11</td>
<td>18.6 ± 1.0</td>
<td>1.27 x 10^{-5}</td>
<td>1.12 x 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>B13</td>
<td>1.8</td>
<td>52.4 ± 2.0</td>
<td>1.33 x 10^{-5}</td>
<td>4.408</td>
<td></td>
</tr>
<tr>
<td>B18</td>
<td>18</td>
<td>18.1 ± 0.9</td>
<td>1.43 x 10^{-5}</td>
<td>6.3 x 10^{-3}</td>
<td></td>
</tr>
</tbody>
</table>

* Annealing process was carried out under fixed length at 180 °C for 2 hrs.

Enhancement in the electrical conductivity of polymer/CNT composites has been reported with annealing above the polymer glass transition temperature or above the polymer crystallization temperature [45, 62, 63, 78-81]. In some studies [78-80], annealing of the composites was even conducted above the melting temperature. When polymer chains obtain more mobility at higher temperatures, carbon nanotubes also get the opportunity to rearrange themselves. This process results in increased nanotube contacts and enhanced electrical conductivity. After annealing the current bi-component fibers at a fixed length at 180 °C (a temperature between T_g and T_m for PAN) for 2 h, the conductivity of A7 and B13 fiber with low draw ratio increased by more than four orders of magnitude while those of the highly drawn fiber A8 and B18, it only increased by one to two orders of magnitude (Table 2.9).
2.3.5 Effect of Annealing Process on Structure and Mechanical Properties

The mechanical properties and structure parameters of PAN – PAN/CNT (10 wt%) bi-component fibers were investigated and analyzed by tensile test and WAXD after annealing process. Figure 2.7 illustrates the WAXD diffraction plots for A7 (as spun) and A8 (drawn) fibers before and after annealing and the mechanical properties as well as structural data for various fibers are given in Tables 2.10 and Table 2.11. The annealing process did not significantly affect their tensile properties. However, the PAN crystallite size for all the as spun fiber increased significantly on annealing from approximately 3 nm to approximately 10 nm, and the PAN orientation factor increased from approximately 0.25 to above 0.55, while PAN crystallinity increased only moderately, from approximately 45 to 50%. Therefore for the as spun fiber, there was significant polymer chain re-arrangement and orientation during annealing. However, on annealing fully drawn fibers only exhibited moderate change in PAN crystallinity, crystal size, and orientation, as these drawn fibers already possess high crystallinity, large crystal size, and high polymer alignment even before annealing. Thus the significant polymer chain re-arrangement on annealing in the as spun fiber provides opportunity for the CNTs to re-arrange themselves, and this CNT re-arrangement results in four orders of magnitude increase in electrical conductivity for the as spun fiber (Table 2.9). On the other hand, there is only very moderate PAN molecular re-arrangement in the drawn fibers, which limits opportunity for CNT re-arrangement. As a result, electrical conductivity of the fully drawn fiber only increased by a factor of 10. The schematics of the structural re-arrangement of the annealing process for the low and high draw ratio nano composite fibers are illustrated in Figure 2.8.
Figure 2.7 WAXD diffraction patterns and equatorial intensity plots of (a) sample A7 and (b) sample A8 fibers before and after annealing.
Table 2.10 Structure and properties of selected PAN/MWNT (90/10) core and PAN sheath bi-component fibers after annealing.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Draw Ratio</th>
<th>Tensile Strength (MPa)</th>
<th>Tensile Modulus (GPa)</th>
<th>Elongation at break (%)</th>
<th>Structure parameters&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Xc (%)</td>
</tr>
<tr>
<td>A1</td>
<td>2</td>
<td>195 ± 5</td>
<td>8.0 ± 0.2</td>
<td>25.3 ± 4.5</td>
<td>51.4</td>
</tr>
<tr>
<td>A3</td>
<td>22</td>
<td>536 ± 67</td>
<td>19.8 ± 2.1</td>
<td>5.4 ± 0.8</td>
<td>52.9</td>
</tr>
<tr>
<td>A4</td>
<td>2</td>
<td>173 ± 10</td>
<td>8.7 ± 1.1</td>
<td>21.8 ± 3.0</td>
<td>53.1</td>
</tr>
<tr>
<td>A6</td>
<td>21</td>
<td>523 ± 81</td>
<td>15.2 ± 1.9</td>
<td>7.0 ± 0.8</td>
<td>52.7</td>
</tr>
</tbody>
</table>

<sup>a</sup> Xc and Lc (2θ ≈ 17°) represents crystallinity and crystal size, respectively. f<sub>PAN</sub> (2θ ≈ 17°) and f<sub>CNT</sub> (2θ ≈ 26°) are Herman’s orientation factors for PAN crystal and CNT.

Table 2.11 Structure and properties of selected PAN core and PAN/MWNT (90/10) sheath bi-component fibers after annealing.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Draw Ratio</th>
<th>Tensile Strength (MPa)</th>
<th>Tensile Modulus (GPa)</th>
<th>Elongation at break (%)</th>
<th>Structure parameters&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Xc (%)</td>
</tr>
<tr>
<td>A7</td>
<td>1.6</td>
<td>183 ± 21</td>
<td>9.6 ± 1.0</td>
<td>9.5 ± 1.5</td>
<td>51.8</td>
</tr>
<tr>
<td>A8</td>
<td>11</td>
<td>400 ± 52</td>
<td>15.0 ± 2.0</td>
<td>6.7 ± 0.9</td>
<td>52.4</td>
</tr>
</tbody>
</table>

<sup>a</sup> Xc and Lc (2θ ≈ 17°) represents crystallinity and crystal size, respectively. f<sub>PAN</sub> (2θ ≈ 17°) and f<sub>CNT</sub> (2θ ≈ 26°) are Herman’s orientation factors for PAN crystal and CNT.

Figure 2.8 Schematics of the PAN/CNT structures for the as-spun and drawn fibers before and after annealing.
2.3.6 Thermal Conductivity

It has been reported that carbon nanotubes can enhance not only electrical conductivity but also thermal conductivity [82] of nano composites. Thermal conductivity of carbon nanotubes (2000–6000 Wm⁻¹K⁻¹) [24-26] is much higher than that of conventional polymers (0.2 ~ 0.5 Wm⁻¹K⁻¹)[83]. Thermal conductivity of bi-component fibers (10 wt% CNT content in PAN/CNT component) was measured using steady-state DC thermal bridge method (DCTBM) [61]. Figure 2.9 illustrates thermal conductivity is approximately 3 Wm⁻¹K⁻¹ before annealing, and is approximately 7 Wm⁻¹K⁻¹ after annealing at 180 °C for 2 h. This thermal conductivity is much higher than the thermal conductivity of pure PAN (~ 0.2 Wm⁻¹K⁻¹), glass (0.8~0.9 Wm⁻¹K⁻¹), liquid water (0.56 Wm⁻¹K⁻¹), and wood (0.04 Wm⁻¹K⁻¹) [83] at room temperature. The results in Figure 2.9 illustrates the increase in thermal conductivity with increasing temperature from 300 to 380 K and is consistent with previous polymer/CNT composite studies in the vicinity of room temperature [84, 85], where thermal conductivity was reported to be approximately linearly dependent on temperature.

For carbon nanotubes and graphite, the main contribution to thermal conductivity is phonons [26, 86], and the thermal conductivity is proportional to specific heat capacity ($C_p$), phonon velocity ($v_p$), and phonon mean free path ($l_p$) as per Debye equation. At temperatures significantly below room temperatures, Umklapp scattering is restrained and inconspicuous, and phonon transportation is almost ballistic. Therefore in this low temperature range, thermal conductivity of graphite and carbon nanotubes (as per acoustic models and experimental results) is proportional to (Temperature)$^{2.5}$ [25, 26, 86, 87]. However, when the temperature approaches room temperature, phonon-phonon
Umklapp scattering on the surface of carbon nanotubes becomes effective and the Umklapp scattering mean free length approaches static scattering mean free length, and the thermal conductivity of carbon nanotubes is constrained and no longer exhibits \((\text{temperature})^{2.5}\) dependence. Thus due to Umklapp scattering, overall thermal conductivities of the composite fibers around room temperature illustrate an approximate linear dependence with respect to temperature (Figure 2.9).

Thermal conductivity is affected significantly by interfacial resistance [88-90] and the geometrical overlap between carbon nanotubes [91]. For the interface between carbon nanotubes and the polymer matrix, the dissimilarity of atomic structure, density, and phonon velocity between polymer and carbon nanotubes are primary factors affecting thermal conductivity. According to the diffusive mismatch model [92], this acoustic mismatch reduces the coupling and induces Umklapp scattering at the interface, which results in an inevitable interfacial resistance or the so-called Kapitza resistance [88] for filler-matrix system. In the previous studies [93-95], it has been reported that the interfacial thermal resistance between carbon nanotubes and matrix can be approximately \(10^{-8} \text{ m}^2\text{KW}^{-1}\), which is approximately equal to the thermal resistance of approximately 20 nm-thick layer of the polymer, and it reduces the overall thermal conductivity considerably [88]. In addition, high geometrical overlap between the tubes is also necessary for successful phonon transfer. That is, if carbon nanotubes are not parallel to each other, then the inter-tube thermal resistance [85, 96, 97] is still high in spite of high carbon nanotube content. Therefore high draw ratio fibers have high CNT orientation and high thermal conductivity as can be seen in Figure 2.9.
Figure 2.9 Thermal conductivity of the (a) as-spun and (b) fully drawn A1, A2, A7, and A8 fibers measured by DCTBM method [61].
As discussed earlier, polymer chains and carbon nanotubes rearrange themselves during annealing and result in improved carbon nanotube network. Therefore, carbon nanotubes obtained higher junction probability and a more effective pathway for heat transfer upon annealing. However, in contrast to the electrical conductivity behavior, where improvement in conductivity upon annealing was higher in the as spun fiber as compared to the highly drawn fiber, thermal conductivity illustrated reverse behavior. On annealing, thermal conductivity of the as spun fiber increased by less than 1 Wm\(^{-1}\)K\(^{-1}\) while for the drawn fiber it increased by approximately 3 Wm\(^{-1}\)K\(^{-1}\) (Figure 2.9).

### 2.4 Conclusions

PAN/MWNT sheath with PAN core and PAN sheath with PAN/MWNT core bi-component fibers have been processed using gel spinning. All the bi-component fibers exhibited improved drawability as compared to the single component fibers spun at the same carbon nanotube concentration (10 wt% and 20 wt%). Tensile strength and modulus of the bi-component fibers were as high as 720 MPa and 20 GPa at 10 wt% CNT, and as high as 560 MPa and 18 GPa at 20 wt% CNT. In addition, the electrical conductivity for the thermally annealed fibers was as high as 0.366 S/m (10 wt% CNT content) and 4.408 S/m (20 wt% CNT content), and thermal conductivity was as high as ~7 Wm\(^{-1}\) K\(^{-1}\) (10 wt% CNT content). The combination of the mechanical properties and electrical and thermal conductivities of these MWNT containing bi-component fibers should enable new applications for such fibers.
2.5 References


CHAPTER 3
ELECTRICAL CONDUCTIVITY AND JOULE HEATING OF PAN/CNT COMPOSITE FIBERS

3.1 Introduction

Carbon nanotubes (CNTs) [1, 2] can exhibit high strength and high electrical conductivity, and therefore CNTs can not only enhance mechanical properties but also introduce electrical conductivity into polymers. With the polymer properties of flexibility, low-density, and ease-of-use, the electrically conductive polymer/CNT materials can be utilized for wearable electronics or sensors [3-6]. For example, polymer/CNT composite can respond to the surrounding temperature or external force. In addition, when we apply electrical current through the conductive materials, electrical current induces Joule heating effect (self-heating). CNTs have shown significant self-heating effect due to the applied electric current [7-19], and the temperature can be enhanced high enough to burn out conductive CNTs and leave semi-conductive CNTs for computer application [20]. This active heating effect also appears in polymer/CNT composites, as reported for composite films with polyethylene [21], silicone elastomer [22], epoxy [23], and maramid [24].

Previously, polyacrylonitrile (PAN) and carbon nanotube composite fibers have been reported with well-dispersed and aligned CNTs along the fiber axis [25-28]. CNTs not only improved mechanical properties but also introduced electrical conductivity to composite fibers. Since the electrons are transferred through the CNT network, both the concentration and orientation [29-32] of CNTs in the composite fibers determined the
structure of CNT network and therefore influenced the electrical conductivity. However, the structure of composite fibers can also be affected by other factors such as the surrounding temperature or external force on the fibers. The electrical conductivity of fibers can be changed when the fibers are placed in different temperature or stretched. This research covers the discussion on the influence of temperature and stretching process on the electrical conductivity of PAN/CNT composite fibers. In addition, since Joule heating effect also occurs when electrical current is applied on the PAN/CNT composite fibers, the self-heating behavior is also investigated in this research. The change of fibril structure and physical properties such as electrical conductivity owing to the Joule heating effect are also discussed in this Chapter.

### 3.2 Experimental Procedure

Polyacrylonitrile (PAN, molecular weight: $10^5$ g/mol) with 6.7% methyl acrylate as a copolymer was obtained from Japan Exlan Co. and dried under vacuum at 80$^\circ$C before being used. Carbon nanotubes (multi-wall carbon nanotubes) were obtained from Iljin Nanotech Co. (Korea) and used as received. The PAN powder was dissolved in dimethylformamide (DMF, Sigma-Aldrich Co.) using an impeller at 90$^\circ$C, and the CNT powder was dispersed in DMF using a bath sonicator (Branson, 3510-MT). CNT/DMF dispersion was subsequently mixed with the PAN solution for fiber spinning, and the PAN/CNT composite fibers were fabricated using a dry-jet wet spinning unit (Bradford University Research, UK) with a spinneret of 250 μm diameter and two coagulation (DMF/water) baths. The fibers were subsequently drawn in boiling water and dried in an
oven at 50 °C for 7 days [26]. The draw ratios and diameters of the PAN/CNT composite fibers were listed in Table 3.1.

Table 3.1 Listing of compositions, draw ratios, diameters, and linear density for the fibers investigated in this study [26].

<table>
<thead>
<tr>
<th>Sample</th>
<th>MWNT Content [wt%]</th>
<th>Draw Ratio</th>
<th>Diameter [μm]</th>
<th>Linear Density a [tex]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>15</td>
<td>4</td>
<td>60</td>
<td>3.6</td>
</tr>
<tr>
<td>B</td>
<td>20</td>
<td>2.5</td>
<td>44</td>
<td>2.0</td>
</tr>
</tbody>
</table>

*a tex equals the weight in grams of 1000 m length of fiber

PAN/CNT composite fibers at a fixed length were annealed in an oven at 65, 135, 165, and 180 °C for two hours before the electrical conductivity was measured. Fibers were fixed using a silver paste (Electron Microscopy Sciences), and electrical conductivity along the fiber axis was measured using the four-point probe method (Signatone probe and Keithley 2400 Sourcemeter) [33]. The response of electrical conductivity to the annealing process at 180 °C was observed by connecting the fiber to a source meter unit (Keithley 2400 Sourcemeter) using silver paste and copper wires in a temperature-controlled oven (Rheometric Scientific Co.). In addition, fibers annealed at 180 °C for two hours were used to investigate the response of electrical conductivity to tensile strain. The electrical conductivity was measured at room temperature using the same setup used for the annealing effect, and the fibers were stretched simultaneously using RSA III solids analyzer (Rheometric Scientific Co.) at a cross-head speed of 0.0127 mm/s with a fiber gauge length of 25.4 mm.

Joule heating effect was induced by applying electrical current using the same source meter unit (Keithley 2400 Sourcemeter). The fiber structure was measured by
real-time wide angle X-ray equipment during Joule heating process, as illustrated in Figure 3.1. Wide angle X-ray diffraction (WAXD) using \( \text{CuK}_\alpha (\lambda = 0.1542 \text{ nm}) \) was conducted with an X-ray generator (Rigaku Micromax-002) with 45 KV operating voltage and 0.65 mA current. Diffraction patterns were recorded by a detection system (Rigaku R-axis IV++) and analyzed by AreaMax (version 1.00), and MDI Jade (version 9.0). From the WAXD data, PAN crystallinity, PAN crystal size, and the Herman’s orientation factors of the polymer and of carbon nanotubes were calculated following previously described methods [25, 27]. Before and after Joule heating process, infra-red spectra (IR) of fibers were collected using an infra-red microscope (Spectrum One, PerkinElmer) with a resolution of 1 cm\(^{-1}\) and 256 scans, and analyzed with IR software (Spectrum, version 5.3, PerkinElmer). The temperature of the composite fibers during the self-heating process was also observed by the InfraScope II infra-red temperature measurement microscope system (Quantum Focus Instruments Co.).

![Figure 3.1 Illustration of real time measurement of electrical conductivity and wide angle x-ray diffraction of PAN/CNT fiber.](image-url)
3.3 Results and Discussion

3.3.1 Effect of Annealing Process

The conductivity of PAN/CNT composite fibers with 15 and 20 wt% CNT content was measured by the four-point probe method and the results are listed in Table 3.2. For composite fibers before the annealing process, the conductivity was around $10^{-5}$ S/m. Although CNT electrical conductivity is in the range of $10^5 \sim 10^6$ S/m and the CNT content was up to 20 wt% in these fibers, the considerable Schottky barrier [34, 35] between adjacent tubes may severely reduce conductivity, and the appropriate CNT orientation [29-32, 36, 37] was required for effective CNT network. Electrical conductivity was significantly improved by using the annealing process [28, 38-44], and after annealing at 180 °C for two hours, the conductivity was as high as 4.83 S/m and 27.63 S/m for fibers with 15 and 20 wt% CNT content, respectively. According to the data in Table 3.2, electrical conductivity increased with increase in annealing temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>MWNT Content [wt%]</th>
<th>Conductivity $^a$ [S/m]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>original</td>
</tr>
<tr>
<td>A</td>
<td>15</td>
<td>$2.21 \times 10^{-5}$</td>
</tr>
<tr>
<td>B</td>
<td>20</td>
<td>$3.14 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

$a$ The composite fibers were annealed at various temperature under fixed length for two hours before the measurement of electrical conductivity.

The response of conductivity to the annealing process was observed using a power source meter and a temperature-controlled oven. Composite fibers with 20 wt% CNT content were controlled at 180 °C and 10 μA current was applied. The voltage and the calculated electrical conductivity with annealing time are shown in Figures 3.2 and 3.3. The response of voltage in the beginning was fast. After only one minute, the applied
voltage was reduced to 40% and the electrical conductivity increased to approximate 2 S/m. After two hours of annealing time, the voltage decreased by 95 % and the conductivity approached 25 S/m.

Figure 3.2 Voltage of PAN/CNT composite fibers with 20 wt% CNT content during annealing process at 180 °C with 10 μA applied current at a constant length of 25.4 mm.

Figure 3.3 Electrical conductivity of PAN/CNT composite fibers with 20 wt% CNT content during the annealing process at 180 °C with 10 μA applied current at a constant fiber length of 25.4 mm.
In order to investigate the structure change due to annealing, composite fibers before and after being annealed for two hours at 180 °C were also observed using X-ray diffraction. Figure 3.4 reveals that the WAXD diffraction patterns were changed after annealing process, and the corresponding structural parameters are summarized in Table 3.3. According to the structural parameters in Table 3.3, the crystallinity and crystal size of PAN polymer increased from 50 to 60 % and from 5.8 to 11.8 nm, respectively. According to previous research [28, 38-44], the annealing process induced a re-crystallization process of polymer chains, resulting in higher crystallinity and a larger crystal size. This induced the re-arrangement of CNT network and lowered their orientation. The re-arrangement increased the number of CNT inter-tube connections, and therefore enhanced the electrical conductivity significantly.

Figure 3.4 WAXD diffraction patterns and integrated radial scans of PAN/CNT composite fibers with 20 wt% MWNT before and after annealing at 180 °C for 2 hours.
Table 3.3 Structural parameters of PAN/CNT composite fibers with 20 wt% MWNT before and after annealing at 180 °C for 2 hours.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PAN Structural Parameters</th>
<th>CNT Structural Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Xc (^a)</td>
<td>f(_P)(^b)</td>
</tr>
<tr>
<td>Original fibers</td>
<td>50</td>
<td>0.51</td>
</tr>
<tr>
<td>Annealed fibers</td>
<td>60</td>
<td>0.56</td>
</tr>
</tbody>
</table>

\(^a\) Xc: PAN crystallinity  
\(^b\) f\(_P\) and f\(_C\): Herman’s orientation factors of PAN crystal and CNT  
\(^c\) L\(_P\): crystal size (2\(\theta\) ~ 17°) according to Scherrer’s equation with K = 0.9

3.3.2 Effect of Stretching

After the annealing process, the response of conductivity to tensile strain was measured with a stretching test. According to Figure 3.5, the elongation at break was ~6% and ~3% for composite fibers with 15 and 20 wt% CNT, respectively. Both fibers exhibited tensile strength higher than 130 MPa and similar tensile modulus of approximate 9 GPa. During the stretching test, the electrical conductivity was reduced when elongation was increased. The conductivity changed from 27 to 15 S/m for fibers with 20 wt% CNT at 3 % elongation, and from 4.5 to 0.4 S/m for fibers with 15 wt% CNT at 6% elongation. That means only 3% elongation can reduce electrical conductivity by 50% when the composite fibers were stretched. This phenomenon is expected for the polymer/CNT composite [31, 36, 37, 45], and the decrease is a result of breakdown in the CNT network. During the stretching process, CNTs inside polymer matrix were orientated, and higher alignment of CNTs caused lower probability of inter-tube connection [29-32]. Lower CNT connection impaired the ability of transferring electrons and led to lower conductivity. The response of electrical conductivity to strain also implies that the PAN/CNT composite fibers can be utilized as sensors to interact with the surroundings when an external force is applied on the fibers.
3.3.3 Effect of Joule Heating

The electrical properties in Table 3.2 were measured when the applied current was less than 0.1 mA per filament (~ 6 x 10^4 A/m^2) at a fixed length. When the applied current was higher than 1 mA per filament though (~ 6 x 10^5 A/m^2), the conductivity was significantly enhanced by increasing the electrical current. As shown in Figure 3.6, the conductivity of annealed composite fibers with 20 wt% CNT content was ~ 25 S/m originally at the electrical current less than 1 mA. The electrical conductivity of fibers increased with increasing applied electrical current and reached 800 S/m at an applied current of 7 mA. The composite fibers finally broke down when the applied current was in the range of 8 to 10 mA. Figure 3.7 shows the original PAN/CNT composite fibers before test and the same fibers broke down by the input electrical current. The increasing
electrical conductivity and the breakdown phenomenon by electrical current suggest the intrinsic properties of the composite fibers were changed by electricity. The electrical power induced Joule heating effect [21-24] in the fibers. Therefore, the properties of fibers were changed by the induced electrical heating behavior.

Figure 3.6 Electrical conductivity of PAN/CNT fibers under various applied current.

Figure 3.7. Photographs of (a) original and (b) electrically broken down PAN/CNT composite fibers. A bundle of PAN/CNT filaments was used for this experiment.
The influence of electrical power on the composite fibers was further investigated by using Fourier transform infrared spectroscopy (FT-IR). The FT-IR spectra of composite fibers before and after Joule heating treatment is given in Figure 3.8. The FT-IR spectra of stabilized PAN fibers and PAN fibers carbonized at 700, 1000, and 1450 °C are also given in Figure 3.8. Spectra peaks [46-50] at 3000 ~ 2850 cm\(^{-1}\) (C–H, stretch), 2240 cm\(^{-1}\) (C–N, stretch), and 1452 cm\(^{-1}\) (CH\(_2\), bend) decreased or disappeared in composite fibers after applying the electrical current. However, a broad peak at 1600 cm\(^{-1}\) (C=C or C=N, conjugate) appeared, and so did other peaks in the fingerprint area between 1600 and 500 cm\(^{-1}\) associated with C=C, C=N, C=O, –OH, and N–H groups for heteroatomic rings.

![FT-IR spectra of PAN/CNT composite fibers with 20 wt% CNT content (a) before and (b) after Joule heating treatment, (c) stabilized PAN fibers and carbonized PAN fibers with carbonization temperature of (d) 700, (e) 1000, and (f) 1450 °C, respectively.](image)

Figure 3.8 FT-IR spectra of PAN/CNT composite fibers with 20 wt% CNT content (a) before and (b) after Joule heating treatment, (c) stabilized PAN fibers and carbonized PAN fibers with carbonization temperature of (d) 700, (e) 1000, and (f) 1450 °C, respectively.
Comparing the composite fibers after Joule heating treatment with stabilized and carbonized fibers, Figure 3.8 shows the composite fibers were stabilized after electrical treatment at a fixed length. When the electrical current passed through the fibers, the temperature of the composite fibers was increased by Joule heating effect [21-24]. The increased temperature by the electrical power was high enough to stabilize composite fibers, and therefore composite fibers were thermally metamorphosed by the electrical current.

Wide angle X-ray diffraction (WAXD) was also used to observe the Joule heating effect on the composite fibers. When different electrical currents passed through the composite fibers with 20 wt% CNT content, two dimensional WAXD patterns (Figure 3.9) were recorded in real time. The integrated radial scans of two dimensional WAXD patterns in Figure 3.9 are illustrated in Figure 3.10. These diffraction patterns show visible change of diffraction peaks at ~ 17° and ~ 30° when the applied electrical current is higher than 1 mA. These two peaks represent PAN (200, 110) and (310, 020) crystal planes [25, 51]. When the electrical current is higher than 1.6 mA, the diffraction peaks at ~ 17° and ~ 30° disappear and the diffraction patterns are totally different from the patterns of those original fibers. These WAXD patterns verify the suggestion from the FT-IR observation that the PAN polymer structure was gradually changed with the increasing electrical current. The electrical power induced the Joule heating effect, and the heating effect thermally metamorphosed PAN crystal structure when the fiber temperature increase by electricity was high enough to destroy PAN crystal structure and stabilized the composite fibers.
Figure 3.9 Two dimensional WAXD diffraction patterns of PAN/CNT fibers at various electrical currents.

Figure 3.10 Integrated radial scans of WAXD diffraction patterns of PAN/CNT fibers at various electrical currents.
The structural parameters of PAN polymer crystal obtained from WAXD patterns [25, 27] with the electrical current no higher than 1.6 mA are listed in Table 3.4. The structure was stable at low applied current, and only crystallinity and orientation of PAN polymer slightly increased. However, when the current was higher than 1 mA, the PAN crystallinity and orientation decreased. After the electrical current was increased to 1.6 mA, the crystallinity changed from 60% to 18% and the orientation factor decreased from 0.56 to 0.37. The d-spacing of \( \theta \sim 17^\circ \) plane also changed from 0.525 to 0.539 and the crystal size increased from 11.8 to 16.6 nm. The above phenomena also happened to stabilized PAN fibers, while PAN crystal structure was destroyed and transformed to ladder or graphite structure [52, 53] during the stabilization and carbonization process.

Table 3.4 Structural parameters of PAN polymer crystal of composite fibers with 20 wt% CNT content at different applied current.

<table>
<thead>
<tr>
<th>Current [mA]</th>
<th>PAN Structural Parameter</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( X_c^a )</td>
<td>( f_{PAN}^b )</td>
</tr>
<tr>
<td>0.0</td>
<td>60</td>
<td>0.56</td>
</tr>
<tr>
<td>0.3</td>
<td>61</td>
<td>0.58</td>
</tr>
<tr>
<td>1.0</td>
<td>47</td>
<td>0.55</td>
</tr>
<tr>
<td>1.6</td>
<td>18</td>
<td>0.37</td>
</tr>
</tbody>
</table>

\( X_c^a \): PAN crystallinity  
\( f_{PAN}^b \): Herman’s orientation factor  
\( d_{2\theta \sim 17^c} \): d-spacing of PAN polymer chains (2\( \theta \sim 17^\circ \))  
\( L_{PAN}^d \): crystal size (2\( \theta \sim 17^\circ \)) according to Scherrer’s equation with K = 0.9

The WAXD integrated radial scan of composite fibers at 1.6 mA is further deconvoluted and shown in Figure 3.11. PAN crystal structure was undergoing the thermal-transformation process as the electrical current was 1.6 mA, and one additional peak at 2\( \theta \sim 15^\circ \) is observed (Figure 3.11). The change of WAXD patterns indicated the
transformation of PAN crystal during the Joule heating process. This additional peak also suggested the structural change may start from portion of PAN polymer region. As illustrated in Figure 3.12, since electrons mainly passed through CNTs inside the polymer matrix, the Joule heating process occurred around CNTs initially, resulting in a higher temperature region around CNTs. Therefore, the thermal transformation of PAN may start in this high temperature zone next to CNTs and gradually occurs in the entire composite. The other reason is that amorphous PAN and PAN crystal with smaller crystal size may have lower thermal stability and may be transformed first, while the PAN crystal with a larger crystal size may sustain for a longer time during Joule heating. When the electrical current is higher than 3 mA, all PAN crystals are converted, and both peaks at $2\theta \sim 15^\circ$ and $\sim 17^\circ$ disappear (Figure 3.10).

![Figure 3.11 Deconvoluted profile of WAXD integrated radial scans of PAN/CNT fibers at electrical currents of 1.6 mA per filament.](image-url)
After the PAN structure disappeared at an electrical current higher than 3 mA, the peak around 26° became more dominant (Figures 3.9 and 3.10). This shows that the stabilization of composite fibers was induced by the electrical current and the PAN polymer was converted to a ladder structure [53]. The structural parameters of stabilized composite fibers induced by Joule heating effect are also analyzed and listed in Table 3.5. During the Joule heating process, the PAN structure was converted gradually with increased current, and the orientation factor of stabilized ladder structure [53] was changed from 0.44 to 0.51, while the d-spacing and crystal size were almost the same at different applied currents.

The electricity-induced stabilization process suggests a new energy-saving process to manufacture carbon fibers. In general, fabrication of polyacrylonitrile (PAN)-based carbon fibers requires large furnaces to stabilize and carbonize precursor PAN fibers. These fibers typically go through stabilization in air in the temperature range of 180 °C to 350 °C and carbonized in inert environment between 350 °C to 1700 °C [52]. Stabilization time typically varies between 1 and 3 hours [52]. This research provides an
alternative method to locally heat the fiber without heating the surroundings, which can save significant energy and space for the carbon fiber manufacturing industry.

<table>
<thead>
<tr>
<th>Current [mA]</th>
<th>( f_{\text{Ladder}} )</th>
<th>( d_{\text{Ladder}} )</th>
<th>( L_{(26)} )</th>
<th>( L_{(43)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.44</td>
<td>0.346</td>
<td>3.9</td>
<td>2.3</td>
</tr>
<tr>
<td>5</td>
<td>0.46</td>
<td>0.348</td>
<td>3.8</td>
<td>2.1</td>
</tr>
<tr>
<td>7</td>
<td>0.46</td>
<td>0.348</td>
<td>3.8</td>
<td>2.4</td>
</tr>
<tr>
<td>&gt; 8</td>
<td>0.51</td>
<td>0.342</td>
<td>4.2</td>
<td>2.1</td>
</tr>
</tbody>
</table>

\( a \) \( f_{\text{Ladder}} \): orientation factor of stabilized PAN
\( b \) \( d_{\text{Ladder}} \): d-spacing for \( 2\theta \sim 26^\circ \)
\( c \) \( L_{(26)} \) and \( L_{(43)} \): crystal size for \( 2\theta \sim 26^\circ \) and \( 2\theta \sim 43^\circ \) according to Scherrer’s equation with \( K = 0.9 \)

3.3.4 Estimation of Thermal Conductivity

The estimation of thermal conductivity of polymer/CNT composite was proposed by Nan et al. [54, 55]. According to their method, the thermal conductivity along the composite fiber can be expressed as follows:

\[
K = K_m \frac{1+f[\beta_{11}(1-L_{11})(1-\langle \cos^2 \theta \rangle)+\beta_{33}(1-L_{33})(1-\langle \cos^2 \theta \rangle)]}{1-f[\beta_{11}L_{11}(1-\langle \cos^2 \theta \rangle)+\beta_{33}L_{33}(1-\langle \cos^2 \theta \rangle)]}
\]

(1)

with

\[
\beta_{ii} = \frac{K_{ii} - K_m}{K_m + L_{ii}(K_{ii} - K_m)}
\]

(2)

\[
\langle \cos^2 \theta \rangle = \frac{\int \rho(\theta) \cos^2 \theta \sin \theta d\theta}{\int \rho(\theta) \sin \theta d\theta}
\]

(3)
where $K_m$ is the thermal conductivity of the polymer matrix, $K_{11}^c$ and $K_{33}^c$ are the effective thermal conductivities of CNT in radial and axial direction, $\theta$ is the angle between the fiber axis and the CNT axis, $\rho(\theta)$ is the distribution function of CNT orientation, $f$ is the volume fraction of CNT, and $p$ is the aspect ratio (length/diameter = $l/t$) of CNT. CNT orientation and $\langle \cos^2 \theta \rangle$ can be obtained by analyzing the graphite (002) peak from WAXD diffraction patterns of composite fibers. However, since atomic structure, density, and phonon velocity between polymer and carbon nanotubes are so different, it causes Umklapp scattering [54, 56] of phonons at the interface and induced the so-called Kapitza resistance ($R_K$) for the CNT-matrix system. Therefore, the effective thermal conductivity is modified and expressed as [54, 55],

$$K_{11}^c = \frac{K_c}{1 + \frac{2a_K K_c}{\mu K_m}}, \quad K_{33}^c = \frac{K_c}{1 + \frac{2a_K K_c}{\mu K_m}}, \quad a_K = R_K K_m$$

where $a_K$ is Kapitza radius, and $K_c$ is the thermal conductivity of CNT. According to previous reports [57-59], Kapitza resistance between CNTs and polymer was around $8 \times 10^{-8}$ m²K/W. In this calculation, we can use $K_m = 0.2$ W/mK for general polymer [60] and $K_c = 3000$ W/mK for MWNT [61, 62], while the diameter and length of CNT was set as 20 nm and 10 μm [63]. The estimation of thermal conductivity is showed in Figure 3.13, and the thermal conductivity of polymer/CNT composites with 20 wt% CNT and at various orientation factors from 0.3 to 0.5 [26] is approximately in the range of 20 ~ 40 Wm⁻¹K⁻¹.
3.3.5 Estimation of Joule Heating Effect

To estimate the temperature distribution of fibers with applied electricity, one-dimensional steady-state Poisson’s equation [13, 64, 65] was adopted as the heat transfer model. Electrical power (Q) generated homogeneously by electrical current is assumed and expressed as,

\[ Q = j \times F = \frac{I^2}{A^2 \sigma} \]  

(6)

where \( j \) is current density equal to current (I) divided by the effective cross section area (A), and \( F \) is the electrical field equal to applied voltage divided by fiber length (L), and \( \sigma \) is the electrical conductivity of fibers. The schematic diagram of the joule heating phenomenon is illustrated in Figure 3.14. We assume that the heat is conducted one-
dimensionally through composite fibers, and transferred to the environment at the fiber ends, as well as through the surroundings via air convection.

Figure 3.14  Schematic diagram of the Joule heating phenomenon.

The temperature distribution \( \theta(x) \) is defined as the difference between the local temperature \( T(x) \) and the surrounding temperature \( T_\infty \) (background temperature). Therefore, the heat transfer equation is expressed as,

\[
\nabla^2 \theta - \frac{\gamma}{K} \theta + \frac{Q}{K} = 0
\]

where \( K \) is fiber thermal conductivity. Also, \( \gamma \) is assumed as \( 4h/d \), where \( h \) is the air convection coefficient and \( d \) is the effective fiber diameter. If we assume natural air convection for this model, the convection coefficient can be estimated by natural convection correlations [66, 67], and the value is assumed 200 W/m\(^2\)K. We also set \( \theta = 0 \) at both fiber ends \( (x = \pm L/2) \) and define \( x = 0 \) as the mid-point of the fiber. For the above boundary conditions, the temperature distribution along the fibers is expressed as
\[ \theta = \frac{Q}{Km^2} \left[ 1 - \frac{\cosh(mx)}{\cosh\left(\frac{mL}{2}\right)} \right] \]  

(8)

Where \( m \) is defined as \( \sqrt{y/K} \).

To utilize the above equation, fiber thermal conductivity is also needed. According to previous research [68], CNTs improve thermal conductivity in polymer fibers, and the thermal conductivity of CNT/Poly(ether ketone) fibers with 10 ~ 30 wt% CNTs is in the range of 10 ~ 30 Wm\(^{-1}\)K\(^{-1}\) at 300 ~ 400 K. The estimation of thermal conductivity by the approach proposed by Nan et al. [54, 55] showed values in the range of 20 to 40 Wm\(^{-1}\)K\(^{-1}\) for 20 wt% CNT content in composite fibers (Figure 3.13). The annealing and Joule heating processes also changed the structure of the composite fibers. This change should result in further increase in thermal conductivity [28]. As a result, thermal conductivity for composite fibers is assumed as 30 Wm\(^{-1}\)K\(^{-1}\) in this calculation.

With electrical conductivity form Figure 3.6, the temperature profile of a 5 mm long composite fiber containing 20 wt% CNT can be estimated and is illustrated in Figure 3.15. Temperature at both ends is lower because the heat is dissipated faster than in the middle region of the fiber, and the fiber temperature increases with a higher applied current. When the current is higher than 1 mA, temperature is predicted to higher than 200 °C, and as high as 1000 °C at 7 mA. These results are in quantitative agreement with the FT-IR and WAXD results discussed above. When the current is higher than 1 mA, Joule heating can increase the fiber temperature high enough to stabilize or carbonize the composite fibers. The one-dimensional heat transfer equation also provides a quantitative method to estimate Joule heating effect and the increased fiber temperature owing to the input electricity. The estimated temperature profile influenced by other parameters,
including fiber length and diameter, electrical and thermal conductivities, and air convection coefficient, are given in Appendix B.

Figure 3.15 Temperature profile of a composite fiber along the fiber length with 20 wt% CNT content at various electrical currents (L = 0.005 m, h = 200 W/m²K, K = 30 W/mK, d = 44 μm, and σ obtained from Figure 3.6).

3.3.6 Measurement of Joule Heating Effect by Infrared camera

The temperature profile resulting from Joule heating was observed by an infrared microscope. Various electrical currents were applied to composite fibers with 20 wt% CNT content. For example, 150 μA of electrical current induced 4.5 degrees higher than background temperature, as illustrated in Figure 3.16. Following the temperature trace-line from X to Y in Figure 3.16 (a), the temperature distribution along the trace-line is given in Figure 3.16 (b). The temperature profile indicates temperature was higher in the fiber and gradually decreased axially to the surroundings.
Figure 3.16 (a) Temperature profile of single composite fiber with 20 wt% CNT content (fiber length L= 5mm) measured by an infra-red camera and (b) temperature distribution along the trace-line from X to Y.

Electrical conductivity and maximal temperature difference ($\Delta T_{\text{max}}$) between the composite fibers and the background at different currents are summarized in Table 3.6. Temperature increased with increasing electrical current. At 1 mA current, the maximum temperature difference was 153 °C. With the background temperature set at 47 °C, fiber temperature can be even higher than 200 °C, which is high enough to induce stabilization process. In other words, only applying the electrical power with 1 mA and 60 V can provide enough energy to thermally transform PAN/CNT composite fibers. Other polymer/CNT composites, such as epoxy[23] and m-aramid[24], also showed that the temperature can easily increase to 150 °C or higher by applying electricity.
Table 3.6 Summary of electrical conductivity and maximal temperature difference of composite fibers with 20 wt% CNT content with various input currents and voltages.

<table>
<thead>
<tr>
<th>Current [μA]</th>
<th>Voltage [V]</th>
<th>Conductivity [S/m]</th>
<th>$\Delta T_{\text{max}}$ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>4.3</td>
<td>38</td>
<td>0.9</td>
</tr>
<tr>
<td>100</td>
<td>8.6</td>
<td>38</td>
<td>2.3</td>
</tr>
<tr>
<td>150</td>
<td>13</td>
<td>38</td>
<td>4.5</td>
</tr>
<tr>
<td>200</td>
<td>17</td>
<td>39</td>
<td>8.7</td>
</tr>
<tr>
<td>300</td>
<td>25</td>
<td>39</td>
<td>18.7</td>
</tr>
<tr>
<td>500</td>
<td>41</td>
<td>40</td>
<td>53.6</td>
</tr>
<tr>
<td>800</td>
<td>66</td>
<td>40</td>
<td>130.6</td>
</tr>
<tr>
<td>1000</td>
<td>60</td>
<td>55</td>
<td>153.1</td>
</tr>
</tbody>
</table>

$\Delta T_{\text{max}}$ represents the maximal temperature difference between the fibers and the background. The background temperature was set at 47 °C.

Figure 3.17 also exhibits the relationship between applied current and the maximum temperature differences ($\Delta T_{\text{max}}$). According to the heat transfer equation (Eq. 8), the temperature difference is proportional to the electrical power. Since the electrical power is also proportional to the square of electrical current, the experimental $\Delta T_{\text{max}}$ obtained by the infrared camera is expected to be linear when fitted as a function of the square of electrical current ($I^2$) in Figure 3.17. The measured $\Delta T_{\text{max}}$ is also compared with the predictions from the heat transfer equation (Eq. 8) in Figure 3.17. The predicted temperature is approximately 40% higher than the measured. The reasons may be due to inconsistent fiber diameters, radiation dissipation, or higher thermal conductivity resulting from lower interfacial resistance between CNT and polymer or higher CNT aspect ratio. The structural re-arrangement during heating may also influence the thermal conductivity and therefore cause the discrepancy between experimental and estimated $\Delta T_{\text{max}}$ values.
The above results suggest that the temperature increased slightly when the applied current was small, and increased significantly for currents higher than 0.5 mA. As a result, with an appropriate applied electrical power, the fiber temperature can be controlled from few degrees to hundreds of degrees. That is, by applying electricity, these flexible and light-weight fibers can be used as heating fabrics for human bodies or for buildings. Because the electricity usage of commercial and residential buildings accounts for more than 70% of all electricity used in the United States [69], if we can utilize heating fabrics on human bodies and therefore set more than 5 °C lower temperature in buildings, then the consumption of building heating energy can be decreased by 10% [70]. This saving corresponds to around 1% of the total energy consumed in the United States [71]. Although we still need more investigation and further research about the amount of CNT
in fabric and the effect of structure on Joule heating, CNT/polymer composite fibers provide a potential way for temperature regulation and energy conservation.

### 3.3.7 Influence of Fiber Length on Joule Heating Effect

The electrical properties of PAN/CNT composite fibers with 20 wt% CNT were also observed to investigate the effect of fiber length on Joule heating behavior. Longer fibers require higher voltage to overcome higher electrical resistance (Figure 3.18). For example, fibers shorter than 4 mm only require voltage less than 50 V to reach electrical current of 1 mA, but fibers with a length of 76 mm require 500 V to reach electrical current of 1 mA. Because high voltage as well as high electrical power can damage the fibers, fibers with a length of 76 mm only showed the results with applied current as high as 4 mA, while the fibers broke down at 4 mA. Since the required voltage and the generated power are different for fibers with various lengths, if these fibers are applied as heating fibers, optimizing the fiber connection and weaving methods are crucial for obtaining a controllable and uniform temperature profile.

Figure 3.18 reveals that both fibers with lengths of 25 mm and 76 mm exhibited a voltage threshold at the current of 1 ~ 2 mA. Fibers with a length of 4 mm also show the similar threshold, but the voltage is much smaller than those of 25 mm and 76 mm owing to the smaller fiber length. The voltage threshold results from the increase of electrical conductivity caused by the Joule heating effect. Figure 3.19 shows that the conductivities of fibers with lengths of 4, 25, and 76 mm begin to increase significantly when the current is higher than 1 mA. The estimated temperature (calculated from one-dimensional steady-state heat transfer equation) for these fibers as a function of various currents is
also shown in Figure 3.20, where the estimated temperature is higher than 200 °C and high enough to thermally transform these fibers with a current higher than 1 mA. Therefore, the electrical conductivity begins to increase when the current is higher than 1 mA. The increased electrical conductivity also reduces the required voltage and results in an up-and-down voltage profile for fibers with lengths of 25 mm and 76 mm.

For the fibers with a length of 2 mm, the behavior in Figures 3.18 to 3.20 is different from other fibers. Although the estimated maximum temperature difference is higher than 200 °C when the current is higher than 2 mA, the voltage threshold occurs and the electrical conductivity starts to increase when the current is higher than 5 mA. According to the heat transfer model discussed previously, the thermal energy generated by electricity is dissipated through fibers at both ends, as well as through the surroundings via air convection. The heat is dissipated faster at both ends and the temperature at both ends is lower than the temperature in the middle region of the fibers. When the fiber length is long, the heat is mostly dissipated by air convection through the entire fiber and only a small part at both fiber ends shows lower temperature. However, when the fiber length is very short, heat dissipation through both ends becomes dominant, leading to a non-uniform temperature profile with lower temperature at both fiber ends. Most portion of fiber shows lower temperature than the temperature in the middle. Therefore, although the estimated maximum temperature (at the middle point) of 2 mm fibers is higher than 200 °C in Figure 3.20, the temperature in most of the fiber may not be high enough to induce thermal transformation. Only after the current is higher than 5 mA, the 2 mm fiber can undergo thermal conversion to induce a significant increase in conductivity (Figure 3.19). The increased conductivity also suggests a lower electrical
power, which is inversely proportional to electrical conductivity, input in fibers and reduces the increasing fiber temperature at 6 mA. As a result, the conductivity and heating temperature are influenced by the length, and the careful control of input current and voltage is necessary for the application of Joule heating.

![Figure 3.18](image1.png) **Figure 3.18** Voltage of PAN/CNT composite fibers with 20 wt% CNT at different lengths and at various applied currents.

![Figure 3.19](image2.png) **Figure 3.19** Electrical conductivity of PAN/CNT composite fibers with 20 wt% CNT at different lengths and at various applied currents.
3.4 Conclusions

Electrical conductivity of PAN/CNT composite fibers was examined, and fibers with 20 wt% CNT content showed conductivity from around 25 S/m up to higher than 800 S/m. Annealing the composite fibers can re-arrange the fiber structure as well as CNT network and enhance electrical conductivity. When the composite fibers were stretched, the electrical conductivity of the fibers can be a function of elongation, and can be reduced 50% by only 3% elongation. In addition, electrical currents induced Joule heating, and thermally converted PAN/CNT composite fibers with the application of 1 to 7 mA of electrical current. As predicted by one-dimensional steady-state heat transfer equation, the fiber temperature can gradually increase to 1000 °C, before the fibers were broken down. As a result, an electrical current can induce the stabilization of the composite fiber in air. Fabrication of PAN-based carbon fibers is an energy intensive process, and this research provides an alternative processing method to save significant
energy for the manufacturing of PAN-based carbon fibers. Additionally, with Joule heating behavior, composite fibers can be used for heating fabrics.

3.5 References


CHAPTER 4
HIGH-STRENGTH SUPERPARAMAGNETIC COMPOSITE FIBERS

4.1 Introduction

A variety of nano-scaled materials have been developed over the past two decades. A large part of these novel materials exist in the form of nanoparticulate powder. Although nanoparticles have great potentials for applications in their native phases, their powder form limits many of their applications as solid components in various devices. Polymer composites of nanoparticles can facilitate many practical applications of nanoparticles, especially for magnetic nanoparticles. Magnetic interactions are based upon field induction and can be conducted over the physical barriers in a relatively long range. Therefore, the polymer composites of magnetic nanoparticles can be possibly used in a bulk form but preserving all the novel characteristics of magnetic nanoparticles such as superparamagnetic behavior.

By incorporating Fe₃O₄ nanoparticles into polymer matrix, Fe₃O₄/polymer composites can exhibit both magnetic properties and conventional polymer properties, such as light-weight, ease of use, and flexibility. Various Fe₃O₄/polymer fibers were also fabricated by wet spinning and electro-spinning technology as discussed in Chapter 1. For PAN-based polymer, previous research has also shown electro-spun Fe₃O₄/PAN fibers [1-7] and some of them can be stabilized, carbonized, and transferred into magnetic carbon nanofibers. These literature studies have been summarized in Table 4.1. However, fabrication of continuous Fe₃O₄ (or other nano-particles)/polymer composite fibers with good mechanical properties is still a challenge today. In contrast, dry-jet-wet
spinning technology has previously been employed to fabricate composite fibers with good mechanical properties. In this study, Fe$_3$O$_4$/PAN composite fibers with 10 wt% Fe$_3$O$_4$ nanoparticles were fabricated by dry-jet-wet spinning. This novel composite fiber can exhibit high tensile strength and tensile modulus while simultaneously maintaining the superparamagnetic properties of the Fe$_3$O$_4$ nanoparticles. This research not only shows promising magnetic applications, including actuator, inductor, EMI shielding, microwave absorption, and hyperthermia behavior, but also realizes the fabrication of composite polymer fibers and the potential for composite carbon fibers with various nanoparticles.
Table 4.1 Summary of recent research on electro-spun Fe$_3$O$_4$/PAN composite fibers.

<table>
<thead>
<tr>
<th>Year</th>
<th>Reference</th>
<th>Journal/Proceeding</th>
<th>Author</th>
<th>Institute</th>
<th>Particle conc.</th>
<th>Particle diameter</th>
<th>Particle Supplier</th>
<th>PAN Fiber diameter</th>
<th>Ms</th>
<th>Hc</th>
<th>Carbonization</th>
<th>Carbon fiber diameter</th>
<th>Ms</th>
<th>Hc</th>
</tr>
</thead>
<tbody>
<tr>
<td>2009</td>
<td>[1]</td>
<td>Polymer Mater. Lett.</td>
<td>D. Zhang, et al.</td>
<td>Larmar U, USA</td>
<td>9 wt%</td>
<td>13 nm</td>
<td>Ocean NanoTech</td>
<td>500 nm</td>
<td>1.1 emu/g</td>
<td>206.7 G</td>
<td>No</td>
<td>N/A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2010</td>
<td>[3]</td>
<td>Proc. SPIE</td>
<td>D. Munteanu, et al.</td>
<td>Valahia U, Romania</td>
<td>10 wt%</td>
<td>10 nm</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2011</td>
<td>[4]</td>
<td>Polymer</td>
<td>M. Bayat, et al.</td>
<td>U. British Columbia, Canada</td>
<td>15 ~ 25 nm</td>
<td>22 nm</td>
<td>Nanostructure and Amorphous Inc.</td>
<td>538 nm</td>
<td>0.3 emu/g</td>
<td>30 G</td>
<td>No</td>
<td>370 nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2011</td>
<td>[5]</td>
<td>Polymer</td>
<td>J. Zhu, et al.</td>
<td>Lamar U, USA</td>
<td>1 ~ 10 wt%</td>
<td>N/A</td>
<td>QuantumSphere Inc.</td>
<td>300 ~ 1000 nm</td>
<td>5.9 emu/g</td>
<td>235 G</td>
<td>Yes</td>
<td>N/A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2012</td>
<td>[6]</td>
<td>Polymer</td>
<td>T. Zhang, et al.</td>
<td>Tsing Hua U, China</td>
<td>0.5 ~ 9 wt%</td>
<td>N/A</td>
<td>Home-made</td>
<td>1000 nm</td>
<td>N/A</td>
<td>N/A</td>
<td>No</td>
<td>N/A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2013</td>
<td>[7]</td>
<td>J. Appl. Polym. Sci.</td>
<td>Y. Yang, et al.</td>
<td>MIT, USA</td>
<td>2, 7, and 17 wt%</td>
<td>7 ~ 50 nm</td>
<td>Home-made</td>
<td>0.5 ~ 2.5 μm</td>
<td>N/A</td>
<td>1.5 ~ 12.3 emu/g</td>
<td>N/A</td>
<td>N/A</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes:
- a Porous structure was formed after carbonization.
- b Particle size increased and Fe$_3$C was formed after carbonization.
- c Particles used in [5] were Fe@FeO.
- d Fe$_3$O$_4$ can be in-situ synthesized from iron (III) acetylacetonate.
4.2 Experimental Procedures

4.2.1 Fe₃O₄/PAN Composite Solution

PAN (homopolymer, viscosity average molecular weight: 2.5×10⁵ g/mol) was obtained from Japan Exlan Co. and dried in a vacuum oven at 100 °C for two days. PAN powder was dissolved in dimethylformamide (DMF from Sigma-Aldrich Co.) at a concentration of 15 g/100 ml at 90 °C. Iron oxide nanoparticles (Fe₃O₄, diameter: 10 ~ 15 nm) were purchased from SkySpring Nanomaterials Inc., and separately dispersed in DMF (100 mg/300 mL) via bath sonication (3510-MT, Bransonic). Fe₃O₄ dispersion was later mixed with the PAN solution, and the excess solvent was evaporated using a vacuum distillation process. The addition of Fe₃O₄ dispersion and solvent removal process was repeated until the desired Fe₃O₄ concentration to PAN was equal to 10 wt%. The final solid content of PAN + Fe₃O₄ used for fiber spinning was 15 g/100 mL.

4.2.2 Gel-Spinning of Fe₃O₄/PAN Composite Solution

Fe₃O₄/PAN composite fibers were spun using a spinning unit manufactured by Hills, Inc (Melbourne FL). Composite solutions were maintained at 70 °C in the solution reservoir and extruded through a single-hole spinneret with a diameter of 200 μm maintained at 80 °C. The extrudate was passed through 25 mm air gap and then through a methanol gelation bath maintained at -50 °C. The as-spun fiber was collected with a draw ratio of one, stored in a methanol bath at -50 °C overnight, and was then drawn at room temperature with a draw ratio of two. The fiber is later hot-drawn at 165 °C in a glycerol bath. Pure PAN fibers were spun by similar processing method. Fe₃O₄/PAN (10/90) core and PAN sheath bi-component fibers are also spun using the similar method described in
Chapter 2. Corresponding processing parameters for different samples are listed in Tables 4.2 and 4.3. All fibers were washed with methanol and dried in an oven at 70 °C before characterization.

**Table 4.2** Processing parameters of Fe₃O₄/PAN composite fibers and control PAN fibers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solution Conc. (g/100 mL)</th>
<th>Solution flow rate (mL/min)</th>
<th>Draw ratio</th>
<th>Diameter (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>CDR</td>
<td>HDR</td>
</tr>
<tr>
<td>Fe₃O₄/PAN Composite fibers</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fₐ</td>
<td>15</td>
<td>2</td>
<td>8.5</td>
<td>17</td>
</tr>
<tr>
<td>Fₙ</td>
<td>15</td>
<td>2</td>
<td>7.5</td>
<td>15</td>
</tr>
<tr>
<td>F₁</td>
<td>15</td>
<td>2</td>
<td>7.5</td>
<td>15</td>
</tr>
<tr>
<td>F₀</td>
<td>15</td>
<td>2</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>Control PAN fibers</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S₂</td>
<td>15</td>
<td>2</td>
<td>7.5</td>
<td>15</td>
</tr>
<tr>
<td>S₁</td>
<td>15</td>
<td>2</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>S₀</td>
<td>15</td>
<td>2</td>
<td>--</td>
<td>2</td>
</tr>
</tbody>
</table>

*a F₀ and S₀ were as-spun fibers, and others were drawn fiber from the corresponding as-spun fibers.

**Table 4.3** Processing parameters of Fe₃O₄/PAN (10/90) core and PAN sheath bi-component fibers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Core component Fe₃O₄/PAN (10/90)</th>
<th>Sheath component PAN</th>
<th>Draw ratio</th>
<th>Diameter (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>CDR</td>
<td>HDR</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(r₂/r₁*b: 2.0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FA₃</td>
<td>Solution Conc.: 15.5 g/dL</td>
<td>Solution Conc.: 15.5 g/dL</td>
<td>2</td>
<td>11.5</td>
</tr>
<tr>
<td>FA₂</td>
<td>Flow rate: 0.5 cc/min</td>
<td>Flow rate: 1.5 cc/min</td>
<td>2</td>
<td>7.5</td>
</tr>
<tr>
<td>FA₁</td>
<td></td>
<td></td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>FA₀</td>
<td></td>
<td></td>
<td>2</td>
<td>-</td>
</tr>
</tbody>
</table>

|         |                                  | (r₂/r₁*b: 1.4)       |     |     |     |               |
| FB₃     | Solution Conc.: 15.5 g/dL       | Solution Conc.: 15.5 g/dL       | 2   | 8.5  | 19  | 14.3 ± 0.7    |
| FB₂     | Flow rate: 0.6 cc/min           | Flow rate: 0.6 cc/min     | 2   | 7.5  | 15  | 16.7 ± 0.5    |
| FB₁     |                                  |                       | 2   | 5    | 10  | 20.1 ± 0.4    |
| FA₀     |                                  |                       | 2   | -    | 2   | 43.9 ± 1.3    |

|         |                                  | (r₂/r₁*b: 1.2)       |     |     |     |               |
| FC₃     | Solution Conc.: 15.5 g/dL       | Solution Conc.: 15.5 g/dL       | 2   | 9    | 18  | 16.0 ± 0.3    |
| FC₂     | Flow rate: 0.5 cc/min           | Flow rate: 0.5 cc/min     | 2   | 7.5  | 15  | 16.6 ± 0.7    |
| FC₁     |                                  |                       | 2   | 5    | 10  | 20.7 ± 0.3    |
| FC₀     |                                  |                       | 2   | -    | 2   | 44.4 ± 2.0    |

*a FA₀, FB₀, and FC₀ were as-spun fibers, and others were drawn fiber from the corresponding as-spun fibers.

*b r₂/r₁ is the ratio of overall fiber radius (r₂) to core radius (r₁).
4.2.3 Characterization

Fiber bundles were embedded in epoxy resin (Epo-Fix, Electron Microscopy Sciences) and then sliced in 10 – 15 μm thick sections using a microtome (Leica, RM2255). Fiber cross-sections were observed using a scanning electron microscope (SEM, Zeiss Ultra60). Fe₃O₄/PAN fiber was mounted on a copper 3 post Omniprobe lift-out grid (Electron Microscopy Sciences) with epoxy resin (Epo-Tek, Gatan, Inc.), and then transverse sections were etched by focus ion beam (FEI Nova Nanolab 200 FIB/SEM) at ion accelerating voltages of 30 keV and 5 keV. Samples were thinned until electron transparency was achieved and observed using a transmission electron microscope (TEM, FEI Tecnai F30), operated at 80 keV. As-received Fe₃O₄ nanoparticles were also observed by TEM (JEOL JEM 100C), and the samples were prepared by slowly evaporating a drop of nanoparticle suspension in hexane on an amorphous carbon-coated copper grids at room temperature.

The tensile properties of single-component fibers were measured at a gauge length of 25.4 mm and at a cross-head speed of 0.127 mm/s, using RSA III solids analyzer (Rheometric Scientific Co.). For tensile testing, fibers were fixed on testing paper tabs (45X10 mm) with a single hole (25X6 mm) in the middle using a super glue. These samples were clamped on the RSA III solids analyzer and the two sides of the paper tab were cut away before testing. The tensile properties of bi-component fibers were measured at a gauge length of 25.4 mm and at a cross-head speed of 0.25 mm/s, using Favimat (Textechno H. Stein GmbH & Co. KG). Dynamic mechanical analysis (DMA) was also carried out using RSA III with frequency of 0.1, 1, 10, and 80 Hz at a heating rate of 1 °C/min on a bundle (25.4 mm length) of 100 filaments.
Thermogravimetric Analysis (TGA, TA Q500) was conducted at a heating rate of 5 °C/min from 25 to 900 °C under air or nitrogen gas. Wide angle X-ray diffraction (WAXD) using CuKα (λ=0.1542 nm) manufactured by Rigaku Micromax-002 (operating voltage and current 45KV and 0.65mA) was conducted on fiber bundles. Diffraction patterns were recorded by a detection system (Rigaku R-axis IV++) and analyzed by AreaMax (version 1.00), and MDI Jade (version 9.0). From this WAXD data, PAN crystallinity (Xc), PAN crystal size (L_{PAN}), and the Herman’s orientation factors of PAN (f_{PAN}) fibers were determined following previously described methods [8, 9]. Both temperature and magnetic field-dependent magnetization measurements were done on a superconducting quantum interference devices (SQUID) magnetometer (Quantum Design MPMS-5S) with a magnetic field up to 5 T[10].

4.3 Results and Discussion

4.3.1 Morphology of Fe₃O₄/PAN Magnetic Fibers

Using dry-jet-wet spinning, continuous Fe₃O₄/PAN composite fibers were fabricated successfully with 10 wt% Fe₃O₄ nanoparticles. These fibers had an approximate overall density of about 1.28 g/cm³. Figure 4.1(a) shows the spools of Fe₃O₄/PAN composite fibers and Figure 4.11(b) shows a bundle of 100 composite filaments attracted to the magnetic bar. Various single component composite and control fibers prepared in this study are designated and listed in Table 4.2. The SEM surface images of composite fibers are shown in Figure 4.2. At low magnification SEM image, fiber surface appears to be relatively smooth. However, at high magnification, nanoparticles embedded in polymer matrix can be observed. The optical micrographs and the SEM images of the
cross sections of composite fibers are shown in Figure 4.3 and Figure 4.4. These micro-scale fibers exhibit noncircular cross sections [11], due to the non-uniform counter-diffusion of DMF and methanol during the coagulation/gelation process at -50 °C. The average effective diameter of composite fibers was decreased by increasing draw ratios, and the smallest diameter of 16 μm was achieved at the highest draw ratio of 17.

Figure 4.1 (a) Spools of Fe₃O₄/PAN composite fibers and (b) a bundle of Fe₃O₄/PAN composite fibers attracted by a magnet bar.

Figure 4.2 (a) SEM images of F₅ composite fiber and (b) fiber lateral surface under higher magnification.
Fe₃O₄ nanoparticles (as bright nano-spots in gray polymer matrix) were dispersed throughout the fiber cross-section (Figure 4.4(b)). TEM Imaging of the transverse fiber cross-section (Figure 4.5(a)) shows individual and clusters of Fe₃O₄ nanoparticles dispersed in the polymer matrix and the particle diameter ~10 nm. For comparison, TEM images of the as-received Fe₃O₄ nanoparticles are also shown in Figure 4.5(b).

Figure 4.4 SEM images of (a) Fₘ fiber cross section and (b) corresponding SEM image under higher magnification.
4.3.2 Structure of Fe₃O₄/PAN Magnetic Fibers by WAXD

Figure 4.6 shows WAXD patterns and integrated radial scans of as-received Fe₃O₄ nanoparticles and control PAN fibers. Fe₃O₄ nanoparticles exhibited typical WAXD diffraction patterns of ferrite identified with ICDD PDF reference (#00-019-0629) in Figure 4.6(a). WAXD patterns and integrated radial scans of Fe₃O₄/PAN composite fibers are shown in Figure 4.7(a), including deconvoluted peaks attributed to semi-crystalline PAN and Fe₃O₄ nanoparticles. The equatorial and meridional scans are also shown in Figure 4.7(b) and Figure 4.7(c). The corresponding structural parameters of the PAN fibers determined from the WAXD patterns are listed in Table 4.4. Higher draw ratios resulted in increased crystallinity, larger crystal size, and higher orientation of PAN crystallites. Fe₃O₄/PAN composite fiber (total draw ratio of 17) exhibits PAN crystallinity (Xc) of 56%, PAN crystal size (Lc) of 12.4 nm, and PAN polymer chain orientation (f_PAN) of 0.76. The results also showed the presence of Fe₃O₄ nanoparticle had moderate or no influence on PAN crystallinity and crystal size under similar draw ratios. However, it was observed that at a given draw ratio composite fibers exhibited lower

Figure 4.5 TEM images of (a) Fe₃O₄ nanoparticles in PAN matrix from Fm fibers and (b) as-received Fe₃O₄ nanoparticles.
PAN orientation (Table 4.4). In addition, according to the equatorial scans from WAXD patterns in Figure 4.6(b), d-spacing of crystal planes (200, 010) at $2\theta \sim 17^\circ$ and crystal planes (310, 020) at $2\theta \sim 30^\circ$ [8, 12] can be calculated and are listed in Table 4.4.

Figure 4.6 Wide angle x-ray diffraction patterns and integrated radial scans of (a) as-received Fe$_3$O$_4$ nanoparticles with PDF reference (#00-019-0629), and (b) $S_1$ PAN fibers.
Figure 4.7 Wide angle x-ray diffraction patterns and integrated radial scans of (a) F₁ composite fibers with corresponding equatorial (b) and meridional (c) scans.
Table 4.4 Structural parameters of Fe₃O₄/PAN composite and control PAN fibers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Draw ratio</th>
<th>PAN Structural parameters</th>
<th>Xc (%)</th>
<th>L_PAN (nm)</th>
<th>f_PAN (-)</th>
<th>d₁θ~17° (nm)</th>
<th>d₂θ~30° (nm)</th>
<th>2θ_{meridional} (degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₃O₄/PAN Composite fibers</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fₘ</td>
<td>17</td>
<td>56</td>
<td>12.4</td>
<td>0.76</td>
<td>0.523</td>
<td>0.304</td>
<td>39.0</td>
<td></td>
</tr>
<tr>
<td>F₂</td>
<td>15</td>
<td>53</td>
<td>11.0</td>
<td>0.75</td>
<td>0.526</td>
<td>0.305</td>
<td>39.1</td>
<td></td>
</tr>
<tr>
<td>F₁</td>
<td>10</td>
<td>47</td>
<td>9.1</td>
<td>0.72</td>
<td>0.529</td>
<td>0.306</td>
<td>39.3</td>
<td></td>
</tr>
<tr>
<td>F₀</td>
<td>2</td>
<td>46</td>
<td>3.4</td>
<td>0.28</td>
<td>0.529</td>
<td>0.306</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>Control PAN fibers</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S₂</td>
<td>15</td>
<td>50</td>
<td>10.6</td>
<td>0.83</td>
<td>0.523</td>
<td>0.303</td>
<td>39.0</td>
<td></td>
</tr>
<tr>
<td>S₁</td>
<td>10</td>
<td>49</td>
<td>9.6</td>
<td>0.81</td>
<td>0.526</td>
<td>0.303</td>
<td>39.1</td>
<td></td>
</tr>
<tr>
<td>S₀</td>
<td>2</td>
<td>46</td>
<td>3.5</td>
<td>0.32</td>
<td>0.528</td>
<td>0.306</td>
<td>--</td>
<td></td>
</tr>
</tbody>
</table>

a Effective diameter of fibers were calculated from SEM cross section images.
b Xc: crystallinity from integrated radial scans.
c L_PAN: crystal size (2θ ~ 17°) according to Scherrer’s equation with K = 0.9.
d f_PAN: orientation factor of PAN polymer chains.
e & f: d₂θ: d-spacing for 2θ ~ 17° and 30°.
g 2θ_{meridional}: Meridional peak position.

Since d-spacing represented the packing condition of polymer chains, higher draw ratio resulted in closer packing and more stretched structure, leading to a lower d-spacing value. Similarly, the meridional peak also provides information of chain conformation along fiber axis [13]. The meridional PAN peak ~ 40° was shifted to lower angles with increasing draw ratio (Table 4.4). This shift indicates the tendency for the presence of increasing planar zigzag structure at higher draw ratios[12]. From WAXD results in Figure 4.7 and in Table 4.4, we can also investigate the influence of Fe₃O₄ nanoparticles on fiber structure. The presence of nanoparticles resulted in higher d-spacings (corresponding to equatorial 2θ ~ 17° and ~ 30° peaks) and higher 2θ value for the ~ 39° meridional peak at a given draw ratio. This shows the influence on the polymer chain packing in the presence of nanoparticles.
4.3.3 Mechanical Properties of Fe$_3$O$_4$/PAN Magnetic Fibers

Mechanical properties of Fe$_3$O$_4$/PAN composite fibers and PAN control fibers at various draw ratios were measured using single filament tensile tests and the results are listed in Table 4.5. Fe$_3$O$_4$/PAN composite fibers have good mechanical properties with tensile strengths as high as 630 MPa and tensile modulus as high as 16 GPa, and the elongation to break of 7% at a draw ratio of 17. Due to the influence of Fe$_3$O$_4$ nanoparticles on the polymer orientation and overall structure, Fe$_3$O$_4$/PAN composite fiber (F$_2$) showed lower modulus (by ~18%) and strength (~10%) as compared to the similarly drawn control PAN fibers (S$_2$). The composite fibers in the current study show much higher mechanical properties as compared to other literature reports on Fe$_3$O$_4$/polymer composite fibers. For example, tensile strength and tensile modulus of wet-spun Fe$_3$O$_4$/Alginate fibers [14] was reported to be ~100 MPa and ~3GPa, while Fe$_3$O$_4$/cellulose fibers[15] exhibited a tensile strength of ~200 MPa. The magnetic Fe$_3$O$_4$/PAN composite fibers in this study showed mechanical properties comparable to higher than the mechanical properties of typical textile fibers such as nyansons and polyesters.

Fe$_3$O$_4$/PAN composite fibers and PAN control fibers were tested using dynamic mechanical analyzer (DMA). Storage moduli (at 0.1 Hz) of fibers at various draw ratios are plotted in Figure 4.8(a) and 4.8(b). Fibers at higher draw ratio showed higher storage modulus, and fibers with nanoparticles exhibited lower storage modulus than control fibers at the same draw ratio. This is consistent with the tensile property measurement results discussed above. PAN polymer exhibit multiple thermo-mechanical transitions [12, 13, 16, 17]. Figure 4.8(c) and 4.8(d) shows typical $\beta_c$ transition in the range of 50 to
110 °C, which is reported to be associated with the molecular motion from helical sequences in the para-crystalline regions of both iso- and atactic-PAN. The corresponding \( \beta_c \) transition temperature for various fibers at different frequencies and the relative activation energies (calculated using Arrhenius equation) are listed in Table 4.5.

### Table 4.5 Properties of Fe\(_3\)O\(_4\)/PAN composite and control PAN fibers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Draw ratio</th>
<th>Tensile Strength (MPa)</th>
<th>Tensile Modulus (GPa)</th>
<th>Elongation at break (%)</th>
<th>( \beta_c ) transition temperature at various frequencies (Hz)</th>
<th>( E_A ) ( ^{a} ) (KJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(_3)O(_4)/PAN Composite fibers</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( F_m )</td>
<td>17</td>
<td>630 ± 87</td>
<td>16.2 ± 1.5</td>
<td>7.0 ± 0.6</td>
<td>70.7 74.1 80.9 74.1 73.8 79.9 83.0 88.0</td>
<td>442</td>
</tr>
<tr>
<td>( F_2 )</td>
<td>15</td>
<td>499 ± 49</td>
<td>14.2 ± 0.6</td>
<td>7.4 ± 0.6</td>
<td>73.8 79.9 83.0 88.0 78.8 82.1 88.2 90.0</td>
<td>501</td>
</tr>
<tr>
<td>( F_1 )</td>
<td>10</td>
<td>398 ± 46</td>
<td>11.0 ± 0.9</td>
<td>9.1 ± 1.8</td>
<td>78.8 82.1 88.2 90.0 78.8 82.1 88.2 90.0</td>
<td>576</td>
</tr>
<tr>
<td>( F_0 )</td>
<td>2</td>
<td>139 ± 4</td>
<td>6.2 ± 0.4</td>
<td>47.4 ± 7.6</td>
<td>-- -- -- -- -- -- -- -- -- --</td>
<td>--</td>
</tr>
<tr>
<td>Control PAN fibers</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( S_2 )</td>
<td>15</td>
<td>552 ± 81</td>
<td>17.4 ± 1.8</td>
<td>6.0 ± 0.6</td>
<td>69.9 73.1 81.1 84.1 69.9 73.1 81.1 84.1</td>
<td>435</td>
</tr>
<tr>
<td>( S_1 )</td>
<td>10</td>
<td>514 ± 57</td>
<td>15.4 ± 0.7</td>
<td>7.4 ± 1.0</td>
<td>75.9 79.1 86.1 90.1 75.9 79.1 86.1 90.1</td>
<td>466</td>
</tr>
<tr>
<td>( S_0 )</td>
<td>2</td>
<td>195 ± 25</td>
<td>7.1 ± 0.9</td>
<td>35.1 ± 4.0</td>
<td>-- -- -- -- -- -- -- -- -- --</td>
<td>--</td>
</tr>
</tbody>
</table>

\( ^{a} E_A \) is activation energy calculated using the Arrhenius equation, \( f = Aexp\left(-\frac{E_A}{RT}\right) \), where \( f \), \( A \), \( R \), and \( T \) are frequency, constant, gas constant, and absolute temperature, respectively.

Fibers with higher draw ratios exhibited lower tan \( \delta \) peak temperature with decreased magnitude and somewhat lower activation energy for the \( \beta_c \) relaxation. Previous research for \( \beta_c \) relaxation of atactic-PAN [13] had reported similar tendency and this was attributed to the presence of more zigzag (and hence fewer helical) sequences at higher draw ratios. Figure 4.8(d) also reveals the interesting influence of nanoparticles on composite fibers.
Figure 4.8 Dynamic mechanical storage modulus (a and b) and tanδ (c and d) plots for Fe₃O₄/PAN composite and PAN control fibers as a function of temperature at a frequency of 0.1 Hz.

Compared with control fibers at the same draw ratio, Fe₃O₄/PAN composite fibers exhibited increase in tan δ peak magnitude, and resulted in 2 to 5 ºC higher transition temperature and higher activation energy (Table 4.5). This is because nanoparticles hinder polymer mobility and therefore result in increased β_c transition temperature, as well as increased activation energy. CNTs [12] have been reported to cause the same influence on β_c transition temperature and activation energy. However, in contrast to
CNTs, which result in decreased tan δ peak magnitude, Fe₃O₄ nanoparticles led to an increase in the magnitude of tan δ. The reason is that CNTs can induce higher alignment and zigzag sequences of the polymer chains. On the other hand, existence of Fe₃O₄ interferes with the alignment of polymer chains. As indicated by the increased meridional 2θ peak position in the Fe₃O₄/PAN composite fibers as compared to the control PAN fibers of the same draw ratio in Table 4.4, the crystal region of Fe₃O₄/PAN composite fibers may present more helical (fewer zigzag) sequences. As a result, nanoparticles in fibers resulted in increased tan δ peak magnitude of βc relaxation.

**4.3.4 Morphology of Magnetic Fe₃O₄/PAN (10/90) Core and PAN Sheath Bi-component Fibers**

Bi-component composite fibers with composites as one component and pure PAN as the other component can exhibit higher draw ratio than single-component composite fibers. Previous results in Chapter 2 have demonstrated PAN – PAN/CNT bi-component fibers have higher draw ratios than PAN/CNT single-component fibers, and therefore bi-component fibers can improve mechanical properties. As a result, Fe₃O₄/PAN (with 10 wt% Fe₃O₄) core and PAN sheath bi-component fibers were also fabricated by dry-jet-wet spinning in this study. The optical micrographs of fiber cross sections are given in Figure 4.9. Depending on the ratio of flow rates in core and sheath components listed in Table 4.3, different core-sheath fibers can be produced. These bi-component fibers also show non-circular shape in Figure 4.9 with clear PAN sheath and Fe₃O₄/PAN core structure.
Figure 4.9 Optical micrographs of cross sections of (a) FA₀, (b) FB₀, (c) FC₀, and (d) FC₁ composite bi-component fibers.

With pure PAN as the sheath component to maintain the integrity of fibers during processing, the total draw ratios can be as high as 23 with corresponding fiber diameters around 14 ~ 16 μm (Table 4.3). Because the draw ratio of Fe₃O₄/PAN fibers can only reach as high as 17 with the fiber diameter as small as 16 μm (Table 4.2), the bi-component composite fibers exhibited higher draw ratio and smaller fiber diameters than single-component composite fibers. SEM image of FB₃ bi-component fibers is also given in Figure 4.10 with a cross-sectional schematic to illustrate two different components.
4.3.5 Structure and Mechanical Properties of Magnetic Fe₃O₄/PAN (10/90) Core and PAN Sheath Bi-component Fibers

The structural parameters determined by WAXD are listed in Table 4.6. Fully-drawn bi-component fibers can exhibit crystallinity of 52% ~ 58% and crystal size as high as 12.2 nm, which are similar to the values of Fₘ single-component composite fibers. However, fully drawn bi-component fibers can show higher orientation factor than single-component fibers. For example, the orientation factor of sample FA₄ can approach 0.81, which is much higher than the value (0.76) of Fₘ single-component fiber. Besides, fully-drawn bi-component fibers have smaller d-spacing at 2θ ~ 17° and 2θ ~ 30°, and therefore bi-component fibers show more tightly packed structure than single-component fibers.
Table 4.6 Structural parameters of Fe₃O₄/PAN (10/90) core and PAN sheath bi-component fibers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Draw ratio</th>
<th>Xc (b)</th>
<th>L PAN (c)</th>
<th>f PAN (d)</th>
<th>d₂θ ~ 17° (e)</th>
<th>d₂θ ~ 30° (f)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(%)</td>
<td>(nm)</td>
<td>(-)</td>
<td>(nm)</td>
<td>(nm)</td>
</tr>
<tr>
<td>FA3</td>
<td>23</td>
<td>57</td>
<td>12.2</td>
<td>0.79</td>
<td>0.521</td>
<td>0.302</td>
</tr>
<tr>
<td>FA2</td>
<td>15</td>
<td>53</td>
<td>11.2</td>
<td>0.76</td>
<td>0.518</td>
<td>0.301</td>
</tr>
<tr>
<td>FA1</td>
<td>10</td>
<td>52</td>
<td>9.0</td>
<td>0.74</td>
<td>0.521</td>
<td>0.302</td>
</tr>
<tr>
<td>FA0</td>
<td>2</td>
<td>44</td>
<td>3.3</td>
<td>0.32</td>
<td>0.527</td>
<td>0.306</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(r₂/r₁: 2.0)</td>
<td></td>
</tr>
<tr>
<td>FB3</td>
<td>19</td>
<td>56</td>
<td>12.3</td>
<td>0.78</td>
<td>0.519</td>
<td>0.302</td>
</tr>
<tr>
<td>FB2</td>
<td>15</td>
<td>52</td>
<td>12.0</td>
<td>0.75</td>
<td>0.522</td>
<td>0.303</td>
</tr>
<tr>
<td>FB1</td>
<td>10</td>
<td>50</td>
<td>8.9</td>
<td>0.71</td>
<td>0.525</td>
<td>0.303</td>
</tr>
<tr>
<td>FA0</td>
<td>2</td>
<td>49</td>
<td>3.2</td>
<td>0.35</td>
<td>0.528</td>
<td>0.306</td>
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<tr>
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<td></td>
<td></td>
<td></td>
<td>(r₂/r₁: 1.4)</td>
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</tr>
<tr>
<td>FC3</td>
<td>18</td>
<td>52</td>
<td>11.4</td>
<td>0.74</td>
<td>0.520</td>
<td>0.301</td>
</tr>
<tr>
<td>FC2</td>
<td>15</td>
<td>54</td>
<td>11.2</td>
<td>0.73</td>
<td>0.519</td>
<td>0.301</td>
</tr>
<tr>
<td>FC1</td>
<td>10</td>
<td>49</td>
<td>9.2</td>
<td>0.71</td>
<td>0.522</td>
<td>0.303</td>
</tr>
<tr>
<td>FC0</td>
<td>2</td>
<td>42</td>
<td>3.3</td>
<td>0.33</td>
<td>0.523</td>
<td>0.306</td>
</tr>
</tbody>
</table>

a Effective diameter of fibers were calculated from SEM cross section images.
b Xc: crystallinity from integrated radial scans.
c L PAN: crystal size (2θ ~ 17°) according to Scherrer’s equation with K = 0.9.
d f PAN: orientation factor of PAN polymer chains.
e & f d₂θ: d-spacing for 2θ ~ 17° and 30°.

The mechanical properties of various Fe₃O₄/PAN core and PAN sheath bi-component fibers are listed in Table 4.7. Since fully-drawn bi-component fibers show higher draw ratios as well as higher orientation of polymer chains than fully-drawn single-component fibers, bi-component fibers can reach better mechanical properties. For example, FA₄ fibers exhibit tensile strength as high as 963 MPa and tensile modulus as high as 22.8 GPa, which are 50% and 40% higher than the values of fully drawn F₄m fibers. The mechanical properties of these Fe₃O₄/PAN core and PAN sheath bi-component fibers are much better than the mechanical properties of typical polymer fibers. The results also imply polymer/nanoparticle composite fibers with high strength can be carried out using the same approach of bi-component fiber technology.
Table 4.7 Mechanical Properties of Fe₃O₄/PAN (10/90) core and PAN sheath bi-component fibers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Draw ratio</th>
<th>Mechanical Properties</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Tensile Strength (MPa)</td>
<td>Tensile Modulus (GPa)</td>
<td>Elongation at break (%)</td>
</tr>
<tr>
<td></td>
<td>(r₂/r₁: 2.0)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FA₃</td>
<td>23</td>
<td>909 ± 88</td>
<td>22.8 ± 0.6</td>
<td>5.9 ± 0.9</td>
</tr>
<tr>
<td>FA₂</td>
<td>15</td>
<td>745 ± 59</td>
<td>21.5 ± 1.3</td>
<td>7.9 ± 0.5</td>
</tr>
<tr>
<td>FA₁</td>
<td>10</td>
<td>683 ± 51</td>
<td>17.0 ± 0.3</td>
<td>9.7 ± 0.7</td>
</tr>
<tr>
<td>FA₀</td>
<td>2</td>
<td>243 ± 11</td>
<td>8.1 ± 1.2</td>
<td>42.5 ± 7.8</td>
</tr>
<tr>
<td>FB₃</td>
<td>19</td>
<td>843 ± 137</td>
<td>21.8 ± 0.5</td>
<td>7.2 ± 1.2</td>
</tr>
<tr>
<td>FB₂</td>
<td>15</td>
<td>824 ± 114</td>
<td>19.3 ± 1.4</td>
<td>9.0 ± 0.7</td>
</tr>
<tr>
<td>FB₁</td>
<td>10</td>
<td>580 ± 47</td>
<td>15.0 ± 0.8</td>
<td>10.6 ± 0.7</td>
</tr>
<tr>
<td>FA₀</td>
<td>2</td>
<td>220 ± 24</td>
<td>8.0 ± 0.2</td>
<td>29.7 ± 13.8</td>
</tr>
<tr>
<td>(r₂/r₁: 1.4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FC₃</td>
<td>18</td>
<td>869 ± 37</td>
<td>20.7 ± 0.3</td>
<td>7.7 ± 0.3</td>
</tr>
<tr>
<td>FC₂</td>
<td>15</td>
<td>847 ± 87</td>
<td>19.2 ± 1.4</td>
<td>8.3 ± 0.8</td>
</tr>
<tr>
<td>FC₁</td>
<td>10</td>
<td>618 ± 57</td>
<td>16.4 ± 0.3</td>
<td>9.1 ± 0.7</td>
</tr>
<tr>
<td>FC₀</td>
<td>2</td>
<td>222 ± 12</td>
<td>7.8 ± 0.3</td>
<td>39.4 ± 4.9</td>
</tr>
</tbody>
</table>

4.3.6 TGA Test of Fe₃O₄/PAN Magnetic Fibers

Iron oxide has various forms and chemical compositions [18] in nature, and Fe₃O₄ can be easily transformed to the other forms by oxidation or heating. Therefore, as-received Fe₃O₄ nanoparticles were investigated by TGA at the heating rate of 5 °C/min up to 900 °C under air and nitrogen environment (Figure 4.11). According to the WAXD patterns before and after TGA test (Figure 4.12), Fe₃O₄ nanoparticles heated in nitrogen can maintain their structure and chemical composition, but transform to α-Fe₂O₃ (refer to PDF#00-001-1053) when heated in the air. The reason is that Fe₃O₄ would be oxidized to α-Fe₂O₃ as a result of exposure to oxygen at temperature higher than 500 °C [18]. Previous research also demonstrated that Fe₃O₄ nanoparticles start to convert to α-Fe₂O₃ at 210 °C during TGA investigation in air [19].
Figure 4.11 TGA plots of Fe₃O₄ nanoparticles in air and in nitrogen at a heating rate of 5°C/min up to 900°C.

Figure 4.12 WAXD patterns and integrated scans of as-received Fe₃O₄ nanoparticles and corresponding particles after TGA test in N₂ and in air (TGA was done at a heating rate of 5 °C per/min to 900 °C). PDF reference of Fe₃O₄ (PDF#00-019-0629) and α-Fe₂O₃ (PDF#00-001-1053) are also included.
Composite and control fibers were also investigated by TGA at the heating rate of 5 °C/min up to 900 °C (Figure 4.13). SEM images of heat-treated composite fiber after TGA test in air and in nitrogen are shown in Figure 4.14, respectively. The integrity of heat-treated composite fibers in air was destroyed, and the entire composite fiber became irregular particles in the size of ~ 300 - 400 nm. Existence of these large particles indicates the agglomeration of the nanoparticles during heat-treatment in air, and the residue material was identified as α-Fe₂O₃ (with reference PDF#00-001-1053) according to WAXD measurement (Figure 4.14). However, when the composite fibers were investigated by TGA in nitrogen, the heat-treated fibers maintained their fibrous shape and exhibited porous structure with non-agglomerated nanoparticles on the surface of heat-treated composite fibers (Figure 4.13). TGA test in nitrogen for composite fibers led to a broad WAXD peak of amorphous carbonaceous structure (Figure 4.14).
In previous literature studies, it was proposed that Fe₃O₄ may be transformed with carbonaceous materials into Iron carbide (Fe₃C) [6, 7] during stabilization and carbonization. WAXD results in Figure 4.15 also exhibited that Fe₃O₄ nanoparticles were converted into iron carbide (Fe₃C: PDF#00-035-0772) with carbonaceous materials in heat-treated composite fibers after heating by TGA in nitrogen. This implies that
nanoparticle/PAN fibers can be converted to carbon fibers containing nanoparticles such as iron carbide.

![Figure 4.15 WAXD patterns and integrated scans of Fe₃O₄/PAN (F₁ fiber) after TGA tests.](image)

### 4.3.7 Magnetic Properties of Fe₃O₄/PAN Magnetic Fibers

As-received Fe₃O₄ nanoparticles dispersed in DMF was showed in Figure 4.16. Nanoparticles can be attracted by a magnetic bar and the aggregation of particles was formed next to the magnetic bar. When the magnetic bar is removed, the particle can be re-dispersed by shaking and sonication process. The magnetic properties of native magnetite (Fe₃O₄) particles and composite fibers were studied using a superconducting quantum interference devices (SQUID) magnetometer (Quantum Design MPMS-5S). For temperature dependent measurements, the zero-field-cooled (ZFC) curves were measured by cooling samples to 5K through the use of liquid nitrogen, and followed by measuring the magnetization under external field equal to 100 G at various temperatures. The blocking temperature (Tₘ) is defined as the maximum in the ZFC curve, while the
blocking temperature of a nanoparticle is the temperature above which the particle shows superparamagnetism, and below which shows ferrimagnetism or ferromagnetism.

The magnetic properties of native magnetite (Fe₃O₄) particles and composite fibers were studied using a superconducting quantum interference devices (SQUID) magnetometer (Quantum Design MPMS-5S). The temperature dependent magnetization of native particles shows interesting double humps under an applied magnetic field of 100 G (Figure 4.17). It looks like two peaks convoluting as one peak around 250K and the other above 400K. The magnetization of native particles displays a typical hysteresis of field dependence at 5K (Figure 4.17). Both temperature and field dependences of magnetization are consistent with the superparamagnetic behavior of magnetite particles. The double hump feature in temperature dependent magnetization provides two blocking temperatures for the native magnetite particles, which implies a mixture of two sets of particles with distinctly different average sizes. TEM studies in Figure 4.5(b) corroborate the results of magnetic studies, and Figure 4.18 clearly reveals two groups of magnetite
particles with a difference in size distribution by volume fraction. One group of as-received particles shows diameters in the range of $8 - 15 \mu m$, and the other group of particles shows diameters in the range of $22 - 28 \mu m$. Such a mixture in sizes of magnetite particles did not cause any abnormal field dependence of magnetization at 5K. Since field dependent magnetization was below the blocking temperature, the coercivity of the native particles is small but not zero (inset of Figure 4.17). The small coercivity of 209 G is consistent with the magnetically soft nature of magnetite. Remnant magnetization ($M_R$) and saturation magnetization ($M_S$) were 16.3 and 80.7 emu/g, respectively.

Figure 4.17 (a) Zero-field-cooling magnetization under 100 G magnetic field and (b) Field-dependent magnetization of as-received $\text{Fe}_3\text{O}_4$ nanoparticles at 300K with inserted image showing enlarged partial hysteresis curves.
After the magnetite particles were embedded in composite fibers, their magnetic properties did not deviate much from the native particles. Figure 4.19 displays the temperature dependence of magnetization obtained from the F₀ composite fiber with ~10 wt% Fe₃O₄. The field dependent magnetization of magnetic fibers was also studied at 5K. Remnant magnetization (Mₚ) and saturation magnetization (Mₛ) were 18.0 and 79.7 emu/g, respectively. Since the data were derived from the magnetic fibers based upon the pure amount of Fe₃O₄ nanoparticles in the composite, it is clear that all the magnetic properties of native magnetite particles were well preserved and also consistent with the reports in the literatures [20, 21]. In addition, only a single blocking temperature ~250K
was observed in the temperature dependent magnetization of magnetic fibers (Figure 4.19 (a)), suggesting the composite fibers are superparamagnetic at room temperature.

Figure 4.19 (a) Zero-field-cooling magnetization under 100 G magnetic field and (b) Field-dependent magnetization of F₀ fibers at 300K with inserted image showing enlarged partial hysteresis curves.

Although the size composition of magnetite particles in composite fibers is different from their native particles, the remnant magnetization and saturation magnetization have not shown significant changes. The coercivity has displayed a decrease of about 20%. Such a decrease is very likely due to the ligands attachment onto the surface of magnetite nanoparticles in composite fibers. The large coercivity decreases from the surface chemical modification have been reported on several magnetic nanoparticulate systems [22, 23]. The saturation magnetization of the F₀ composite fiber (with 10 wt% Fe₃O₄) can be calculated as ~ 8 emu/g, which is higher than most studies of Fe₃O₄/PAN composite materials [4-7]. The preservation of magnetic properties in the
embedment of magnetic nanoparticles into composite fibers can greatly facilitate the utilization of magnetic nanoparticles. In the physical form of composite fibers, magnetic nanoparticles truly become a type of ready-for-use engineering materials. By manipulating the magnetic properties of the nanoparticles through chemical composition and particle sizes, the composite fibers can provide new type of engineering materials with desired magnetic properties.

4.4 Conclusion

Magnetic Fe$_3$O$_4$/PAN composite fibers were fabricated using dry-jet-wet spinning technology. The single-component magnetic fibers with diameter as small as ~16 μm can exhibit tensile strength as high as 630 MPa and tensile modulus as high as 16 GPa. For Fe$_3$O$_4$/PAN (10/90) core and PAN sheath bi-component fibers, the tensile strength and tensile modulus were increased to as high as 909 MPa and 23 GPa, respectively. Even though Fe$_3$O$_4$ nanoparticles may slight interfere with the polymer chain orientation, Fe$_3$O$_4$/PAN composite fibers in this research exhibit high mechanical properties. Since Fe$_3$O$_4$ nanoparticles also introduced magnetic properties into fibers, Fe$_3$O$_4$/PAN composite fibers can exhibit superparamagnetic properties. With the coercive force (H$_c$) around 165 G, saturation magnetization (M$_s$) around 80 emu/g, and blocking temperature around 250 K, this novel magnetic fiber provide promising application such as hyperthermia (ferromagnetic resonance heating), microwave-absorption, and electromagnetic interference (EMI) shielding. The success of fabrication of Fe$_3$O$_4$/PAN composite fibers also implies the feasibility for the fabrication of myriad composite fibers with different nanoparticles and various innovative properties in the future.
4.5 References


CHAPTER 5

GRAPHENE OXIDE NANORIBBON REINFORCED PAN-BASED
COMPOSITE FIBERS

5.1 Introduction

Graphene nanoribbon (GNR) has the same flat sp² carbon honeycomb layered structure as graphene [1, 2], but GNR has a strip-like structure with a width less than tens of nanometers. GNR with few layers of graphene can be fabricated by a bottom-up synthesis method [3, 4] or by unzipping or opening carbon nanotubes (CNTs) [5-10]. Tour’s research group proposed a facile method to unzip multi-wall carbon nanotubes (MWNTs) by oxidizing CNTs using a KMnO₄/H₂SO₄ solution [9, 10]. The unzipping direction can be controlled and graphene oxide nanoribbons (GONRs) can be produced directly. The aspect ratio and uniformity of GNRs or GONRs can be controlled by the selection of CNT diameters and lengths. The GONRs can be used directly or further reduced to GNR for desired applications.

With their specific physical properties, GNRs and GONRs have been used in different composite materials and applications[11]. After Rafiee et al.[11] proposed an epoxy-based polymer/GNR composite, various polymers [12-19] have been studied to fabricate polymer/GNR composites. Previously, our research group has successfully fabricated PAN/CNT composite fibers and corresponding composite carbon fibers by using gel-spinning technology [20-22]. In this research, the gel-spinning technology was also adopted to fabricate PAN/GNR composite fibers. Both the reinforcement of GNR in
polymer and the carbonized composite fibers is discussed in this chapter. GONR or GNR can be an alternative nano-filler for reinforcement in polymer fibers and carbon fibers.

5.2 Experimental Procedure

5.2.1 PAN/GONR Composite Solution

PAN (homopolymer, viscosity average molecular weight: \(2.5\times10^5\) g/mol) was obtained from Japan Exlan Co. and dried in a vacuum oven at 100 °C for two days. PAN powder was dissolved in dimethylformamide (DMF from Sigma-Aldrich Co.) at a concentration of 15 g/100 ml) at 90 °C. Graphene oxide nanoribbon (GONR) fabricated from multi-wall carbon nanotubes (MWNT, Baytubes with a length of 0.2 ~ 1 μm and an outer diameter of 13 nm) [9, 10] was obtained from Tour’s group at Rice University. GONR was dispersed in DMF at a concentration of 100 mg/300 mL using bath sonication (3510-MT, Branson). The UV-visible absorption of GONR dispersion was obtained using a UV-visible spectrometer (Lambda 35, PerkinElmer). The GONR dispersion was later mixed with the PAN solution, and the excess solvent was evaporated using a vacuum distillation process. The GONR dispersion was added and the solvent removal process was repeated until the desired GONR concentration to PAN was equal to 1 wt%. The final solid content of PAN + GONR and the control PAN solution are listed in Table 5.1.
Table 5.1 Processing parameters of PAN/GONR fibers and PAN fibers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SDR</th>
<th>CDR</th>
<th>HDR</th>
<th>TDR</th>
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<tr>
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<td></td>
<td></td>
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<tr>
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<tr>
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<td>2</td>
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<td><strong>Control PAN Fibers</strong></td>
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</tr>
<tr>
<td>Spinning Flow Rate: 1 mL/min</td>
<td></td>
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<td></td>
<td></td>
</tr>
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<td>B30</td>
<td>3</td>
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<td>A02</td>
<td>1</td>
<td>2</td>
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</tbody>
</table>
| **a** SDR – spin draw ratio, CDR – draw ratio at room temperature, HDR – draw ratio at 165 °C, TDR – total draw ratio.

### 5.2.2 Gel Spinning PAN/GONR Composite Fibers

The PAN/GONR composite fibers were spun using a spinning unit manufactured by Hills, Inc (Melbourne FL). Composite solution was maintained at 70 °C in the solution reservoir and extruded through a single-hole spinneret with a diameter of 200 μm maintained at 90 °C. The extrudate was passed through a 25-mm air gap and then through
a methanol gelation bath maintained at –50 °C. The as-spun fibers were collected with a spin draw ratio of 1 and 3 and then stored in methanol bath at –50 °C overnight. The composite fibers were subsequently drawn at room temperature and later drawn at 165 °C in glycerol. The control PAN fibers were spun with the same processing method. The spinning condition and the draw ratios of different PAN/GONR fibers and control PAN fibers are listed in Table 5.1.

5.2.3 Stabilization and Carbonization of Composite Fibers

The stabilization of the composite fibers was carried out in a box furnace (Blue M Electric) in air. A bundle of fibers was clamped at a stress of 25 MPa. The fibers were heated from room temperature up to 270 °C at a heating rate of 3 °C/min and held at 270 °C for 400 minutes. Then, they were heated up to 315 °C at a heating rate of 3 °C/min and held at 315 °C for 15 minutes. The stabilized fibers were subsequently carbonized by heating up to 1000, 1200, and 1300 °C at a heating rate of 5 °C/min in nitrogen at the same stress of 25 MPa (based on precursor fiber diameters), and the temperature was hold at 1000, 1200, and 1300 °C for 5 minutes, respectively. The carbonized fibers were finally cooled down by purging nitrogen in the furnace.

5.2.4 Characterization

Fiber bundles were embedded in epoxy resin (Epo-Fix, Electron Microscopy Sciences) and then sliced into 10 – 15 μm thick sections using a microtome (Leica, RM2255). These fiber cross-sections were then observed using a scanning electron microscope (SEM, Zeiss Ultra60). Epoxy resin (Epo-Tek, Gatan, Inc.) was used to mount the PAN/GONR fibers on a copper 3-post Omniprobe lift-out grid (Electron Microscopy Sciences). Transverse fiber sections were etched by focus ion beam (FEI Nova Nanolab...
200 FIB/SEM) at ion accelerating voltages of 30 keV and 5 keV. Samples were thinned until electron transparency was achieved and observed using a transmission electron microscope (TEM, FEI Tecnai F30), operated at 80 keV. As-received GONRs were also observed by TEM (JEOL JEM 100C), and the samples were prepared by slowly evaporating a drop of GONR suspension in DMF on an amorphous carbon-coated copper grid at room temperature. The Raman spectra of composite fibers were collected using an optical microscope (Olympus BX41) and the XploRA system (HORIBA) using a 785 nm excitation laser with a polarizer and an analyzer parallel to each other. The composite fibers were placed parallel (0°) or perpendicular (90°) to the polarizer and analyzer during measurement.

Tensile properties were measured at a gauge length of 25.4 mm and at a cross-head speed of 2 mm/min using Favimat (Textechno Herbert Stein GmbH & Co. KG.). Fiber diameters were calculated from their linear density, which was also measured with Favimat. The PAN density was assumed to be 1.18 g/mL and the carbon fiber density was assumed to be 1.8 g/mL. Dynamic mechanical analysis (DMA) was carried out using RSA III with frequencies of 0.1, 1, 10, and 80 Hz at a heating rate of 1 °C/min on a bundle (25.4 mm length) of 100 filaments. Wide angle X-ray diffraction (WAXD) was conducted on fiber bundles using CuKα (λ=0.1542 nm), which is generated by Rigaku Micromax-002 (operating voltage and current 45 KV and 0.65 mA). Diffraction patterns were recorded by a detection system (Rigaku R-axis IV++) and analyzed by AreaMax (version 1.00) and MDI Jade (version 9.0). From the WAXD data, the structural parameters, including polymer crystallinity (Xc), crystal size (L) from equatorial scans,
full width at half maximum (Z) from azimuthal scans, and the Herman’s orientation factors (f), were determined according to previously described methods [23-25].

5.3 Results and Discussion

5.3.1 Dispersion of GONR

GONR was fabricated by unzipping MWNT, whose original length and diameter were 0.2 ~ 1 μm and 13 nm, respectively. The SEM images of as-received GONR and the corresponding width distribution of GONR width are shown in Figure 5.1. The average width of GONR is 39 nm ± 4 nm, which matches the diameter (13 nm) of the un-zipped MWNT.

![Figure 5.1 (a) SEM images of as-received GONR and (b) the number fraction of GONR width distribution.](image)

Figure 5.1 (a) SEM images of as-received GONR and (b) the number fraction of GONR width distribution.

The TEM image of partial un-zipped CNT is given in Figure 5.2. We can observe the part of un-opened CNT with the diameter ~ 15 nm and the other part of un-zipped CNT (GONR) with a width from 20 nm to higher than 40 nm owing to the flexibility of graphene sheets.
Before mixed with the PAN solution, GONR was dispersed in DMF by sonication. The GONR dispersion was investigated using UV-visible spectroscopy, and the UV-visible absorption spectra are given in Figure 5.3. For graphene oxide, several studies [26-28] have reported a typical absorption peak ~ 280 nm due to $n - \pi^*$ transition of C=O bond [28, 29]. When the sonication time increases, the characteristic peak grows. The increase of UV-visible absorption during the sonication process has also been found in carbon nanotube dispersion [30] and carbon black dispersion [31]. This is because the sonication process assists the dispersion of aggregated GONR and therefore increases the total GONR surface area exposed to UV radiation. As a result, the absorption peak grows
at the beginning of sonication, and the magnitude gradually reaches maximum when sonication time is longer than 12 hours. The absorption peak intensity for 12 and 24 hours of sonication are almost the same, indicating that dispersion conditions over 12 hours and 24 hours of sonication are similar. In this research, GONR dispersion was sonicated for 24 hours before it was mixed with the PAN solution in order to improve the dispersion and homogeneity of the GONR.

![Absorption spectra of GONR dispersion in DMF with various sonication times.](image)

Figure 5.3 UV-Visible absorption spectra of the GONR dispersion in DMF with various sonication times. The inset figure shows the maximal absorption at 270 ~290 nm with various sonication times.

### 5.3.2 Morphology of Gel-Spun PAN/GONR Composite Fibers

PAN/GONR composite fibers were fabricated successfully by using gel-spinning technology. However, the solid content of the PAN/GONR solution (18 g/100 mL) was higher than that of control PAN solution (15 g/100 mL) in Table 5.1. This is because the viscosity of the PAN/GONR solution with a solid content of 15 g/100 mL was too low to
spin. Therefore, it became necessary to adopt a higher solid content for the composite fiber during spinning process. Figure 5.4 (a) shows the spool of gel-spun fibers, and the GB₀₃ composite fibers were sectioned using a microtome and then observed by an optical microscope (Figure 5.4 (b)). Note that the shape of the cross section is irregular owing to the non-uniform counter-diffusion of DMF and methanol during the coagulation/gelation process [32].

Figure 5.4 (a) A spool of PAN/GONR composite fiber and (b) micrograph of GB₀₃ fiber cross sections.

SEM image (Figure 5.5 (a)) shows that the fiber lateral surface of GB₀₃ composite fibers is smooth. According to the SEM image (Figure 5.5 (b)) of the fractured surface from the same GB₀₃ fiber, some GONRs can be found and are indicated by arrows in Figure 5.5 (b). The average width of these strip-like materials is 41.3 ± 5.6 nm. Figure 5.6 shows SEM images of cross sections of GB₃₀ composite fibers, and one can see noncircular cross sections [32], which are similar to the results in Figure 5.4 (b). The diameter of GB₃₀ composite fibers is smaller than 15 μm, and the effective diameter of fibers can be calculated from fiber linear density obtained via Favimat and PAN density of 1.18 g/ml. The diameters of both composite and control fibers are listed in Table 5.2.
(Section 5.3.4), and the fiber diameter value varies from 11 ~ 67 μm, depending on the fiber draw ratios.

Figure 5.5 SEM images of (a) fiber lateral surface of a GB_{03} fiber and (b) fractured surface with GONRs protruding from the surface indicated by arrows. The image of fractured surface is taken from the broken fiber in the inset image.

Figure 5.6 SEM images of GB_{30} fiber cross-sections.

The longitudinal cross-section of GB_{30} composite PAN/GONR fibers were observed in TEM after preparation using a focused ion beam. Figure 5.7 reveals that GONR (as dark gray strip) is embedded in the polymer matrix and aligned along the fiber direction. The schematic also illustrates the width of GONR in the fibers varies from 10 nm to 30 nm, which is less than the original GONR width of ~ 40 nm. Since the GONRs
may be twisted, folded, or rotated in the fibers, the GONR width shown in the TEM image obtained from the transverse section of fibers is less than the width of flat or expanded GONRs.

Figure 5.7 (a) TEM image of GB30 fiber with an arrow indicating the fibril axial direction and (b) a schematic illustrating the GONR strip in the TEM image.

5.3.3 Dissolution of PAN/GONR Composite Fibers

PAN/GONR composite fibers were partially dissolved in DMF solvent to investigate the interior structure. GA02 composite fibers (draw ratio = 2) were placed in DMF at room temperature for various lengths of time, and the images of the fibers are shown in Figure 5.8. After 3 minutes, the fibers begin to dissolve, and the polymer was diffusing out of the fibers. After 7 minutes, because partial polymer was removed, the middle part of the fibers could not sustain the weight of the bottom fibers, and finally the bundle broke. The broken bundle floated and retained its shape in the solvent.
Interestingly, when the remaining part of the fibers is observed in SEM, the fibers exhibit porous structure in Figure 9. This image suggests some of the polymer inside the fiber dissolved out of the composite and left porous network structure. The remaining GONR maintained the frame, and some of the polymer was still patched on the GONRs. By analyzing the SEM image, Figure 10 reveals the distribution of strip width and the distribution of the void size. The average width of these strips was 88 ± 22 nm. Since the original GONRs showed an average width of 40 nm, at least approximately 20 nm in thickness of polymer is still coated on the GONRs, suggesting that there is interaction between PAN and GONR. A similar phenomenon has already been reported for polymer/CNT composite materials [22, 33, 34]. In addition, the porous structure consisted of voids of various sizes from as small as approximately 200 nm to as large as
700 nm, and the average size was 394 ± 105 nm. This implies the composite fibers can be harnessed for more promising research and applications, such as in filtration, fuel cells, and capacitors.

Figure 5.9 SEM images of GA_{02} PAN/GONR composite fibers after being placed in DMF for 15 minutes.

Figure 5.10 Number fraction of (a) strip width distribution and (b) void size distribution analyzed from Figure 5.9 (b).
GA_{20} PAN/GONR composite fibers (draw ratio = 20) were also placed in DMF at room temperature. However, the composite fibers with higher draw ratios show higher resistance to the solvent. In contrast to GA_{02} composite fibers (draw ratio = 2) dissolved in DMF within one hour, Figure 5.11 (a) exhibits GA_{20} composite fibers still survived even after the fibers were put in DMF for one week. The reason is high draw ratio improves the fiber structure such as higher crystallinity, inducing higher resistance to the solvent, and therefore fibers with higher draw ratio can exist in DMF for a longer time. In addition, A_{20} control PAN fibers (draw ratio = 20) were also put in DMF for one week, but Figure 5.11 (b) shows most control fibers were dissolved. According to SEM images (Figure 5.12) of GA_{20} composite fibers after being placed in DMF for one week, the fiber surface was only slightly etched and there was no porous morphology on the fiber lateral surface. This implies that the existing of GONRs in fibers can help to maintain the fiber integrity and improve the resistance to the solvent.

Figure 5.11 (a) GA_{20} PAN/GONR composite fibers and (b) A_{20} control PAN fibers after being placed in DMF for one week.
5.3.4 Structure of PAN/GONR Composite Fibers

Raman spectra of GB30 composite are given in Figure 5.13. The fiber was measured parallel (0°) or perpendicular (90°) to the polarized incident beams, and both peaks of the $D$-band ($A_{1g}$, disorder or defect carbonaceous structure) at $\sim 1300 \text{ cm}^{-1}$ and the $G$-band ($E_{2g}$, graphite) at $\sim 1580 \text{ cm}^{-1}$ [35-37] are exhibited in the spectra. Since graphene nanoribbon was oxidized, the peak of the $D$-band is obvious. The ratio between $D$ and $G$ peak intensities, which is denoted as $I_D/I_G$ [38-40] and used as a measure of the quantity of ordered graphitic structure, is around 0.37. In addition, the peak intensity is much higher when the fiber was parallel to the polarization direction, suggesting high GONR orientation to the fiber axis.
Figure 5.13 Raman spectra of GB$_{30}$ composite fibers parallel (0°) and perpendicular (90°) to the polarization direction.

The influence of GONRs on the fiber structure is investigated by analyzing 2-dimensional wide-angle X-ray diffraction (WAXD), and the structural parameters of the fiber under various draw ratios are listed in Table 5.2. Generally, a higher draw ratio results in higher crystallinity ($X_c$), larger crystal size ($L_c$), and higher polymer chain orientation ($f_{\text{PAN}}$). However, GONRs in composite fibers also induce higher crystallinity and a larger crystal size. The orientation factor of PAN is also slightly increased owing to GONRs. For example, GB$_{30}$ composite fibers exhibit crystallinity of 75% and a crystal size of 11 nm, which are 19% higher and 10% larger than the values from B$_{30}$ control fibers. The orientation factor of PAN is also increased from 0.831 to 0.851. In addition, investigating the d-spacing of crystal planes (200, 010) at $2\theta \sim 17^\circ$ and crystal planes (310, 020) at $2\theta \sim 30^\circ$ [20, 23] from the WAXD equatorial scans reveals that GONR also induced a slight decrease in d-spacing. Because d-spacing represents the packing...
condition of polymer chains, smaller d-spacing indicates closer packing. For example, fibers with higher draw ratios have more aligned polymer chains and closer packing, and therefore the d-spacing decreases with the increase of draw ratios [20].

Table 5.2 Structural parameters of PAN/GONR composite and control PAN fibers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Effective Diameter (^a) (µm)</th>
<th>PAN Structural Parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>GB(_{30})</td>
<td>13.0 ± 0.7</td>
<td>(X_c^\text{b}) (%)</td>
<td>75</td>
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<tr>
<td>GB(_{20})</td>
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<td>GB(_{15})</td>
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<td>10.9</td>
</tr>
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<td>GA(_{01})</td>
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<td>3.2</td>
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</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Effective Diameter (^a) (µm)</th>
<th>PAN Structural Parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>GB(_{30})</td>
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<td>(L_{\text{PAN}}^\text{c}) (nm)</td>
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<td>GB(_{20})</td>
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<td>9.2</td>
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<td>16.0 ± 0.9</td>
<td>56</td>
<td>9.2</td>
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<td>49.4 ± 4.0</td>
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</table>

\(^a\) The effective diameters of fibers were calculated from the linear density obtained by Favimat and the density of PAN (1.18 g/mL).
\(^b\) \(X_c\): crystallinity from integrated radial scans.
\(^c\) \(L_{\text{PAN}}\): crystal size (2\(\theta\) ~ 17\(^o\)) according to Scherrer’s equation with \(K = 0.9\).
\(^d\) \(f_{\text{PAN}}\): orientation factor of PAN polymer chains.
\(^e\) & \(^f\) \(d_{2\theta}\): d-spacing for 2\(\theta\) ~ 17\(^o\) and ~ 30\(^o\).
\(^g\) \(2\theta_{\text{meridional}}\): meridional peak position.
Composite fibers exhibit smaller d-spacing than control fibers under the same draw ratio, suggesting that GONRs induces a closer packing condition and a more orientated structure. This phenomenon can be also observed from the meridional PAN peak at ~ 40° ($2\theta_{\text{meridional}}$), which provides information of chain conformation along the fiber axis and indicates the tendency of the presence of planar zigzag sequences [20, 41, 42]. Fibers with a higher draw ratio [20] or under higher strain [42] show a more stretched structure, and the meridional PAN peak at ~ 40° decreases slightly. Since the existence of GONR increases the orientation of PAN and induces a closer packing structure, composite fibers also exhibit a decrease in $2\theta_{\text{meridional}}$, suggesting a more stretched planar zigzag structure.

### 5.3.5 Mechanical Properties of PAN/GONR Composite Fibers

The mechanical properties of composite and control fibers at various draw ratios are listed in Table 5.3. The tensile strength and modulus of PAN/GONR (GA series) and PAN (A series) fibers are also shown in Figure 5.14. The PAN/GONR fibers exhibit better mechanical properties than PAN fibers. For example, GA$_{20}$ fibers show tensile strength and modulus 35 % and 18 % higher than A$_{20}$ PAN fibers. When the draw ratio is 30, GB$_{30}$ PAN/GONR fibers show the tensile strength as high as 0.9 GPa and the tensile modulus as high as 21.3 GPa with the elongation at break of 7.4%. According to the structural parameters in Table 5.2, since GONRs can induce higher crystallinity with a larger crystal size and increase orientation of PAN, the existence of GONR can reinforce the fibers and improve the mechanical properties.
Table 5.3 Mechanical Properties of PAN/GONR composite and control PAN fibers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile Strength (GPa)</th>
<th>Tensile Modulus (GPa)</th>
<th>Elongation at Break (%)</th>
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<td>66.2 ± 7.3</td>
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<td>119.9 ± 14.2</td>
</tr>
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<td>20.6 ± 0.6</td>
<td>6.0 ± 0.8</td>
</tr>
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<td>19.6 ± 0.8</td>
<td>7.5 ± 0.4</td>
</tr>
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<td>0.67 ± 0.05</td>
<td>17.4 ± 0.5</td>
<td>9.1 ± 0.6</td>
</tr>
<tr>
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<td>0.23 ± 0.03</td>
<td>7.4 ± 0.2</td>
<td>64.9 ± 6.3</td>
</tr>
<tr>
<td>GA01</td>
<td>0.12 ± 0.03</td>
<td>5.8 ± 0.3</td>
<td>121.8 ± 16.5</td>
</tr>
<tr>
<td><strong>Control PAN Fibers</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B30</td>
<td>0.83 ± 0.04</td>
<td>19.1 ± 0.6</td>
<td>6.9 ± 0.3</td>
</tr>
<tr>
<td>B20</td>
<td>0.76 ± 0.06</td>
<td>16.7 ± 0.6</td>
<td>7.9 ± 0.5</td>
</tr>
<tr>
<td>B15</td>
<td>0.67 ± 0.06</td>
<td>16.4 ± 1.0</td>
<td>9.0 ± 0.3</td>
</tr>
<tr>
<td>B10</td>
<td>0.42 ± 0.03</td>
<td>11.6 ± 0.6</td>
<td>10.6 ± 1.0</td>
</tr>
<tr>
<td>B05</td>
<td>0.28 ± 0.04</td>
<td>9.4 ± 0.5</td>
<td>25.5 ± 6.9</td>
</tr>
<tr>
<td>A20</td>
<td>0.59 ± 0.10</td>
<td>17.5 ± 0.7</td>
<td>5.9 ± 0.5</td>
</tr>
<tr>
<td>A15</td>
<td>0.55 ± 0.08</td>
<td>17.4 ± 0.8</td>
<td>6.0 ± 0.6</td>
</tr>
<tr>
<td>A10</td>
<td>0.51 ± 0.06</td>
<td>15.4 ± 0.7</td>
<td>7.4 ± 1.0</td>
</tr>
<tr>
<td>A02</td>
<td>0.20 ± 0.03</td>
<td>7.1 ± 0.9</td>
<td>35.1 ± 4.0</td>
</tr>
</tbody>
</table>

Figure 5.14 (a) Tensile strength and (b) tensile modulus of PAN/GONR (GA series) and PAN (A series) fibers at various draw ratios.
The composite and control fibers were also investigated using a dynamic mechanical analyzer (DMA) at different frequencies of 0.1, 1, 10, and 80 Hz. Similar to the tensile properties, fibers with higher draw ratios and fibers with GONR show higher storage moduli (at 10 Hz) as plotted in Figure 5.15 (a) and (b). In addition, the plots of tan δ show typical βc transition [41] in the range of 60 to 110 °C in Figure 5.15 (c) and (d). βc transition is one of the multiple thermo-mechanical transitions [20, 41, 43, 44] for PAN, and this transition temperature is associated with the molecular motion from helical sequences in the para-crystalline regions. Table 5.4 lists the βc transition temperatures for composite and control fibers at various frequencies. The corresponding activation energies calculated using the Arrhenius equation are also listed in Table 5.4. In general, when the draw ratio is increased, the βc transition temperature decreases, and both the magnitude of tan δ peak and the activation energy of the βc relaxation are reduced. Take GB15 and GB30 as examples. The transition temperature of βc is decreased from 93 °C to 80 °C, and the activation energy was reduced from 701 to 509 KJ/mol. This is because of the presence of more zigzag (and hence fewer helical) sequences at higher draw ratios [41].

According to Figure 5.15 (d), GONRs also affect tan δ peak and slightly increased βc transition temperature. In Table 5.4, the transition temperatures of the composite fibers are 3 ~ 8 °C higher than those of the control fibers under the same draw ratios, suggesting that GONRs can hinder or constrain the mobility of PAN polymer chains. The activation energy indicates the same influence and shows a higher value for the composite fibers in Table 5.4. The composite fibers also showed a slight decrease in the magnitude of tan δ peak. Since βc transition represents the molecular motion of helical sequences, and since
the existence of GONRs induced more zigzag structure as a result of the closer packing structure and decreased meridional 2θ peak position, more stretched polymer chains and hence less helical structure was induced in the composite fibers. Therefore, the magnitude of tan δ is decreased in Figure 5.15 (d). The above phenomenon is similar to the influence of CNT [20] on PAN composite fibers, suggesting that GONRs have somewhat similar influence on polymer chains.

Figure 5.15 Dynamic mechanical storage modulus (a and b) and tan δ (c and d) plots for PAN/GONR composite and PAN control fibers as a function of temperature at a frequency of 10 Hz.
Table 5.4 Dynamic mechanical analysis results of PAN/GONR and PAN fibers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \beta_c ) transition temperature at various frequencies (Hz)</th>
<th>( E_A^{a} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( 0.1 )</td>
<td>( 1 )</td>
</tr>
<tr>
<td>PAN/GONR Composite fibers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GB30</td>
<td>67</td>
<td>71</td>
</tr>
<tr>
<td>GB20</td>
<td>78</td>
<td>83</td>
</tr>
<tr>
<td>GB15</td>
<td>84</td>
<td>89</td>
</tr>
<tr>
<td>GA20</td>
<td>70</td>
<td>75</td>
</tr>
<tr>
<td>GA15</td>
<td>74</td>
<td>78</td>
</tr>
<tr>
<td>GA10</td>
<td>79</td>
<td>84</td>
</tr>
<tr>
<td>Control PAN fibers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B30</td>
<td>63</td>
<td>67</td>
</tr>
<tr>
<td>B20</td>
<td>76</td>
<td>81</td>
</tr>
<tr>
<td>B15</td>
<td>80</td>
<td>85</td>
</tr>
<tr>
<td>B10</td>
<td>84</td>
<td>88</td>
</tr>
<tr>
<td>A20</td>
<td>63</td>
<td>68</td>
</tr>
<tr>
<td>A15</td>
<td>70</td>
<td>73</td>
</tr>
<tr>
<td>A10</td>
<td>76</td>
<td>79</td>
</tr>
</tbody>
</table>

\( ^{a} \) \( E_A \) is activation energy calculated using the Arrhenius equation, \( f = Aexp\left(-\frac{E_A}{KT}\right) \), where \( f \), \( A \), \( R \), and \( T \) are frequency, constant, gas constant, and absolute temperature, respectively.

5.3.6 PAN/GONR Composite Carbon Fibers

Composite (GB30) and control PAN fibers (B30) with the highest draw ratios were selected for stabilization and carbonization. A bundle of fibers was stabilized under a stress of 25 MPa in air at 270°C for 400 minutes and then at 315 °C for another 15 minutes. Stabilized fibers were subsequently carbonized in nitrogen at 1000, 1200, and 1300 °C for 5 minutes. Fibers with different stabilization and carbonization process are summarized and designated in Table 5.5. According to SEM images of GC1 composite carbon fibers in Figure 5.16, the size of the fibers is approximately 7 μm in diameters.
after the carbonization process. Figure 5.16 also reveals higher magnified SEM images and shows graphitic structure on the fractured surface of composite carbon fibers. GONR may be reduced to GNR [19] and emerged into graphitic structure after stabilization and carbonization process.

![SEM images of GC1 composite carbon fiber. (b) ~ (d) high magnification images of selected regions in (a).](image)

Stabilized fibers and carbonized fibers were also investigated by using wide angle x-ray, and the diffraction patterns and the integrated radial scans of GB$_{30}$ fibers in different stages are illustrated in Figure 5.17. During the stabilization process, PAN structure is converted to ladder structure, and subsequently transformed into graphite during carbonization process [25, 45]. Therefore, typical diffraction peaks of PAN (at 2θ ~ 17° and 30°) disappear after stabilization and carbonization processes, and the
diffraction peaks of carbon ladder (at \(2\theta \sim 26^\circ\)) and graphitic structure (at \(2\theta \sim 26^\circ\) and \(43^\circ\)) occurs for stabilized and carbonized fibers.

The corresponding structural parameters of different stabilized and carbonized fibers are calculated and summarized in Table 5.5. The orientation factors of the stabilized fibers are lower than that of the precursor fibers and the final carbonized fibers, which has been reported previously [25, 46]. If we compare PAN/GONR and PAN fibers after stabilization and carbonization process, composite fibers show closer packing of graphitic structure (lower d-spacing at \(2\theta \sim 26^\circ\)) and a slightly larger crystal size with a smaller FWHM (full width at half maximum) of graphite (002) plane from azimuthal scans. This means GONRs can improve the graphitic structure, and therefore leads to decreased d-spacing and increased crystal size. Fibers at different carbonization
temperature show similar structural parameters, but higher carbonization temperature induces a slightly larger crystal size, suggesting the carbonization temperature can also influence the graphitic structure.

Table 5.5 Structural parameters of stabilized and carbonized PAN/GONR and PAN fibers.

<table>
<thead>
<tr>
<th>Sample Description (holding temperature/time)</th>
<th>Structural parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Stabilized fibers</strong></td>
<td></td>
</tr>
<tr>
<td>PAN/GONR composite fibers (GB30)</td>
<td></td>
</tr>
<tr>
<td>GS1 (1)270 °C/400 min (2)320 °C/15 min</td>
<td>f_{Ladder}^b Z_{Ladder}^c d_{2θ<del>26°}^d L_{2θ</del>26°}^e L_{2θ~43°}^f</td>
</tr>
<tr>
<td></td>
<td>0.449 45.6 3.399 1.1 1.2</td>
</tr>
<tr>
<td>PAN fibers (B30)</td>
<td></td>
</tr>
<tr>
<td>S1 (1)270 °C/400 min (2)320 °C/15 min</td>
<td>f_{Ladder}^b Z_{Ladder}^c d_{2θ<del>26°}^d L_{2θ</del>26°}^e L_{2θ~43°}^f</td>
</tr>
<tr>
<td></td>
<td>0.418 46.7 3.433 1.1 1.2</td>
</tr>
<tr>
<td><strong>Carbonized fibers</strong></td>
<td></td>
</tr>
<tr>
<td>PAN/GONR composite fibers (GB30)</td>
<td></td>
</tr>
<tr>
<td>GC1 1300 °C/5 min</td>
<td>f_{(002)}^a Z_{(002)}^b d_{2θ<del>26°}^c L_{2θ</del>26°}^d L_{2θ~43°}^d</td>
</tr>
<tr>
<td></td>
<td>0.684 29.3 3.492 1.5 1.9</td>
</tr>
<tr>
<td>GC2 1200 °C/5 min</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.682 29.5 3.496 1.3 1.7</td>
</tr>
<tr>
<td>GC3 1000 °C/5 min</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.687 30.0 3.499 1.2 1.4</td>
</tr>
<tr>
<td>GC4 1300 °C/50 min</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.689 29.9 3.501 1.5 2.0</td>
</tr>
<tr>
<td>PAN fibers (B30)</td>
<td></td>
</tr>
<tr>
<td>C1 1300 °C/5 min</td>
<td>f_{(002)}^a Z_{(002)}^b d_{2θ<del>26°}^c L_{2θ</del>26°}^d L_{2θ~43°}^d</td>
</tr>
<tr>
<td></td>
<td>0.673 30.7 3.518 1.2 1.8</td>
</tr>
<tr>
<td>C2 1200 °C/5 min</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.679 29.7 3.520 1.3 1.4</td>
</tr>
<tr>
<td>C3 1000 °C/5 min</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.678 30.1 3.516 1.1 1.4</td>
</tr>
</tbody>
</table>

- \( f \): orientation factor of stabilized ladder structure and carbonized graphite (002) plane.
- \( Z \): Full width at half maximum (FWHM) from azimuthal scans of a stabilized ladder structure and carbonized graphite (002) plane at \( 2θ \sim 26° \).
- \( d_{2θ~26°} \): d-spacing for peak at \( 2θ \sim 26° \).
- \( L \): crystal size (\( 2θ \sim 26° \) and \( 2θ \sim 43° \)) according to Scherrer’s equation with \( K = 0.9 \).

The diameters and the mechanical properties of carbonized fibers are listed in Table 5.6. The effective diameters of various carbon fibers obtained via Favimat are approximately 6.5 ~ 8 μm, and higher carbonization temperature results in a slightly
smaller fiber diameter. Carbonized composite fibers exhibit somewhat better mechanical properties than control fibers. For examples, GC\textsubscript{2} composite carbon fibers exhibit a tensile strength of 1.82 GPa and a tensile modulus of 229 GPa, which are 17\% and 13\% higher than the results from the control C\textsubscript{2} fibers under the same carbonization process. This value is also better than the commercial P-25 carbon fibers, which has a tensile strength 1.38 GPa and a tensile modulus of 159 GPa [47].

Table 5.6 Mechanical properties of carbonized PAN/GONR composite fibers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Effective Diameter (a) (μm)</th>
<th>Tensile Strength (GPa)</th>
<th>Tensile Modulus (GPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN/GONR composite fibers (GB\textsubscript{30})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GC\textsubscript{1}</td>
<td>6.8 ± 0.4</td>
<td>1.62 ± 0.24</td>
<td>230 ± 9</td>
<td>0.66 ± 0.11</td>
</tr>
<tr>
<td>GC\textsubscript{2}</td>
<td>7.0 ± 0.3</td>
<td>1.82 ± 0.38</td>
<td>229 ± 9</td>
<td>0.79 ± 0.20</td>
</tr>
<tr>
<td>GC\textsubscript{3}</td>
<td>7.3 ± 0.5</td>
<td>1.72 ± 0.26</td>
<td>196 ± 5</td>
<td>0.84 ± 0.16</td>
</tr>
<tr>
<td>GC\textsubscript{4}</td>
<td>6.8 ± 0.3</td>
<td>1.17 ± 0.20</td>
<td>232 ± 6</td>
<td>0.49 ± 0.10</td>
</tr>
<tr>
<td>PAN fibers (B\textsubscript{30})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{1}</td>
<td>6.5 ± 0.5</td>
<td>1.58 ± 0.23</td>
<td>222 ± 7</td>
<td>0.72 ± 0.10</td>
</tr>
<tr>
<td>C\textsubscript{2}</td>
<td>7.3 ± 0.7</td>
<td>1.56 ± 0.21</td>
<td>203 ± 7</td>
<td>0.75 ± 0.10</td>
</tr>
<tr>
<td>C\textsubscript{3}</td>
<td>7.8 ± 0.7</td>
<td>1.64 ± 0.22</td>
<td>184 ± 10</td>
<td>0.86 ± 0.15</td>
</tr>
</tbody>
</table>

\(a\) The effective diameters of the fibers were calculated from linear density measured by Favimat and the density of carbon fiber (1.8 g/cm\textsuperscript{3}).

Table 5.6 also reveals the influence of carbonization temperature on mechanical properties. Because higher carbonization temperature induces a larger crystal size of PAN (Table 5.5), tensile moduli are higher when both composite and control fibers are carbonized at higher temperature. For example, GC\textsubscript{1} fibers (carbonized at 1300 °C) exhibit tensile modulus of 230 GPa, which is 17\% higher than the value of GC\textsubscript{3} fibers.
(carbonized at 1000 °C). However, higher carbonization temperature also lowers the elongation at break. Therefore, tensile strength decreases with increasing carbonization temperature. When composite fibers are carbonized at 1300 °C for 50 min (ten times carbonization time than GC₁ fibers), GC₄ fibers become significantly brittle with only 0.49 % elongation at break. Although the tensile modulus is 232 GPa similar to that of GC₁ fiber, the tensile strength (1.17 GPa) decreased by 28%. As a result, appropriate control of carbonization temperature and length of carbonization time are crucial for obtaining better mechanical properties.

5.4 Conclusions

The gel-spinning method was used to successfully fabricate PAN/GONR composite fibers with a diameter as small as 13 μm with 1 wt% GONRs in the polymer. GONRs influenced the structure of PAN and induced higher crystallinity and a larger crystal size in fibers. These GONR-reinforced composite fibers can achieve a tensile strength as high as 0.9 GPa and a tensile modulus as high as 21.3 GPa, which is 8.4% and 11.5% increase over the control PAN fiber at the same draw ratio of 30. PAN/GONR composite fibers were also stabilized at 270 °C and 315 °C in air, and subsequently carbonized in nitrogen in the temperature range of 1000 ~ 1300 °C. After the stabilization and carbonization process, the fiber diameter was reduced to approximately 7 μm, and the tensile strength and tensile modulus of composite carbon fibers increased to as high as 1.82 GPa and 232 GPa, respectively.
5.5 References


CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

PAN – PAN/CNT core-sheath bi-component fibers with a diameter of < 20 μm were fabricated successfully by using gel-spinning technology. When the bi-component fiber method is used, the pure PAN component could maintain the integrity of the fibers during the drawing process and therefore induce higher draw ratios and better mechanical properties. Composite fibers with 20 wt% CNT exhibited fiber tensile strength as high as 560 MPa and tensile modulus as high as 18 GPa, and Composite fibers with 10 wt% CNT exhibited fiber tensile strength as high as 720 MPa and tensile modulus as high as 20 GPa. In addition, because of the re-arrangement of CNTs, the annealing process enhanced both electrical and thermal conductivity of composite fibers. The electrical conductivity of annealed composite fibers was as high as 0.366 S/m at 10 wt% CNT content and 4.408 S/m at 20 wt% CNT content, and thermal conductivity was as high as ~7 Wm⁻¹ K⁻¹ at 10wt% CNT content.

The electrical properties of PAN/CNT composite single-component fibers with 15 wt% and 20 wt% CNT content were investigated and discussed. The electrical conductivity of PAN/CNT fibers was enhanced by the annealing process at different temperatures and changed with time. The conductivity of composite fibers with 20wt% CNT increased from ~ 10⁻⁵ S/m to higher than ~ 25 S/m. These fibers could also respond to stretching, and the electrical conductivity decreased by 50 % when the elongation reached 3%. In addition, electrical current could induce Joule heating effect and
thermally stabilize composite fibers in the air. The conductivity of composite fibers also increased from 25 S/m to higher than 800 S/m when the applied current was increased from 1 mA to 7 mA. The temperature of composite fibers can increase from room temperature to higher than hundred degrees Celsius as measured by an IR camera. Joule heating effect can also be estimated according to one dimension steady-state Poisson’s Equation, which reveals the temperature can be high enough to stabilize or even carbonize the fibers. Since fabrication of PAN-based carbon fibers is an energy-intensive process and the increase of fiber temperature by Joule heating is high enough to stabilize the fibers, this research provides a new carbon fiber manufacturing process to save energy.

Magnetic Fe$_3$O$_4$/PAN composite fibers with a diameter as small as ~14 μm were fabricated with 10 wt% Fe$_3$O$_4$ nanoparticles. The magnetic fibers exhibited tensile strength as high as 630 MPa and tensile modulus as high as 16 GPa for single-component Fe$_3$O$_4$/PAN composite fibers, and tensile strength as high as 900 MPa and tensile modulus as high as 22 GPa for PAN – Fe$_3$O$_4$/PAN bi-component fibers. In addition, PAN/Fe$_3$O$_4$ can be heat-treated by TGA at 900 °C in nitrogen. The composite fibers could keep their shape, and the materials were converted to iron carbide (Fe$_3$C) with some amorphous carbonaceous structure. The Fe$_3$O$_4$/PAN composite fibers can also exhibit superparamagnetic properties at room temperature with the coercive force ($H_c$) around 165 G, saturation magnetization ($M_s$) around 80 emu/g, and blocking temperature around 250 K.

GONR/PAN composite fibers with diameter as small as 13 μm were successfully fabricated with 1 wt% GONRs in polymer matrix. PAN crystallinity was higher with
larger crystal size and higher orientation factor in PAN/GONR fibers. GONRs reinforced composite fibers and enhanced the tensile strength and tensile modulus up to 0.9 GPa and 21.3 GPa, respectively. After the stabilization and carbonization process, the fiber diameter was reduced to ~ 7 μm, and the tensile strength and tensile modulus of the composite carbon fibers were as high as 1.82 GPa and 232 GPa, respectively.

6.2 Recommendations for Future Study

1. In the study of thermal conductivity of PAN/CNT composite fibers, because of the inevitable interfacial resistance or so-called Kapitza resistance between CNTs and polymer matrix, the ability of CNTs to enhance thermal conductivity is significantly diminished. In order to enhance thermal conductivity in polymer/CNT composites, further research is required to reduce the interfacial resistance. For example, we can investigate the relationship between the interfacial resistance and CNT-polymer interaction by selecting surface-modified CNTs or utilizing different polymer matrix. The influence of polymer structure adjusting CNTs on phonon transferring can also be discussed. This study can provide crucial information of factors determining thermal resistance, and therefore we can further enhance thermal conductivity of polymer/CNT composites.

2. According to the study of Joule heating effect, fiber geometrical factors (length and diameter) and thermal and electrical conductivity of fibers influence the heating process significantly. Therefore, fibers with different diameters or fibers mixed with different electrical conductive fillers (such as different CNTs or other nanoparticles) can be investigated to further control the Joule heating effect. In addition, since the study has
showed the temperature increased by Joule heating effect is high enough to stabilize or carbonize PAN fibers, the electrical heating experiment can also be conducted in specific environment, such as in nitrogen, to further control the stabilization and carbonization process.

3. For the application of heating fabrics, providing a safe and uniform heating power is necessary. A controllable and uniform heating temperature without any electrical short circuit or leakage will be the first requirement for heating fabrics. Since the conductive fibers should be woven as textiles or embedded in other matrix as heating materials, the influence of different weaving techniques as well as connection methods on heating ability will be the next topic. In addition, Joule heating can be applied to other polymer/CNT composites for different applications. For example, PMMA/CNT composite fibers can be fabricated first, and PMMA can be subsequently removed by increasing the temperature. The residual CNTs may maintain the conductive network to establish a circuit of CNTs.

4. Fe₃O₄ nanoparticles can absorb microwave, and the wavelength of microwave absorbed by Fe₃O₄ nanoparticles is overlapped in X-band (8 ~ 12 GHz). Therefore, the Fe₃O₄/PAN composite fibers can be used as electromagnetic interference (EMI) shielding materials. The ability of microwave absorption and the EMI shielding effect can be further studied for Fe₃O₄/PAN composite fibers. Other magnetic nanoparticles can also be selected to fabricate composite fibers to provide higher saturation magnetization. In addition, since Fe₃O₄/PAN composite can be converted to iron carbide with carbonaceous materials and iron carbide is still a magnetic material, Fe₃O₄/PAN composite fibers can be used as precursor fibers to fabricate magnetic composite carbon fibers. The
stabilization and carbonization process as well as the physical properties of magnetic carbon fibers can be investigated to understand the influence of nanoparticles on the fiber structure and properties.

5. During the fabrication process of PAN/GONR composite fibers, because the viscosity of the PAN/GONR solution was reduced by GONRs, the solid content of the PAN/GONR spinning solution was higher than that of the control PAN solution. Therefore, the influence of GONRs on the rheology of PAN should be studied further. The results can also be compared with other nano-fillers, such as CNTs and graphenes, to understand the influence of various filler types and shapes on the viscosity.

6. In this research only CNT, Fe$_3$O$_4$, and GONR were used as the nano-fillers in PAN fibers. Myriad nano-fillers and polymers can be chosen to fabricate different composite fibers. Since different nanoparticles exhibit distinct properties, some possible research topics of composite fibers are listed in Table 6.1. In addition, different polymer or different geometry of the two components on the cross section can also be chosen to fabricate new bi-component fibers. For example, PMMA – PAN/CNT core-sheath bi-component fibers are discussed in Appendix C. These fibers with different materials/fillers or distinct cross sections may provide different applications and play important roles for the next generation fibers.
Table 6.1 Possible nanoparticles or polymer candidates for different properties and applications.

<table>
<thead>
<tr>
<th>Polymer or Nanoparticles</th>
<th>Properties</th>
<th>Benefits &amp; Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA / CNT</td>
<td>Sacrificed PMMA</td>
<td>CNT circuit</td>
</tr>
<tr>
<td>PEO - PAN</td>
<td>Phase change materials</td>
<td>Temperature regulation</td>
</tr>
<tr>
<td>Metal nanoparticles (e.g. Au, Ag, Cu)</td>
<td>Electrical conductivity</td>
<td>Conductive fibers</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Thermal management</td>
</tr>
<tr>
<td>Spinel family</td>
<td>Magnetism:</td>
<td>Microwave-adsorption</td>
</tr>
<tr>
<td>Garnet family</td>
<td>Ferromagnetic</td>
<td>Magneto-resistance</td>
</tr>
<tr>
<td>Rare earth elements</td>
<td>Ferrimagnetic</td>
<td>Data-recording</td>
</tr>
<tr>
<td>Metal (e.g. Fe, Co, and Ni)</td>
<td>Superparamagnetic</td>
<td>Security and Labeling</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Self-heating</td>
</tr>
<tr>
<td>Lignin</td>
<td>Bio-degradability</td>
<td>Green and Cost Reducing</td>
</tr>
<tr>
<td>Nano-whisker (e.g. Cellulous nanocrystal)</td>
<td>High mechanical properties</td>
<td>Mechanical reinforcement</td>
</tr>
<tr>
<td>Au nanorod/wire</td>
<td>Coherent surface plasma oscillation</td>
<td>Sensor, Security, Labeling</td>
</tr>
<tr>
<td>Pt</td>
<td>H₂ - adsorption</td>
<td>Fuel cell</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Specific chemical reactions</td>
<td>Photo-catalysis</td>
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<td>Uv-visible wave absorption</td>
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<td>Pt, ZnO, Ag</td>
<td>Anti-bacteria,</td>
<td>Sanitation</td>
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<td>Ordor-eliminating</td>
<td>Deodorization</td>
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<tr>
<td></td>
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<td>Air conditioning</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Refrigeration</td>
</tr>
<tr>
<td>ZnO nano-rod/nano-wire</td>
<td>Piezoelectricity</td>
<td>Sensor, generator</td>
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<tr>
<td>Quantum Dot/rod/tetra-pod</td>
<td>Light-emitting</td>
<td>Textile-LED</td>
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<td></td>
<td>Light-harvesting</td>
<td>Textile-solar cell</td>
</tr>
<tr>
<td>Silicon oxide (chemical/biological modification)</td>
<td>Specific chemical reactions</td>
<td>Sensor</td>
</tr>
<tr>
<td></td>
<td>Biomaterials interaction</td>
<td>Reaction agent</td>
</tr>
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<td>Catalyst</td>
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APPENDIX A

DISSOLUTION OF PAN CORE AND PAN/CNT SHEATH BI-COMPONENT FIBERS

A.1 Dissolution at Room Temperature

PAN core and PAN/MWNT sheath bi-component fibers with 10 wt% MWNT introduced in Chapter 2 were placed in DMAc to observe the fiber dissolution behavior at room temperature. After different lengths of dissolution time, the fibers were dried and placed on conductive carbon tapes for SEM investigation. The original A7 fibers with draw ratio of 1.6 are shown in Figure A.1. The lateral surface of fiber is smooth and CNTs are embedded in the polymer matrix.

![Figure A.1 SEM images of A7 fibers before dissolution process. (b) is higher magnification image of denoted region in (a).](image)

After the A7 fibers were placed in DMAc, the fibers were gradually dissolved in the solvent and PAN polymer started to diffuse out of the fibers. Figure A.2 and A.3
exhibit the SEM images of A7 fibers after the fibers were placed in DMAc for 5 min and 30 min. The integrity of fiber was destroyed and only fractured structure with CNTs coated with PAN can be observed. A7 fibers finally disappeared after the fibers were placed in the solvent over one hour.

Figure A.2 SEM images of partially dissolved A7 fibers after being placed in DMAc for 5 minutes. (b) is higher magnification image of denoted region in (a).

Figure A.3 SEM images of partially dissolved A7 fibers after being placed in DMAc for 30 minutes. (b) is higher magnification image of denoted region in (a).
In contrast to A7 fibers, A8 fibers with draw ratio of 11 can remain as fibers in the solvent after three days (Figure A.4). Although some polymer was dissolved from the surface of the fibers, A8 fibers with higher draw ratios exhibit better solvent resistance and retain their integrity in the solvent for a longer time as compared to the fibers with lower draw ratios. Figure A.4 also shows CNTs appearing on the fiber surface and portions of the CNTs were embedded in the polymer matrix, as partial polymer on the fiber surface was removed by the solvent. The presence of CNTs may also improve the resistance to the solvent and maintain the fiber integrity in DMAc.

![Figure A.4 SEM images of A8 fibers after being placed in DMAc for three days. (b) is lower magnification image of A8 fibers, and (c) is higher magnification image of denoted region in (a).](image)

A.2 Recovered CNT after Dissolution Process

After PAN/CNT composite fibers were dissolved in the solvent, MWNT can be recovered through filtration process. A7 fibers were placed in boiling DMAc until the fibers were dissolved completely. Half of boiling solution with dissolved fibers was
filtered via a PTFE membrane filter (Whatman GmbH, TE37) directly, and the other half of boiling solution was naturally cooled down to room temperature before filtration. The residual materials on the membranes from both procedures were later dried and observed by using SEM. According to the SEM images in Figure A.5 and A.6, when the temperature of DMAc was different during filtration process, the recovered CNTs from the DMAc with dissolved fibers were different. As the solution was filtered at DMAc boiling temperature, PAN was dissolved in the solvent and only CNTs was filtered on the membrane (Figure A.5). The diameter of CNTs is $21 \pm 3.9$ nm, which is similar to the pristine CNT diameter of $21.0 \pm 3.1$ nm revealed in Figure 2.6 (a). The result indicates PAN including the polymer coating on the CNT surface discussed in Section 2.3.2 was dissolved completely in the solvent. However, if the DMAc with dissolved A7 fibers was naturally cooled down to room temperature before filtration, the diameter of recovered CNTs increases to $44.8 \pm 5.3$ (Figure A.6). Partial dissolved PAN was re-coated on the CNT surface and the thickness of PAN coating on the CNT surface was approximate $12$ nm. This result reveals that the recovered CNTs will be coated with PAN if the fiber-dissolved solution is cooled down before filtration. This observation has important implication in polymer/CNT processing.
Figure A.5 SEM images of recovered CNTs from boiling DMAc with dissolved A7 fibers.

Figure A.6 SEM images of recovered CNTs from naturally cooled down DMAc with dissolved A7 fibers at room temperature.
APPENDIX B

ESTIMATION OF TEMPERATURE PROFILE OF COMPOSITE FIBERS AS A RESULT OF JOULE HEATING

Joule heating effect was introduced in Chapter 3, and the temperature profile along the composite fibers with applied electricity can be estimated by one-dimensional steady-state heat transfer equation. According to the theory, various parameters can affect Joule heating and the resulting temperature profile. This appendix discusses several different parameters, including applied electrical current, fiber length and diameter, electrical and thermal conductivities, and air convection coefficient.

Figure B.1 shows the estimated temperature along the fiber axis under different applied electrical currents. Higher electrical current induces higher electrical energy along the fiber and therefore increases fiber temperature. In addition, the temperature is higher in the middle than at both fiber ends. According to the heat transfer equation, thermal energy is dissipated through fibers at both ends, as well as through the surroundings via air convection. Because the heat is dissipated faster at both ends and therefore the temperature at both ends is lower. However, when the fiber length is much longer (Figure B.2), the heat generated along the fibers is dissipated rather through the surroundings than through the two fiber ends. Since heat dissipated by air convection is slower than by thermal conduction, the fiber temperature increases when the fiber length is longer (Figure B.2), while the temperature profile is also changed from arc to square shape. In contrast, when the fiber length is shorter, more heat can be quickly dissipated through thermal conduction to both fiber ends, and therefore the entire fiber temperature
decreases. Since fiber diameter and fiber electrical conductivity are two crucial factors to control Joule heating behavior, Figures B.3 and B.4 also reveal the influence of fiber diameter and fiber electrical conductivity on Joule heating behavior.

Figure B.1 Temperature profile of a composite fiber along the fiber length with 20 wt% CNT content at various electrical currents (L = 0.005 m, h = 200 W/m²K, K = 30 W/mK, d = 44 μm, and σ is obtained from Figure 3.6).
Figure B.2 Temperature profile of a composite fiber along the fiber length with 20 wt% CNT content at various fiber lengths (I = 1 mA, h = 200 W/m²K, K = 30 W/mK, d = 44 μm, and σ = 45 S/m).

Figure B.3 Temperature profile of a composite fiber along the fiber length with 20 wt% CNT content at various fiber diameters (L = 0.005 m, I = 1 mA, h = 200 W/m²K, K = 30 W/mK, and σ = 45 S/m).
Figure B.4 Temperature profile of a composite fiber along the fiber length with 20 wt% CNT content at various electrical conductivities (L = 0.005 m, I = 1 mA, h = 200 W/m²K, d = 44 μm, and K = 30 W/mK).

Figures B.5 and B.6 exhibit the influence of thermal conductivity and air convection coefficient. Since the heat generated by electrical power is only dissipated through the fiber at both ends or through the surrounding by air convection, higher thermal conductivity and higher air convection coefficient lead to faster heat dissipation and therefore lower fiber temperature. However, Figure B.5 also shows the shape of temperature profile is changed from arc to square when thermal conductivity is too low. Low thermal conductivity implies less heat is transferred by thermal conduction. Therefore, the heat prefers to be dissipated through air conduction, which is similar to the condition when fiber length is long. As a result, the temperature profile is changed and the fiber temperature increases with decreasing thermal conductivity.
Figure B.5 Temperature profile of a composite fiber along the fiber length with 20 wt% CNT content at various thermal conductivities ($L = 0.005$ m, $I = 1$ mA, $h = 200$ W/m$^2$K, $d = 44$ μm, and $σ = 45$ S/m).

Figure B.6 Temperature profile of a composite fiber along the fiber length with 20 wt% CNT content at various convection coefficients ($L = 0.005$ m, $I = 1$ mA, $K = 30$ W/mK, $d = 44$ μm, and $σ = 45$ S/m).
APPENDIX C

PMMA CORE AND PAN/CNT SHEATH BI-COMPONENT FIBERS

PMMA core and PAN/CNT sheath bi-component fibers were fabricated by gel spinning. PMMA (homopolymer, molecular weight: $3.5 \times 10^5$ g/mol) was obtained from Sigma-Aldrich, Co., while PAN (homopolymer, molecular weight: $2.5 \times 10^5$ g/mol) was obtained from Japan Exlan Co. PAN powder was dried in an oven at 100 °C for two days before used. Multi-wall carbon nanotubes (MWNT), with an average diameter of $21.0 \pm 3.1$ nm were obtained from Cheap Tubes Inc. PMMA powder was dissolved in dimethyl formamide (DMF) obtained from Sigma-Aldrich, Co. PAN/CNT composite solution was prepared according to the same procedure described in Section 2.2.1. The final concentrations of both PMMA and PAN/CNT solutions for spinning process are listed in Table C.1.

PMMA core and PAN/CNT sheath composite fibers were spun using bi-component fiber spinning unit manufactured by Hills, Inc (Melbourne FL). The spinning process and set-up is similar to the one used for PAN/CNT bi-component fibers described in Section 2.2.2. However, after the as-spun PMMA core and PAN/CNT bi-component fibers were stored in a methanol bath at $-50$ °C overnight, the fibers were drawn at room temperature followed by drawing in three stages at 100, 135, and 165 °C in a glycerol bath. The information of fiber spinning and drawing process are listed in Table C.2. The characterization procedure for the bi-component fibers were also similar to the one used for PAN/CNT bi-component fibers described in Section 2.2.3.
Table C.1 Processing parameters of PMMA core and PAN/CNT (90/10) sheath bi-component fibers.

| Sample | Core component     | Sheath component       | Draw ratio  
|--------|--------------------|------------------------|-------------
|        | PMMA               | PAN/CNT (90/10)        | DR₁ | DR₂ | DR₃ | DR₄ | TDR |
| M₀     |                    |                        | 2   | -   | -   | -   | 2   |
| M₁     | Solution Conc.: 30 g/dL | Solution Conc.: 14 g/dL | 2   | 2.4 | -   | -   | 5   |
| M₂     | Flow rate: 0.7 cc/min  | Flow rate: 0.4 cc/min  | 2   | 2.4 | 1.7 | -   | 8   |
| M₃     |                    |                        | 2   | 2.4 | 1.7 | 1.2 | 10  |

- The ratio of overall fiber radius to core radius is 1.1.
- DR₁ – draw ratio at room temperature, DR₂ – draw ratio at 100 °C, DR₃ – draw ratio at 135 °C, DR₄ – draw ratio at 165 °C, TDR – total draw ratio. Spin draw ratio is equal to 1.

Figure C.1 shows the optical micrographs of the cross section of bi-component fibers. PMMA as the core component is transparent and the cross section of the bi-component fibers is slight irregular. Figure C.2 also shows the SEM image of fiber cross section, and two distinguished component can be observed. The fractured surface of bi-component fibers was also investigated using SEM, and numerous CNTs can be observed from the fractured surface of PAN/CNT sheath component in Figure C.3.
Figure C.2 (a) SEM image and (b) cross-sectional schematic of M₀ PMMA core and PAN/CNT sheath bi-component fibers.

Figure C.3 SEM images of fractured surface of M₀ PMMA core and PAN/CNT (90/10) sheath bi-component fibers. (b) is lower magnification image of M₀ fibers, and (c) is higher magnification image of denoted region in (a).

Figures C.4 and C.5 show wide angle x-ray diffraction patterns and the corresponding integrated radial and equatorial scans of PMMA powder and the bi-component fibers with different draw ratios. When the draw ratio of bi-component fiber is 2, the diffraction pattern of amorphous PMMA is dominant and the peaks of PAN crystal structure are un-clear. When the draw ratio of bi-component fibers increases, the
peaks of PAN (200, 110) and (310, 020) crystal planes become more obvious. Their fiber structural parameters can be calculated according to the similar method described in Section 2.2.3 and the values are listed in Table C.2. PAN crystallinity and crystal size as well as the orientation parameters for both PAN and CNT increase when the fiber draw ratio increases.

Table C.2 also shows the fiber diameter and mechanical properties of the bi-component fibers with different draw ratios. M₁ fibers with draw ratio of 5 show highest tensile strength and tensile modulus of 165 MPa and 6 GPa, respectively. When fiber draw ratio increases to 10, the elongation at break decreases considerably, and the tensile strength decreases to only 144 MPa. This is because amorphous PMMA has lower contribution to tensile strength and tensile modulus than semi-crystal PAN, and the mechanical properties of PMMA core PAN/CNT sheath bi-compoenent fibers are less than those of the control PAN fibers, while the tensile strength and tensile modulus for control PAN fibers with draw ratio of 2 is 195 MPa and 7.1 GPa (Table 4.5 in Section 4.3.3).
Figure C.4 Wide angle x-ray diffraction patterns of PMMA powder and PMMA core and PAN/CNT sheath bi-component fibers with different draw ratios.

Figure C.5 (a) Integrated radial scans and (b) equatorial scans of wide angle x-ray diffraction patterns of PMMA powder and bi-component fibers with different draw ratios.
Table C.2 Mechanical properties and structural parameters of PMMA core and PAN/MWNT (90/10) sheath bi-component fibers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Diameter (μm)</th>
<th>Tensile Strength (MPa)</th>
<th>Tensile Modulus (GPa)</th>
<th>Elongation at break (%)</th>
<th>Structural parameters a</th>
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</thead>
<tbody>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Xc (%)</td>
</tr>
<tr>
<td>M₀</td>
<td>57.2 ± 2.3</td>
<td>127 ± 6</td>
<td>5.9 ± 0.4</td>
<td>8.0 ± 1.8</td>
<td>44.0</td>
</tr>
<tr>
<td>M₁</td>
<td>41.9 ± 1.2</td>
<td>165 ± 6</td>
<td>6.0 ± 0.3</td>
<td>5.9 ± 0.4</td>
<td>48.3</td>
</tr>
<tr>
<td>M₂</td>
<td>34.0 ± 2.9</td>
<td>139 ± 7</td>
<td>5.5 ± 0.1</td>
<td>4.4 ± 0.4</td>
<td>50.6</td>
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<tr>
<td>M₃</td>
<td>29.7 ± 1.9</td>
<td>144 ± 5</td>
<td>5.8 ± 0.2</td>
<td>4.4 ± 0.5</td>
<td>53.5</td>
</tr>
</tbody>
</table>

a Xc and Lc (θ ≈ 17°) represents crystallinity and crystal size, respectively. f_PAN (θ ≈ 17°) and f_CNT (θ ≈ 26°) are Herman’s orientation factors for PAN crystal and CNT.