Exploration of torsional actuation and twist to writhe transition in nanostructured hydrogels

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Exploration of torsional actuation and

twist to writhe transition in

nanostructured hydrogels

By

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Declaration

I, Nicolas Martino, declare that this thesis, submitted in fulfillment of the requirements for awarding the degree of Doctor of Philosophy at Australian Institute of Innovative Materials at the University of Wollongong, is entirely my own, unless otherwise stated, referenced or acknowledged. This document has not been submitted for qualifications at any other academic institution.

Nicolas Martino

March 2018
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Abstract

Torsional artificial muscles are a branch of actuators that react to a stimulus by rotating. This rotation is driven by a change in volume and mechanical properties such as modulus and was shown to be extremely large in the case of twisted fibers due to their helical geometry. The following thesis introduces a new method of fabrication of nanofiber yarns and nanocomposites with the aim of making hydrogel torsional catch actuators that combine responsiveness to pH changes and a high torsional output as well as a systematic approach to the modeling of their behavior using the single helix theory.

Furthermore, the mechanical and torsional properties of our actuators have shown to induce interesting new properties such as the conversion of twist to writhe at a constant length. Increasing the strength of these actuators by making nanocomposites has allowed the synthesis of linear actuators that transform the generated torque during the untwist of the swelling composite nanofiber yarns into a coiling/snarling linear actuator. These interesting new properties are shown to be a consequence of the swelling of the sample as well as its mechanical properties.
Table of Contents

Declaration ........................................................................................................................................... 2
Acknowledgments .............................................................................................................................. 3
Abstract ............................................................................................................................................... 4
Table of Figures .................................................................................................................................. 8
Table of Tables .................................................................................................................................... 14
I. Introduction ....................................................................................................................................... 16
   Historical perspective ...................................................................................................................... 16
   The natural muscle .......................................................................................................................... 16
   The artificial muscles ...................................................................................................................... 18
      Dielectric elastomer .................................................................................................................... 19
      Conducting polymers .................................................................................................................. 19
      Liquid crystal elastomers .......................................................................................................... 19
      Shape memory alloys ............................................................................................................... 20
      Hydrogels ...................................................................................................................................... 20
   Fiber-based artificial muscles .......................................................................................................... 21
      Carbon nanotube actuators ........................................................................................................ 21
      Fishing line actuator ................................................................................................................... 22
      Review conclusion ....................................................................................................................... 22
II. Synthesis of hydrogel nanofiber yarns ............................................................................................ 24
   Introduction ...................................................................................................................................... 24
   State of the art nanofiber yarn spinning .......................................................................................... 24
      Self-assembly ............................................................................................................................. 24
      Phase separation ......................................................................................................................... 25
      Fiber drawing .............................................................................................................................. 26
      Templating .................................................................................................................................. 26
      Blow spinning ............................................................................................................................. 27
      Rotary jet spinning ...................................................................................................................... 28
      Electrospinning .......................................................................................................................... 28
   Results and discussion .................................................................................................................... 34
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Machine design choices</td>
<td>34</td>
</tr>
<tr>
<td>Platform for rapid prototyping</td>
<td>35</td>
</tr>
<tr>
<td>Wire driven collection apparatus</td>
<td>37</td>
</tr>
<tr>
<td>Disk driven nanofiber collection</td>
<td>40</td>
</tr>
<tr>
<td>Synthesis of nanoyarns</td>
<td>46</td>
</tr>
<tr>
<td>Synthesis of PAA hydrogel nanofiber yarns</td>
<td>52</td>
</tr>
<tr>
<td>Conclusion</td>
<td>60</td>
</tr>
<tr>
<td>III. Hydrogel nanofiber yarn torsional actuators</td>
<td>61</td>
</tr>
<tr>
<td>Introduction to torsional artificial muscles</td>
<td>61</td>
</tr>
<tr>
<td>Mechanism of torsional actuation</td>
<td>62</td>
</tr>
<tr>
<td>Change in volume</td>
<td>62</td>
</tr>
<tr>
<td>Deformation in crystalline or semi-crystalline structure</td>
<td>65</td>
</tr>
<tr>
<td>Potential applications of torsional actuators</td>
<td>68</td>
</tr>
<tr>
<td>Hydrogel torsional actuators</td>
<td>69</td>
</tr>
<tr>
<td>Modeling</td>
<td>70</td>
</tr>
<tr>
<td>Results and Discussion</td>
<td>72</td>
</tr>
<tr>
<td>Study layout</td>
<td>72</td>
</tr>
<tr>
<td>One end tethered experiments</td>
<td>73</td>
</tr>
<tr>
<td>Two ends tethered experiments</td>
<td>76</td>
</tr>
<tr>
<td>Single Helix Modelling</td>
<td>82</td>
</tr>
<tr>
<td>Nanofiber yarn snarling and coiling</td>
<td>85</td>
</tr>
<tr>
<td>Conclusion</td>
<td>89</td>
</tr>
<tr>
<td>IV. Composite nanofiber yarn linear actuator</td>
<td>91</td>
</tr>
<tr>
<td>Snap-buckling artificial muscles</td>
<td>91</td>
</tr>
<tr>
<td>Biomimetism a source of inspiration</td>
<td>91</td>
</tr>
<tr>
<td>Theoretical analysis of the bending of filaments</td>
<td>94</td>
</tr>
<tr>
<td>Summary</td>
<td>97</td>
</tr>
<tr>
<td>Results and Discussion</td>
<td>97</td>
</tr>
<tr>
<td>Conclusion</td>
<td>125</td>
</tr>
<tr>
<td>V. Conclusion and suggestions for further work</td>
<td>127</td>
</tr>
<tr>
<td>Literature</td>
<td>134</td>
</tr>
</tbody>
</table>
VI. Appendix microcontroller program ................................................................. 143
    Program for the disk collectors ........................................................................ 143
    Program for the winding unit ............................................................................ 146

VII. Appendix Machine’s Engineering drawing ..................................................... 148
    Engineering drawing of the box and prototyping platform .............................. 148
    Box design ........................................................................................................ 148
    Prototyping platform design ............................................................................ 149
    Disk driven collecting apparatus .................................................................... 150
<table>
<thead>
<tr>
<th>Figure Number</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Skeletal muscle multiscale architecture</td>
<td>17</td>
</tr>
<tr>
<td>2</td>
<td>Three-dimensional simulation of the assembly of myofibrils at the molecular scale</td>
<td>17</td>
</tr>
<tr>
<td>3</td>
<td>Myofibril schematic subassembly.</td>
<td>18</td>
</tr>
<tr>
<td>4</td>
<td>Myofibril radial assembly into a muscle fiber</td>
<td>18</td>
</tr>
<tr>
<td>5</td>
<td>Step actuation of dielectric elastomer.</td>
<td>19</td>
</tr>
<tr>
<td>6</td>
<td>Rolled actuator to provide linear actuation.</td>
<td>19</td>
</tr>
<tr>
<td>7</td>
<td>Coiled carbon nanotubes actuators infiltrated with paraffin wax, with [a] their actuation properties and [b] their microstructure</td>
<td>21</td>
</tr>
<tr>
<td>8</td>
<td>Different microstructure obtained from a filament (a) of nylon 6-6, (b) when coiled, (c,d) when braided and (d) when heat set into a spring</td>
<td>22</td>
</tr>
<tr>
<td>9</td>
<td>Reversible thermal actuation of a coiled nylon filament</td>
<td>22</td>
</tr>
<tr>
<td>10</td>
<td>Self-assembly of nanofiber by hydrophobic driven micelle formation reproduced from on the left (Jun &amp; Yuwono 2005) and on the right (Silva et al. 2004)</td>
<td>25</td>
</tr>
<tr>
<td>11</td>
<td>Different scales of the organization of nylon 6-6 nanofiber made by drawing (reproduced from (Liao et al. 2017))</td>
<td>26</td>
</tr>
<tr>
<td>12</td>
<td>Template synthesis of aligned nanofiber pillars reproduced from (Chakarvarti &amp; Vetter 1998)</td>
<td>27</td>
</tr>
<tr>
<td>13</td>
<td>Blow spun nanofiber mats of PCL showing (A) fiber bundles and (B) uniform mats (reproduced from (Daristotle et al. 2016))</td>
<td>27</td>
</tr>
<tr>
<td>14</td>
<td>Different type of collecting strategies, [a] gravity assisted collection of nanofibers, [b,c] pressure assisted deposition and [d] water bath assisted yarn collector</td>
<td>28</td>
</tr>
<tr>
<td>15</td>
<td>Typical electrospinning setup comprising a high voltage power supply, a syringe pump, and a grounded collector. Reproduced from (Ali Eatemadi, Hadis Daraee, Nosratolah Zarghami 2016).</td>
<td>29</td>
</tr>
<tr>
<td>16</td>
<td>Spinning and whipping motion of a nanofiber jet in an electrospinning context. Reproduced from (Xue et al. 2017).</td>
<td>29</td>
</tr>
<tr>
<td>17</td>
<td>Scale bridging using a combination of nanofiber organization and chemical processing to obtain highly aligned PEDOT microtubes. Reproduced from (Feng et al. 2013).</td>
<td>30</td>
</tr>
<tr>
<td>18</td>
<td>Three-dimensional assemblies relying on the gap alignment technique of electrospun nanofibers, showing on the left the patterned substrate and on the left the resulting nanofibrous layers. Reproduced from (Li et al. 2004).</td>
<td>31</td>
</tr>
<tr>
<td>19</td>
<td>Modulization of the effect of insulator gap in a patterned collector with (a) A schematic view of the electrospinning setup and 9b0 a potential profile at different insulator gap width. Reproduced from (Chaurey et al. 2010).</td>
<td>31</td>
</tr>
<tr>
<td>20</td>
<td>Results of non-solvent bath nanofiber yarn electrospinning without on the left and with on the right the use of a vortex to align nanofibers.</td>
<td>32</td>
</tr>
</tbody>
</table>
Figure 21: Double conjugate electrospinning setup (left) and resulting nanofiber yarn (right) reproduced from (Wei & Qin 2016).

Figure 22: Gap aligned nanofiber yarn with on top the schematics of the electrospinning setup, and on the bottom, the resulting nanofiber yarns at different scales reproduced from (Wu et al. 2014).

Figure 23: Isometric rendered a view of the prototyping platform. The green (an example of a two-floor collection system) and blue (lab jack) objects that fit inside an acrylic box are easily removable through a screwed back panel. Colors were added for contrast.

Figure 24: Engineering drawing showing features of the prototyping platform. Features are (1) Top panel, (2) Screw holes for back panel assembly, (3) Syringe tip hole, (4) Guillotine door rack pair with key holes, (5) Bottom of the second floor, (6) back panel, (7) wire guides mounting and sliding holes, (8) front pillar, (9) bottom of the first floor, (10) lab jack (z position control), (11) guillotine door bottom seal and (12) bottom panel.

Figure 25: Engineering drawing of platform 14, bottom and right side views are virtually identical to the top and left side views. Features described are (1) Cross through hole pillar to top floor holder, (2) Gas inlet hole, (3) Top acrylic floor, (4) Front Pillar (5) Bottom floor and (6) Lab jack. All dimensions are millimeters.

Figure 26: Electrospinning system with wire collectors, [a] shows the collector mechanism where either the fork or the wire can move and [b] the wire path and motor driven collecting reels, features include (1) Silver wire path, (2) Top wire guiding pulley, (3) Platform 14 top floor, (4) Driven reels and (5) Platform 14 bottom floor.

Figure 27: Front view and zoom over the first nanofiber yarn produced of the first working electrospinning system presenting the following features: in [a], (1) Fume hood, (2) Syringe pump, (3) Homemade wire guides, (4) Wire reel and pulley, (5) Electric motor coupled with the wire reel via a green belt and (6) Arduino microcontroller; in [b], (1) grounding copper ring, (2) homemade guide system, (3) grounding wire, (4) First nanofiber yarn, (5) silver wire and (6) top floor wire guiding pulley; in [c] engineering drawing of the center pulley-wire reel.

Figure 28: 3 pulley guide design with [a], (1) on of the three-pulley guiding the silver wire, (2) base on which cloth can be added to clean the wire, (3) grabbing hole, (4) through holes to prevent rocking.

Figure 29: Engineering drawing of the new guides.

Figure 30: Stable machine configuration with two parallel rotating collector disks with meshing autosampler disks. The machine design consists of (1) copper coated collector electrodes, (2) a main slave pulley that powers (3) a central shaft, a stepper motor (4) that powers a pair of rotary autosamplers (5) through a small shaft (6), a master pulley (7) that drives the main collecting system and is powered by a stepper motor (8) and, finally a slip grounding wire (9) and a grounded shaft (10).

Figure 31: Engineering drawing of the disk based nanofiber collector design with from top left to bottom right the isometric, top, front and side views.

Figure 32: Principle of operation of the machine nanoyarn synthesis mechanism, on the left, is shown the first phase of nanofiber collection with the two main collecting disk and the nanofibers forming between them showing (1) the extrusion syringe, (2) the parallel disk electrodes and (3) the rotary auto
sampling disks. On the right is shown the late stage of synthesis, the autosampler has concentrated the nanofiber from the main collector into thin sheets and has rotated to create four samples. .......... 42

Figure 33: Final electrospinning machine placed inside a fume hood (faraday cage and solvent extraction). ................................................................. 44

Figure 34: [a] Series of 5 PAA nanofiber yarns spun and collected on the rotary autosampler for one minute per sample (yarns are at least 5 cm long) and [b] Nanoyarns on an optical microscope plate after twisting and chemical modifications ................................................................. 45

Figure 35: NMR of the different polymers used in this study. The top spectrum is made from diluted polyacrylic acid and the bottom spectrum from diluted polyacrylonitrile both in deuterated DMSO. ...... 47

Figure 36: Low (left) and high (right) magnification of a PAN nanofiber yarn made using optimized conditions (3PANY) at 2000 turns per meter done by SEM on Pt-coated sample.................................. 49

Figure 37: Average diameter of PAN nanofiber yarns prepared at different collection times, for a feed rate of 0.4mL/hour. At least four samples were prepared. Error bars represent one standard deviation. ........................................... 50

Figure 38: PAN nanofibers diameter distribution for 100 counts in 5 independent samples. The pooled statistic is an average diameter of 301 nm and a standard deviation of 74 nm.......................... 50

Figure 39: Physical properties of PAN nanofiber yarns, [a] distribution of metric weight and [b] angle measured by SEM against inserted twist for nanofiber yarns made using PAN standard conditions, 0.4 mL/hr and 3 minutes spin time................................................................. 51

Figure 40: PAN nanofiber yarn mechanical properties against the inserted twist with [a] typical stress and strain curve and [b] the ultimate tensile strength plotted against the yarn helix angle and [c, d] respectively the strain at break and the moduli as a function of the twist angle. .......................... 52

Figure 41: Expected condensation reaction from a polyacrylic acid polymer and a polyetherdiamine (Jeffamine ED600) under heat treatment ................................................................. 53

Figure 42: PAA-Jeffamine nanofiber yarn diameter at different spinning times. Results are reported for the standard PAA-Jeffamine electrospinning conditions ................................................................. 56

Figure 43: Low (left) and high (right) magnification SEM images of PAA-Jeffamine nanofiber yarn. A thin 20nm Pt layer was deposited to reduce electrostatic charging during SEM imaging...................... 56

Figure 44: Swelling experiments of a twisted and crosslinked PAA-Jeffamine nanofiber yarn in [a] the dry state, [b] pH 1.5 buffer solution and [c] pH 10 buffer solution ................................................................. 57

Figure 45: SEM images of PAN nanofiber yarns at different twist densities with [a, b] SEM images of the synthesized nanogels and [c] the observed linear density as a function of the inserted linear density in the sample. ................................................................. 58

Figure 46: SEM image of the nanostructure of the nanogels after swelling experiments. ............... 59

Figure 47: Swelling ratio from pH 1.5 to pH 10 of nanogels made in the standard conditions with a minimum of 4 samples at different crosslink time (hours)........................................................................ 60

Figure 48: Pneumatic torsional actuator (a) before and (b) after the bladder is inflated. Reproduced from (Sanan et al. 2014). ................................................................................................. 62

Figure 49: Torsional actuation of CNT nanofiber yarn, scanning electron microscopy and geometry presented in [a] and resulting actuation under electrochemical stimulation in [b] ........................................ 63
Figure 50: Torsional actuation of two ends tethered CNT yarn with half the actuator infiltrated with wax and the other half used as a return spring. Actuation is the result of Joule heating, [a] shows the remarkable cycling stability and [b] the torsional actuation behavior at different stress against the input power. ................................................................. 64

Figure 51: Twisted nitinol heat activated torsional actuator reproduced from (Mirvakili et al. 2018). ................................................................. 65

Figure 52: Schematic view of the inter-crystalline (B, A and TM) and crystalline (C) regions of a highly drawn semi-crystalline polymer fiber. The former appears as a blend of (B) crystalline bridge molecules, (A) folded polymer chains and oriented tie molecules. Reproduced from (Choy et al. 1981). 67

Figure 53: Untwisting due to the torsional actuation of a twisted 70mm nylon fiber reproduced from (Aziz et al. 2015). ................................................................. 68

Figure 54: Geometry of the swelling of a twisted helical string ......................................................... 70

Figure 55: Effect of the change in volume over the twist density at different initial twist density ($T_0$) in isotropic conditions. Negative numbers indicate an untwist upon swelling............................................. 72

Figure 56: Drawing of the nanofiber yarns characterization techniques with [a] the one end tethered configuration with (1) a steady holding surface, (2) the free to untwist nanofiber yarn and (3) an attached weight allowing to count the turns and indicating the rotation direction. And [b] the two end tethered configuration with (1) A lever arm system to apply constant force and measure length changes, (2) a hook system to hold the sample, (3) a highly twisted nanofiber yarn sample and (4) a steady surface. Note: in this test the sample was only partially immersed in the pH solutions............................................. 73

Figure 57: Untwisting of a hydrogel nanofiber yarn again time as pH changes (black dots indicate the sample under 5mN load in air, dark dots indicate the sample is immersed in a pH=1.5 buffer solution, red dots stand for a pH 10 buffer solution) ............................................................................. 74

Figure 58: Untwisting of a set of hydrogel nanofiber yarn torsional component............................... 75

Figure 59: Average length (with one standard deviation as error bars) of PAA hydrogel nanofiber yarns when exposed to different pH solutions. The initial dry length of the yarns was 20 mm............... 75

Figure 60: Actuation of two end tethered hydrogel nanofiber yarns with different twist inserted and half-immersed in pH 1.5 or pH 10 and at a constant tension of 8 mN. Each point represents a half turn of a paddle attached to the yarn center and the torsional stroke is given as the twist density by normalizing to the immersed length of yarn.............................................................................. 77

Figure 61: Relative torsional actuation of a two-end tethered hydrogel nanofiber yarns crosslinked at 130 degrees for 6 hours with an initially inserted twist of 2000 turns/m............................................. 78

Figure 62: a) Example plot showing length change during successive immersions in different pH solutions, and b) Relative change in length relative to the previous state size............................................. 79

Figure 63: Relative change in volume as a function of the twist density, the red points represent the transition between dry to pH 1.5 and the blue point between pH 1.5 to pH 10................................. 81

Figure 64: Schema of a filament yarn with filament helicoidal path changing from the center to edge of twisted structure [A] and geometrical interpretation [B] of the center and middle filaments with D0, S0 and L0 respectively the diameter, string length and actuator length prior and D, S and L after swelling.. 83
Figure 65: PAA nanofiber yarn sledge experiment forming superstructures and shortening as a result. Scale can be deduced from the 0.5mm nylon fiber. ................................................................. 86

Figure 66: Custom design immersion box for the horizontal two end tethered full immersion experiment showing [a] the isometric view and [b] the longitudinal section with (1) the water line, (2) the sample and (3) the glue points. ................................................................. 87

Figure 67: Coil forming in a PAA nanofiber yarn immersed in pH 1.5 solution. Fiber is ~100μm in the dry state. .............................................................................................................. 87

Figure 68: Progressive reversible snaring of a PAA nanofiber yarn sample micrographs that show the snarl expanding (image a) at pH 10 solutions with the steady state at pH 10 (image b) and reversed state (image c) at pH 1.5. Fiber is ~100μm in the dry state. ................................................................. 87

Figure 69: Formation of coiled structure in the sample immersed at pH 1.5. Image [a] shows the formation of the first coil and [b] the steady state showing a zoom over the three meshing coils. Fiber is ~100μm in the dry state. .............................................................................................................. 88

Figure 70: Formation of a reversible higher order structure a pH. Fiber is ~100μm in the dry state. .............................................................................................................. 89

Figure 71: From left to right, micro-patterned PNIPAM ribbon twisting upon swelling, from (Erb et al. 2013), and actuation of a microscale ribbon warping in differently angled helices from (Jeon & Hayward 2017)... ................................................................. 92

Figure 72: (a and b) Images of V. convallaria in extended and contracted states (22), (c and d) The model in extended and contracted states. The head is modeled by an incompressible sphere, the stalk by an elastic rod (in gray), and the spasmoneme by a thin fiber (in black) winding helically around the stalk. Reproduced from (Misra et al. 2010). .............................................................................................................. 93

Figure 73: Contraction model is showing the mechanics of buckling of the spasmoneme in black and stalk in grey. Reproduced from (Misra et al. 2010). .............................................................................................................. 94

Figure 74: Phase transition in response to winding a rubber cable at constant load. Reproduced from (Ghatak & Mahadevan 2005). .............................................................................................................. 96

Figure 75: Stress against strain curve of a rubber cable exhibiting different phase transition as a function of the applied load. Reproduced from (Ghatak & Mahadevan 2005). .............................................................................................................. 96

Figure 76: Phase transition diagram showing the different phases a function of extension and twist density. Reproduced from (Ghatak & Mahadevan 2005). .............................................................................................................. 96

Figure 77: Image of a composite nanofiber yarn in the dry state made by electrospinning the two component PAN (fine fibers) and PAA (fibers with defects) one and six minutes and twisting the resulting sheet into a yarn at 2000 turns per meter .............................................................................................................. 98

Figure 78: Typical composite nanofiber yarn optical microscopy image swollen in a pH 1.5 buffered solution.............................................................................................................. 99

Figure 79: Typical composite nanofiber yarn optical microscopy image swollen in a pH 10 buffered solution.............................................................................................................. 99

Figure 80: Optical microscopy image of PAN30-PAA 360 composite nanofiber yarn. The PAA component appears translucent and the PAN component appears opaque white .............................................................................................................. 99

Figure 81: Displacement against time of a reversible pH responsive plectoneme actuator. A decrease in length represents a shortening of the actuator .............................................................................................................. 102
Figure 82: Optical microscopy images of a 126 ± 14 µm composite nanofiber yarn during the contraction events at the condition indicated. ................................................................. 104

Figure 83: Close-up characterization of the snap-coiling motion. ................................................................. 105

Figure 84: Optical microscopy images of a composite nanofiber yarn snarling actuator .................. 106

Figure 85: Optical microscopy image of the first cycle of composite nanofiber yarn plectoneme actuator in different pH solutions ................................................................. 107

Figure 86: Experiment design to obtain the mechanical properties of our composite nanofiber yarns (s-s is the short for stress and strain curves) ......................................................................... 108

Figure 87: Characterization setup to extract the mechanical properties from immersed nanofiber
yarns consisting of (1) A microscope, (2) an horizontal lever arm and (3) a syringe body containing
swelling solution and the sample which end can be turned to change the latter's twist density. .......... 109

Figure 88: Axial strain of composite nanofiber yarn swelling in pH 1.5 solution where time was
recorded after the addition. .................................................................................................................. 110

Figure 89: Typical set of stress and strain curves obtained from a composite nanofiber yarn swollen in pH 1.5 with an unaltered 2000 turns per meter twist density ....................................................... 110

Figure 90: Stress and stress curves at decreasing twist for a sample immersed in pH 1.5 solution .. 110

Figure 91: Linear fit of the unloading curve of a sample in a pH 1.5 solution ........................................ 110

Figure 92: Modulii obtained at different twist densities for a sample at pH 1.5 ....................... 111

Figure 93: Modulii obtained at different twist densities for a sample at pH 10 ......................... 111

Figure 94: Modelling of a coil in a twisted structure with [a] a three-dimensional view and [b] the schematic geometrical interpretation. .................................................................................. 112

Figure 95: Composite nanofiber yarns dry diameters at constant components ratio, represented by their total spin time (sum of spin time for both PAA and PAN components) ......................................................... 114

Figure 96: Multistrand nanofiber yarn composite actuator with the tension provided by the lever arm ........................................................................................................................................ 116

Figure 97: Actuator made of two strands of opposite chirality with 36mg applied weight .......... 116

Figure 98: Newly observed plied phase transition in imperfectly torque balanced experiment....... 118

Figure 99: Actuation plotted against the yarn diameter. ................................................................. 121

Figure 100: Contraction speeds as a function of the applied stress .................................................. 121

Figure 101: Still image showing the change in actuation mechanism to a long range buckling in the formation of snarls .................................................................................................................. 124

Figure 102: Representative snarling repeat experiment with PAN 1min (0.4mL/hrs) and PAA 6min at 2000tpm .............................................................................................................................. 125

Figure 103: Section and full preview of the proposed twisting and winding units for making continuous lengths of nanofiber yarn .................................................................................. 130

Figure 104: Code used in the nanoyarn collection apparatus ............................................................. 146

Figure 105: Front view of the box and the prototyping platform ........................................................... 148

Figure 106: View of the collecting apparatus with the collection disks and the autosampler ....... 150
Table of Tables

Table 1: Summary of the design iterations during the development of the nanofiber yarn electropsinning machine. .................................................................................................................. 46

Table 2: Experimental determination of a set of electrospinning variable for different weight concentration of polyacrylonitrile in DMF. ......................................................................................... 48

Table 3: Experimental determination of a set of electrospinning variable for different weight concentration of polyacrylic acid and Jeffamine in DMF. Jeffamine concentration was kept at 0.33% in all experiments ......................................................................................................................... 55

Table 4: Result of the two end tethered experiment with different twist densities of PAA nanofiber yarns made at 130 degrees 6H. T0 and all λ ratios refer to the starting state for the transition from the dry condition to immersion in pH 1.5 and to transition from pH 1.5 to pH 10 condition ........................................ 80

Table 5: Average change in twist density from dry to pH 1.5 and pH 1.5 to 10 where T0 is the twist density at the start of each transition .................................................................................................................. 80

Table 6: Change in swelling and twist for samples prepared at a constant twist density (2000 turns/m). T0 and all λ ratios refer to the starting state for the transition from the dry condition to immersion in pH 1.5 and to transition from pH 1.5 to pH 10 condition. .......................................................................................................................... 82

Table 7: Comparison of the experimental and predicted values for fractional change in twist using the single helix theory. Calculation 1 refers to the results obtained assuming the ‘string length’ remains constant during each transition. Calculation 2 is based on the assumption that the change in string length is the same as the change in the overall yarn length during each transition .................................................................................................................. 85

Table 8: Comparison of diameters in pristine and composite nanofiber yarns ................................. 100

Table 9: Actuation results of composite nanofiber yarns at constant components ratio. Transition between dry to pH 1.5 for ntot samples and n samples showing the buckling and reversibility properties. ..................................................................................................................................... 101

Table 10: Samples actuation characteristics at different crosslinking times. Transition between 1.5 and pH 10. PAA spin time was always 6 times the PAN spin time. ................................................................. 102

Table 11: Ross criterion estimate of the twist density needed to form a coil in the swollen composite nanofiber yarns swollen at pH 10 .............................................................................................................. 111

Table 12: Characterization of remarkable nanofiber composite actuators at different spinning times. ......................................................................................................................................................... 114

Table 13: Small diameters exploration of composite nanofiber yarn actuation ............................... 117

Table 14: Torque balance experiments reversibility and buckling type of the subset of experiments showing a characteristic buckling actuation .................................................................................. 117

Table 15: Typical composite nanofiber yarns actuation one cycle strain for different compositions. .................................................................................................................................................... 119

Table 16: Actuation results of the best performing composite nanofiber yarns at different diameters constant components ratio ........................................................................................................... 120

Table 17: Actuation of a composite nanofiber yarn in response to different applied stress .......... 122
Table 18: Repeat experiment metrics (6 experiments per data point)................................. 123
Table 19: Repeatability experiments pooled dataset of 10 different pH cycles at 0.5MPa. .......... 125
Table 20: Samples failure types at different crosslinking times. Transition between pH 1.5 and pH 10. ................................................................................................................................. 126
I. Introduction

Historical perspective

Linear actuators are objects that transform an energy input into linear mechanical work yielding to a reversible change in size. Their use can be correlated to the advances made in human history with the invention of the slide cars (7000 BC), and the use of horses (3500 BC). The source of motion was the muscles of the animal moving the devices, the role of these tools was to amplify the mechanical work allowing more intensive agriculture, construction of high buildings, cavalry and chariots as war weapons. In modern history, the invention of the piston and the steam engine (beginning of the XVIII century), the electric motor and the combustion motor (XIX century) led to the two industrial revolutions and the technological world we live in today. The actuation was performed using heat to provoke the piston movement yielding to a linear movement transformed in a rotational movement using a crankshaft. The electric motor relies on magnets or electromagnets that consecutively repel and attract to provide rotary motion using Lorentz forces. All these technologies remain today either inefficient in battery-powered autonomous robot because of low power per unit mass or too complex in the transmission design required to transform a continuous movement in an abrupt change of a robot’s motion. In more recent history actuators improvement and robotics led to a breakthrough in automation allowing robots to manufacture from cars to computers covering a large pan of the industry. Moreover, since the first industrial robot in the 1970's (Paz et al. 2010) the rapid growth of automation technologies allowed new promising technologies to develop such as surgical robots (Gastrich et al. 2011) and military robots (Khurshid & Bing-rong 2004). However challenges remain and reside in the battery itself, which, with the current limitations of the lithium polymer technology, among others, would not be able to drive a human skeletal muscle during a full day and the human skeletal muscle is still today the benchmark to beat as it is seen as a very efficient actuator, all-in-one power transmission and chemical energy converting system (Madden 2007).

The natural muscle

Nature is a great source of inspiration in the field of material science. From evolutionary standpoint, genes on which relies the protein production and control, are selected not for their efficiency but their fitness. Fitness is defined as the probability of one genotype or phenotype to be included in the next generation. For simple organisms, such bacteria, which spread by scissiparity fitness and efficiency are highly correlated, in the case of a single environmental niche (Schulz zur Wiesch et al. 2010). However, efficiency in more complex organisms is not the principal trait involved in the selection of offspring as ecological performance depends on several individual counterbalancing factors which can lead to vestigial structures. Nonetheless, the high complexity of living organism has created a movement toward understanding and reproducing the different involved molecular architectures since Da Vinci study of bird’s wings motion (XVth century) (Humphrey 2003), Carothers by the synthesis of Nylon (1935 at
DuPont Ind.) and more recently to the development of superhydrophobic coating mimicking the lotus leave surface chemistry (Sanjay & Annaso 2012; Vincent 2009).

This complexity arises from the nanoscale to the macroscopic scale by layers, mainly usually constructed around repeated clusters. From the angstrom to the millimeter repeating motifs bridge the scale difference, for example, glucose molecule in glycogen polymers, the keratin supramolecular assembly in hairs and the intricated architecture of muscles from repeated muscle fibers. At all those scales, the highly organized architecture is precisely controlled creating highly automated and sophisticated machines. The skeletal muscle, or voluntary muscle, is an example of such sophistication. It consists of multiple tangled fiber bundles at different scales (shown in Figure 1). Starting from bottom, two composite nanoyarns comprised of actin fiber (a composite of a polymer of actin tetramers that organizes in a the F-actin helicoidal filament, 2.17 units per turn, 6nm diameter) (Chen et al. 2013) and myosin filaments (supramolecular homopolymer of myosin, organized head and tail, with different length allowing three heads to be on the same plane) (Rayment et al. 1993) are organized in an unidirectional non twisted bundle (shown in Figure 2). The actuation is the consequence of the actin filament sliding provoked when ATP is dephosphorylated to ADP during the interaction of the myosin cross-bridge (head, in purple) and the actin-binding site1 in a lever-cantilever fashion (Skubiszak 2011).

![Figure 1: Skeletal muscle multiscale architecture.](image1)

![Figure 2: Three-dimensional simulation of the assembly of myofibrils at the molecular scale.](image2)

The different moving parts are tethered either to the cytoskeleton of the cell or with spring-like polypeptides in turn linked to the cytoskeleton (myosin/titin) forming a unit, the sarcomere (shown in Figure 3). The sarcomere is repeated along and parallel to the myocyte axis. These bundles are enclosed in a complex architecture containing the signal transducing system, the sarcoplasmic reticulum and energy supply, the mitochondria (shown in Figure 4). This, in turn, forms a myofibril of 1 to 2 micrometer which is assembled in radially repeated motif forming a muscle fiber of 100 micrometers.
The muscle’s signal transduction and energy supply rely respectively on the electrochemical gradient of ions such as calcium at the cell’s membrane and the diffusion of ATP/creatine produced by oxidation of glucose (Glancy et al. 2015). Nanoyarns can be found in nature as complex layers of polymeric materials in the form of nanofibers in human anatomy, tendons, ligaments, and hairs. Tendons and ligaments, present interesting and similar mechanical properties, as they are both connective tissues made of collagenous fibers (75%) and elastin among others (Frank 2004). Tendons are made of tropocollagen polypeptide, of 285nm length and 1.4nm diameter, which is excreted outside of the cell and can self-assemble into a triple helix polymer made of four repeating units of period 67nm and diameter of 3.5nm. The resulting polymer assembles into fibrils resulting in an overall diameter of 50-500nm and is then subjected to further chemical modifications such as crosslinking, making the fibers bundles strong and insoluble (Doehring 2005). This self-assembly results in spring-like extended and organized structures. The result of this architecture is a nonlinear elastomer with dampening properties that can stretch up to 4% (Lanir 1978) and absorb stress up to 30MPa (Pourcelot et al. 2005) allowing the muscle to be anchored to the bones, but also it allows the load and stress to be propagated as the helical spring fibres compress and stretch in an anisotropic manner.

These highly organized nanostructures are a source of inspiration as they show functionality at all scales.

In particular natural muscles have interesting mechanical properties that translate high power to mass output of 323 W/kg, with 0.1 to 0.3 MPa of stress in isotonic contraction and with a strain varying from 1 to 100%. The efficiency of the human skeletal muscle strain is reported to be 35% with a maximum actuation frequency of 173Hz (Josephson 1993; Josephson 1985).

### The artificial muscles

Artificial muscles are a heterogeneous group of technologies that aim to surpass the natural muscle. The energy source can be electrical, heat usually obtained by Joule heating, or chemical gradients usually powered by batteries or fuel cells that have their limitations. This non-exhaustive literature review provides an insight into the field of artificial muscles and its recent developments.
**Dielectric elastomer**

Dielectric elastomers are devices made of an elastic material coated with compliant electrodes. By charging the two electrodes with different electric charges, in capacitor configuration, the two electrodes attract which causes stress on the elastomer that contracts and change area. This change in area is reversible since the electrodes can be charged with the same electric charge causing the plates to repel and the dielectric material to extend. The energy is expanded during the contraction or extension because of the electrostatic mechanism relying on high voltage, in the kilovolt scale, depending on the thickness on dielectric elastomer film (O’Halloran et al. 2008). This translates in very low current to provoke actuation and allows very large actuation frequencies from 10 to 100hz and in some cases 105 cycles with no drift allowing steps of strain (Figure 5). Their main drawbacks are the prestrain needed, where the elastomer is cycled under MPa range loads, in order to achieve full stroke and the hazard of high voltages. With prestrain acrylic elastomer can reach up to 380% strain, 7.2MPa maximum pressure and a power output of 400W/kg (Fallis 2013).

![Figure 5: Step actuation of dielectric elastomer.](image1)

![Figure 6: Rolled actuator to provide linear actuation.](image2)

**Conducting polymers**

Conducting polymers are oxido-reductibles plastics that rely on the conjugation of pi electrons along the unsaturated polymer backbone to provide conduction. In a supercapacitor setup, while being electrically or chemically oxidized/reduced, they incorporate ions from the electrolyte to balance their stored charge which induces a volume transition (Otero et al. 2012). The mechanical properties of an ingenious open-air linear actuator afforded an actuation frequency 0.005 Hz, 300 mN of peak stress for 3% strain (Plesse et al. 2010). Immersed in an electrolyte conducting polymer actuator based on a tubular geometry can contract up to 19% with a peak strain of 8 MPa and can reach 5% strain for 0.5Hz actuating frequency (Ding et al. 2003). Their main drawback is the low cyclability due to the high localized stresses involved in incorporating large ions in the polymer structure.

**Liquid crystal elastomers**

Liquid crystal elastomer comprising an isotropic crosslinked polymer network in which anisotropic mesogenic structures are oriented but free to move with respect to another. This results in the formation
of crystalline domains within the polymer network, and upon stimulation, these domains can reversibly align and contract preferentially along a direction which yields to the macroscopic strain (Jiang et al. 2013). Their actuation characteristics are large strains up to 40% with maximum stress of 60kPa (Naciri et al. 2003).

**Shape memory alloys**

Artificial muscle shape memory alloys are metal alloys that undergo reversible crystal lattice structural transition upon heating/cooling (Morgan 2004). The resultant strain can be produced even at very high loads with the drawback of a hysteretic behavior, and the slow cooling process implies low actuating frequencies or the use of active cooling which decrease the specific power as the mass of the actuator increases. Their characteristics are a strain up to 10% and a maximum stress of 200MPa, 3 Hz actuation frequency, 10 J/cm3 of work per volume and 30 W/cm3.

**Hydrogels**

Gels are loosely crosslinked polymer network; hydrogels are gels that are hygroscopic and show a large volume transition by swelling water. This is due to the solvation of the polymer chains, and the macroscopic structure is held by the crosslinked network (Calvert 2009). As an artificial muscle, the swelling transition is used to create stress. Hydrogels artificial muscle can be stimulated by heating, electric fields and solution variation such as pH change.

Heat-induced swelling is obtained by having polymers made with hydrophilic and hydrophobic chains that are crosslinked in a hydrogel. This difference in affinity from the polymer chains with the solution results in conformational changes with temperature as the miscibility of the different moiety changes. It follows that thermosensitive hydrogels can contract with upon an increase in temperature (LCST) or expand (UCST) due to the transition between the soluble state where the molecules are randomly organized with incorporated solvent molecules to the insoluble state where molecules are organized in globules with the solvent being expelled. The swelling is then controlled by the temperature as the interaction between the polymer chains, and water changed substantially by small increments or decrements of temperature (Haq et al. 2017).

We are particularly interested in pH transition as it is a way to transform a chemical energy, here a pH gradient, in a mechanical work which origins in the swelling of the polymer. A pH-responsive hydrogel is a polyacrylic acid in which the transition from acid to base creates a repulsion of charges, an insertion of ion and solvation by water causing an abrupt and large deformation (Richter et al. 2008). Usually, slow hydrogels have reported attaining contraction speed up to millisecond by micro-structuration (Lee et al. 2010), and can be made tough (Sun et al. 2012) and conductive (Naficy et al. 2012) by using a second polymer network interpenetrating the hydrogel crosslinked network. The actuation capabilities are interesting with large strain, usually > 50%, power densities that can attain 34mW.g⁻¹ and a stress up to 0.1 MPa. Their ability to be chemically driven, the large deformation and potential fast driven upon size reduction makes them interesting candidates to be electrospun. In the case of heat responsive hydrogels, few seconds were necessary to actuate the electrospun mat. We hypothesize that by aligning the nanofibers in the same direction and twisting them, we can obtain large deformation with fast response as the swelling will be a cooperative anisotropic process (Wang et al. 2011).
Fiber-based artificial muscles

Carbon nanotube actuators

Carbon nanotube actuators yarns are made by twist-drawing carbon multiwalled nanotube forests synthesized by chemical vapor deposition. Their mechanical properties make them very attractive in artificial muscle, in host-guest experiments where the carbon multiwalled nanotube yarn is filled with paraffin (shown in Figure 7) it surpasses mammalian skeletal muscles in several ways, with a contraction speed with 30ms, a contraction pressure of 100MPa and specific power output of 27.9kW/kg for an applied 32V/cm. But the strain is low, with less than 7% and the high electric power reduces the cycle-ability. Several other experiments, especially heat driven results in a reduced strain inferior to 3% when stimulated below 200 degrees Celsius (Lima, Li, Andrade, et al. 2012). The mechanism of the contraction relies on the reversible thermal expansion of the paraffin guest inside the yarn that applies pressure on the stiff carbon nanotube moiety and does not extrude from the porous structure because of the nanostructure. Macroscopically, the change in length is concentrated between the coils with no appreciable change in the total number of coils. In another study, the electrochemical double layer charge injection stimulation resulted in low contraction speeds, with full contraction in 5 seconds and a strain inferior to 1.5%. Interestingly the geometry of the system, with the high inserted twist, allows the rotation by twisting and untwisting upon stimulation yielding to a specific torque of 1.85N.m in the range of commercial electric motors and 590 rpm (Lima, Li, Jung de Andrade, et al. 2012).

Figure 7: Coiled carbon nanotubes actuators infiltrated with paraffin wax, with [a] their actuation properties and [b] their microstructure.
Fishing line actuator

The nylon micro size wire, usually used as a fishing line, is very cost effective and powerful artificial muscle. Heat-driven, their actuation mechanism relies on the semi-crystalline highly ordered polymer chain in the fiber axis which conformation changes upon heating and use the helical geometry provided by twisting to amplify the stroke, Figure 8 and Figure 9. The result is a strain of 4% when straight and increased 7.75 times to 35% when coiled in temperatures ranging up to 250 degrees Celsius. In the case of nylon 6,6, the maximum tensile stress produced was under 90 MPa for 10% of non-loaded length strain at contraction. The maximum reported contraction-extension frequency were 1Hz, under heat stimulation between 25 and 95 degrees Celsius under 8.4 MPa of load performing 1500 reversible actuation cycle and achieving 12% of strain (Haines et al. 2014).

![Image](image.png)

Figure 8: Different microstructure obtained from a filament (a) of nylon 6-6, (b) when coiled, (c,d) when braided and (d) when heat set into a spring.

![Image](image.png)

Figure 9: Reversible thermal actuation of a coiled nylon filament

Review conclusion

Recently the field of artificial muscles has been the witness of several important breakthroughs. The twisted actuators are reversible, fast and very strong, providing both rotational and translational actuation. They are made of highly twisted carbon nanotubes and twisted nylon fiber. These new actuators opened new insight by twisting yarn or fiber, using the helix angle to provide torque and elastic force which allow reversal upon actuation. The main drawback being the use of heat as an energy source which implies that transforming the twisted fibers in a more complex architecture as simultaneously stimulating several of them may require a heat dissipation system to attain maximum actuating frequencies. These two systems rely on the mechanical advantage provided by the twisting to increase the strain of the actuator. We aim to use this advantage by developing a new method to synthesize nanoscale structures that can be winded into yarns. Our model will be hydrogels as their strain is already important to further understand the mechanisms of helical geometry amplification if the actuator varies in volume. Moreover, it has been shown that templating hydrogels in the nanoscale is a source of high speeds motion which may be increased by the helical geometry and the alignment of the nanostructure. Our objective for this
first year was to design, build and test an innovative setup for nanofiber fabrication and orientation which will provide us the necessary ground to study nanoscale artificial muscles.
II. Synthesis of hydrogel nanofiber yarns

Introduction

The objective of this research is to synthesize highly twisted yarn actuators that show large deformation upon stimulation. Previous work (Aziz 2016) has demonstrated that the magnitude of actuation in twisted fibers increases when more twist is inserted into the fiber. To store the maximum amount of twist in the yarn actuators, the fibers will be made from multi-filaments yarns of nanofibers aligned in the fiber’s main axis. Electrospinning will be used to create the nanofibers, and a machine will be designed and fabricated to organize the nanofibers into aligned sheets that can be twisted into yarns. The main focus of the machine fabrication has been on maximizing process reliability, and the most important variables were the nanoyarn’s diameters and nanostructure.

State of the art nanofiber yarn spinning

Nanofiber yarns or nanoyarns are nanostructured hierarchically organized objects, which name was coined back in the 2000s (Fong et al. 2002), resembling the typical microfiber yarns made of cotton or other fibrous materials in the textile industry (Zhou & Gong 2008). Our project is focused on making controllable nanostructure that shows functionality across different scales. We approached the problem by looking at potential technologies to meet this challenge. Our yarns have the following requirements; they should be as strong as possible independently of their material properties and as thin as possible to have the highest twist density while remaining stable in actuation experiments. Filament yarns are in opposition to staple yarns are the strongest independently of material properties as they do not show slippage issues. Slippage of the staples in the yarn is a consequence of the fact that there are not held by tension at their ends but by radial friction due to the pressure exerted by twisting (Pan 1993). It follows that to meet our goal, we must find a reproducible and replicable way to manufacture nanofilament yarns with controllable diameters and subsequently assemble them into yarns. This requires control over the nanostructure and the microstructure in the radial direction of the yarns as well as producing yarn long enough for testing their mechanical and actuation properties.

In this context several technologies show potential to allow for the synthesis of polymer nanoyarns such as self-assembly, phase separation, fiber drawing, templating, blow spinning, centrifugal spinning, electrospinning and electrospinning based techniques (Ali Eatemadi, Hadis Daraee, Nosratolah Zarghami 2016)(Kenry & Lim 2017)(Vasita & Katti 2006)(Nayak et al. 2011).

Self-assembly

The self-assembly of nanofiber is a bottom-up approach where the shape of materials where supramolecular structure are made by the weak noncovalent interaction between molecules (Zhang 2003). Hydrophobic forces are a well-known strategy of assembly (Berndt et al. 1995), here molecules present apolar and polar substituent which depending on their 3d structure will form a variety of different quaternary structures from micelles to single layers. This allows for complex material to be made by Langmuir-Blodgett layer by layer technique. Nanofiber made of nanostructure cylindrical micelles have
been shown to be of controllable diameter and assembly could by the exposure to a ligand (Jun & Yuwono 2005) shown in Figure 10.

![Figure 10: Self-assembly of nanofiber by hydrophobic driven micelle formation reproduced from on the left (Jun & Yuwono 2005) and on the right (Silva et al. 2004).](image)

Gels could also be obtained by this technique (Kim et al. 2009) that were the result of the interaction with a metallic ligand forming the crosslink inside the nanofibers.

The nanostructure is obtained mimicking the processes yielding to complex nanostructured materials in nature at the expense of the range of materials that can be used, the complexity of predicting the material properties from individual molecular constituents and difficult processing steps needed to obtain macroscopic objects. Objects made by this method can be much thinner than made by electrospinning, but the low productivity and complexity of the method hinders its use in macroscopic applications. Furthermore, further processing the materials into macrostructure that emerge from the interaction between the nanofibers are yet to be shown.

### Phase separation

Another possible synthetic set of techniques relies on phase separation. Phase separation is a process by which the miscibility of compounds can be tweaked to obtain different structure by relying on thermodynamic changes. Widely used in tissue engineering this technique that leverages the dependence of miscibility of polymers in a solvent as a function of temperature. When a critical temperature is reached the interaction between polymer chains are thermodynamically favored over solvation it follows that the solution presents two phases comprised of polymer rich and poor constituents. When the solvent is removed, and the polymer solidifies, usually by freeze-drying, the shape is set. The obtained shape is the consequence of the processing and the interaction between polymer chains which allows nanofibrous meshes to be obtained with various degrees of porosity (Ma & Zhang 1998) using a gelation step to stabilize the porous structure before solvent removal.
The main drawback of this technique is the organization of the meshed nanostructures into a macroscopic object, if it is possible to use a mold to achieve the desired shape it is difficult to have a comprehensive method to obtain organization at all scales from the nanometer to the centimeter with control over the microstructure.

**Fiber drawing**

Invented by Hill in the 1930s, fiber drawing relies on mechanical forces to produce fibers from a bulk solution or melt. The viscous liquid is usually extruded through a die or preformed then drawn and solidifies into a fiber. This technique is widely used in the industry to obtain the various type of fiber of sub-micron size using different processing chemistries such as dry spinning, gel spinning, wet spinning and melt spinning (Bigg 1976). Commercial synthetic fibers are frequently made by this method. Recent advances, however, have shown that it is possible to obtain nanofiber by using fiber drawing (Xing et al. 2008) and organize the aligned nanofiber into well-behaved yarns (Liao et al. 2017) shown in Figure 11. The authors of the latter study where able to make kilometers long nanofiber strands by collecting the draw spun nanofibers over a rotating drum. The nanofiber assemblies into yarns show a high degree of alignment dawn to the molecular scale due to the shear driven alignment of polymer chain when the drawing is performed.

![Figure 11: Different scales of the organization of nylon 6-6 nanofiber made by drawing (reproduced from (Liao et al. 2017).](image)

This sophisticated technology has evolved to meet our requirements at the end of our research but should be considered carefully as a potential technique to make nanofiber yarn in any future endeavors.

**Templating**

Similar to casting techniques templating uses a nanostructured material, usually porous as a template which pored are filled with the material of interest, the template is then removed in a subsequent step, and the obtained material is left with the imprint of the negative shape (Chakarvarti & Vetter 1998) as shown in Figure 12. Nanowires can be made in assemblies (Porter et al. 2009) but appear to be short and unorganized. This makes this technique impractical for our application as self-standing nanofiber yarn long enough that they can be processed into yarns are yet to be demonstrated.
Blow spinning

Blow spinning is a technique that uses a gas flow to produce fibers. The compressed gas is forced around a stream of polymer solution creating a drawing force that pushes and deforms the viscous polymer droplet into a conical jet flowing downstream to a target (Daristotle et al. 2016). Simultaneously, as the solvent evaporates, the fiber solidifies as it travels toward the target. This process makes use of the Bernoulli principle where changes in pressure are converted in kinetic energy and allows for production rate several times higher than conventional electrospinning (Medeiros et al. 2009). It follows as it does not rely on high electrical potential coupled with conductive targets for nanofiber generation and transport, thus this technique is applicable to any substrate and can be used as a handheld coating process (Tutak et al. 2013) using pressurized airbrushes. This technology can produce nanofibers of different diameters as well as bundles but lacks a driving force for fiber orientation resulting in poor alignment and nanofibers of unknown lengths.

Figure 12: Template synthesis of aligned nanofiber pillars reproduced from (Chakarvarti & Vetter 1998).

Figure 13: Blow spun nanofiber mats of PCL showing (A) fiber bundles and (B) uniform mats (reproduced from (Daristotle et al. 2016)).

Albeit interesting production rate and versatility, this technique does not allow for the controlled organization of nanofiber in yarns which makes it inapplicable in our research.
**Rotary jet spinning**

Rotary jet spinning uses centrifugal forces to draw a polymer solution or melts into fibers similar to a cotton candy machine. As the rotor is spinning and the centrifugal forces reach a critical value higher than the surface tension of the liquid the droplet deform into a liquid jet the solution flows in the air and undergoes stretching due to the friction forces and drawing forces acting on the viscoelastic polymer solution or melt (Zhang & Lu 2014). This process does not use the high electric field to form the spinning jet and can be applied to different materials. The most important aspect is the scalability of the technique with production rate up 500 times higher than conventional electrospinning. Initially developed by the industry to manufacture fiberglass it was adapted to the production of nanofibers and is used at high scale using commercial apparatus.

Different configuration (shown in Figure 14) allows for the synthesis of different types of nanofiber assemblies from mats to yarns. The latter as an interest in our application but very little comprehensive research can be found on the topic.

![Figure 14: Different types of collecting strategies](image)

Consequently, rotary jet spinning in the context of nanofiber yarn assemblies is a technique in its infancy that show great promise with high production rates and possible application to a wide range of materials from solution to melts. The only reported form of organizing nanostructures into yarns appears to be using a liquid bath as a collection probably leveraging vortex stirring. The problems of a liquid bath are the difficult control over the diameter, staple length and twist insertion which has been shown to be a downside of electro-wet spinning of yarns (Zhou & Gong 2008) as well as the formation of large defects such as loops in the microstructure.

**Electrospinning**

Electrospinning is a technique first described in the early 20th century and became commonly used in labs as means to synthesize nanofiber in the 1990s with the boom of nanotechnology (Teo & Ramakrishna 2006). Conventional electrospinning is a simple process that requires a high voltage power supply, a needle, a syringe pump and a conductive target (shown in Figure 15) which was applied to a very wide range of material to fabricate nanostructure mats, highly organized films, and nanofiber yarns.
The variety of the potential materials and intricate assemblies across scales available has made electrospinning a method of choice in the synthesis of nanofibers which once spun can be further processed into a variety of possible application from transparent conductive mats (Kim et al. 2015) to high strength carbon nanofibers (Yao et al. 2014).

Electrospinning is an electrostatically driven jet spinning technique that leverages the electrostatic repulsion at the surface of flowing viscous liquid to stretch it while the solvent evaporates, or the melt dries and is simultaneously transported it across a voltage gradient usually towards a grounded surface. The electrostatic forces acting on the viscous liquid deform the droplet into a cone called the Taylor cone, make it spin and appear to provoke a whipping motion at high speeds which draws the millimeter-thin stream into the nanometer scale (shown in Figure 16).

It follows from these different inherent properties to electrospinning that several approaches can be undertaken to control the different scale involved in manipulating nanofibers. From the nanometer scale...
controlling the nanofiber’s content can be done using different syringe tip geometries. Subdividing the tip radially can lead to core-shell fibers while feeding different polymer solution in a parallel arrangement can lead to bicomponent to several component fibers arranged, viewed from the cross-section, in a pie slice configuration (Kishan & Cosgriff-hernandez 2017). Furthermore, post-processing can be used to control the nanofiber porosity, content, and chemistry. An example of hierarchical control over various scales is PEDOT microtubes that can be made using a combination of nanofiber arrangement detailed in the section below and nanofiber templating. Here nanostructures are aligned and stacked over a collecting drum, and Edot containing PLGA nanofibers are spun. The resulting highly aligned film is placed in an oxidative bath containing FeCl₃ and in situ oxidative polymerization of Edot happens at the surface of the nanofibers. Lastly, the PLGA is removed in a good solvent allowing for a controlled structure from the nanoscale, organization at the microscale with the alignment of the fiber and results in a macroscale mat (Feng et al. 2013) shown in Figure 17.

![Figure 17: Scale bridging using a combination of nanofiber organization and chemical processing to obtain highly aligned PEDOT microtubes. Reproduced from (Feng et al. 2013).](image)

This example shows the versatility of this well-studied technique that allows control over various scales while simultaneously providing an opportunity to access the nanoscale structures for further chemical processing. Literature is plethoric with different strategies with results spanning from conductive nanofibers to crystalline and semi-crystalline nanofibers with intricate nanometer scale designs (Bhardwaj & Kundu 2010).

Interestingly this electrostatics forces can also be used to organize the nanofiber in different types of assemblies at the microscale. Patterning the grounded surface or placing it below a mask allows for complex controlled patterns of nanofibers to be made (Li et al. 2004). The technique of making different types of three-dimensional assemblies mainly relies on the alignment effect of insulating gaps in the target surface (shown in Figure 18). The alignment effect is due to the concentration of charge at the edge of the conductor or the conductor-insulator interface (shown in Figure 19) and is also known as the Hall effect. The positively charged nanofiber acquires negative charges when it touches the charged edge of
the collector which repels them provoking a hoping motion back and forth through the gap at the edges of the collector forming aligned structures (Kakade et al. 2007).

This effect allowed for different design uses that allow for nanofiber organization in different direction and axis and was instrumental in the making of our electrospinning machine. The aligned nanostructure can also be obtained by other means, such as using a rotating drum or disk which organizes the nanofibers by surface-nanofiber friction driven alignment and to some extent a liquid batch coupled with yarn drawing. But comparative reports appear to suggest that conductor gap alignment is a superior technique for nanofiber organization on a substrate (Liu & Dzenis 2008). Moreover, gap alignment can be used to obtain self-standing nanofiber bundles that can further be processed into bundles (Wu et al. 2014).

We have seen that strategic ordering of nanofiber can be obtained by varying the collector shape thus manipulating electric field. In the recent years, however, techniques designed to obtained nanofiber yarns from polymer solutions and melt have been refined and improved. Three major strategies are allowing for nanofiber yarn synthesis, using a non-solvent bath to collect the nanofibers assisted with vortex spinning, modified gap electrospinning techniques, and double conjugate electrospinning spinning. These techniques can all potentially be applied to our project but have different drawbacks.

The non-solvent bath driven yarn assembly, assisted or not by vortex spinning, also known as electro-wet spinning is a technique that uses a liquid surface as a nanofiber collector by placing the grounded target below a water batch or series or bath. The yarn floating at the surface is then collected and twisted into yarns similarly to common staple yarn making machines. The main drawback is the
presence of a non-solvent that may evaporates and the quality of the fibers that present defective zones of different fiber diameters loops and knots (shown in Figure 20) which would make determining the yarn angle when twisted and effective cross-sectional area is very difficult due to the presence of loops in the structure (Zhou & Gong 2008).

Figure 20: Results of non-solvent bath nanofiber yarn electrospinning without on the left and with on the right the use of a vortex to align nanofibers.

Double conjugate electrospinning is a recent major advance in nanofiber yarn spinning that uses opposite charge high voltage power supply pointing at a target to obtain an electrostatically non-charged mat the is then twisted into a yarn. The system is comprised of two spinneret/power supply assemblies through which the polymer solution is fed with syringe pumps. The two polymer jets are electrostatically oppositely charged, and charge attract attraction provokes the collapse into a mat or bundle usually over a rotating funnel that collects the mat by suction. The mat is thus self-standing between the edges of the rotating funnel and is then pulled into a twisted yarn.

Figure 21: Double conjugate electrospinning setup (left) and resulting nanofiber yarn
The quality of the obtained mats is unprecedented with high alignment at the surface and with little to no defect seen in electrowet spinning. The major drawback of this technique is its complexity. Polymer solutions do not carry the same amount of electrostatic charge when positively or negatively biased which seriously complexifies the process of finding the proper variable set for a given polymer solution at a given concentration. This complexity means that few materials have been successfully made in nanofiber yarns. But this technique is under extensive study due to its industrial potential.

Lastly, nanofiber yarn can be made by gap alignment where the gap is obtained by two grounded thin needles in the cylindrical axis. When electrospinning over this collector happens nanofibers form between the two-grounded needle forming a bundle, which can be made of several centimeters in length as shown in Figure 22.

![Figure 22: Gap aligned nanofiber yarn with on top the schematics of the electrospinning setup, and on the bottom, the resulting nanofiber yarns at different scales reproduced from (Wu et al. 2014).](image)

Here the clear advantage is the simplicity of the technique with only one electrospinning needle, reducing the complexity of the optimization step and excellent quality of the highly aligned bundles. The drawback is that the nanofiber yarns are of fixed length and their diameter is top controlled by the electrostatic repulsion of the fiber that may cause the structure to collapse.

For our project, we need highly aligned filament nanofiber yarns to be made of various materials such as poly (acrylic acid). In the years past our lab has shown that pH-triggered hydrogel nanofibers can be made by electrospinning (Gestos et al. 2010). We aim to apply gap aligned nanofiber yarn synthesis to obtain hierarchically aligned nanofiber yarns. We thus designed a machine that would allow for the synthesis of such yarns by using an industrial grade ionic fan blower to allow for different diameter to be
made and by separating the electrospinning part of the process from the yarn assembly. Such technique has been shown to generate meter long nanofiber yarns although this was not the focus of our endeavor, as well as high aligned nanofiber yarn of different materials with different degrees of twist.

**Results and discussion**

**Machine design choices**

To synthesize actuating nanofiber yarns, we made which an electrospinning machine which aimed to be both versatile and precise. After preliminary electrospinning experiments a machine design was developed iteratively to comply with the following requirements: the electrospinning apparatus has to be enclosed to avoid nanofibers being released into the air; the machine needs to fit in a fume hood to avoid evaporating potentially dangerous solvent in the lab while leveraging it as a Faraday cage; and finally the enclosure has to be relatively airtight as a stream of dry nitrogen coupled with a hygrometer was chosen as a cost-effective way to control the humidity inside the enclosure. The preliminary studies used a polymer that was easy to electrospin: polyacrylonitrile (PAN). Initial experiments used two stationary wires as a collector to take advantage of the alignment effect of this type of gap electrospinning. The electrospinning process was stopped periodically to allow the collection of the nanofibers using a fork. However, it was realized that this method posed problems with the occurrence of holes and defects in the spun nanofibers. It was noticed that as the space between the collectors was filled with the aligned nanofiber mat, the spinneret became increasingly unstable to an extent where fiber spinning was replaced by the ejection of droplets that formed defects in the spun mat.

The potential solution to this problem was developed in two competing designs (Figure 26). One solution involved the automation of the fork collection, by having it mounted on a moving rack. This solution allowed the collection frequency to be increased to avoid droplet ejection. Another potential solution was to automate the wires, by having them moving along their length. This option required an optimization of the speed of movement of the plane formed by the two wires. The latter design option was chosen for four reasons. The first was that the fork would have to pass below the spinneret which would inevitably provoke droplet ejections, the fork design would be made difficult by the potentially high speeds it would need to attain, the second was that once the now highly positively charged fork would have passed below the electrified spinneret it was likely to cause disturbances in the electric field and the new sample formed would then be defective until the spinneret would stabilize. The third reason was that by moving the aligned nanofiber mat away from the spinneret, using the moving wires collection method, enabled the possibility to subsequently twist the mat continuously into a yarn. Finally, the fourth reason was that it was convenient to obtain a very thin layer of nanofiber on top of the wire that would allow for chemical modifications to be performed continuously in a similar fashion as in an industrial conveyor belt; possible chemical changes could include surface chemistry with the deposition of materials or material chemistry such as in situ crosslinking.

If these four reasons made a compelling argument to choose to make an automated wire system, it did not appear to be a much more complex system to build as both solutions would need a custom build system. After few iterations, a design was proposed that only had one wire loop around a multi-floor
collecting system. Consequently, wires forming the spinning target were always moving at the same surface speed in this design (Figure 26.B).

**Platform for rapid prototyping**

To provide a rapid prototyping environment to develop successive iteration of the electrospinning collection apparatus, a lab made prototyping platform was introduced, as rendered in Figure 23.

![Figure 23: Isometric rendered a view of the prototyping platform. The green (an example of a two-floor collection system) and blue (lab jack) objects that fit inside an acrylic box are easily removable through a screwed back panel. Colors were added for contrast.](image)

The integrated prototyping platform system was built with transparent high precision laser cut acrylic sheets solvent welded with chloroform to allow for a rapid and flawless transition between computer-aided design, manufacturing, and integration, while relying on an inexpensive, sturdy and transparent material, for the ease of fabrication and use. The strength of the acrylic sheet allowed for the housing to be manufactured and installed with a thickness screwed removable back panel to fit the collecting machine prototype easily. Transparency helped significantly with fittings and experiments. The housing was built to provide a partially isolated inside environment by using a double sealed guillotine door, and solvent welded side, top and bottom panels that could be fitted with corner rubber seals as needed. The aim was to provide humidity control in the chamber using a dry nitrogen gas flow intake on the sides (Figure 24 and Figure 25). The vertical rack pairs through which the guillotine door was designed to slip where perforated to allow the door to be held in place by a removable key.

The prototyping platform box was compartmented by two internal floors with a removable rack that could move in the z-direction thanks to a lab jack to control the distance between the collecting units and the top hole through which the spinneret syringe was positioned. This height adjustability is an important design element as collection distance must be controlled with fair precision for electrospinning to occur and proceed for extended periods of time. A transparent ruler was thus glued to the right-side panel of the box to measure this variable distance from the top of the box.
Figure 24: Engineering drawing showing features of the prototyping platform. Features are
(1) Top panel, (2) Screw holes for back panel assembly, (3) Syringe tip hole, (4) Guillotine door rack pair with key holes, (5) Bottom of the second floor, (6) back panel, (7) wire guides mounting and sliding holes, (8) front pillar, (9) bottom of the first floor, (10) lab jack (z position control), (11) guillotine door bottom seal and (12) bottom panel.

Figure 25: Engineering drawing of platform 14, bottom and right side views are virtually identical to the top and left side views. Features described are (1) Cross through hole pillar to top floor holder, (2) Gas inlet hole, (3) Top acrylic floor, (4) Front Pillar (5) Bottom floor and (6) Lab jack. All dimensions are millimeters.

The integrated platform prototyping system proved reliable with continuous use for over two years and remains completely functional. Attention was next focused on the design of the electrospinning
collection apparatus with two competing design being built and tested. The first design was a wire-based design forming a loop around the first floor and the second design was based on a pair of disks.

**Wire driven collection apparatus**

Nanofiber collection prototypes that relied on the wire driven collector concept were designed using CAD software and built. The electrospun nanofibers were collected on the plane formed between two parallel wires fed at a constant speed. The two grounded wires are fed on the second floor of the platform and move in the same direction maintaining their spacing as they pass below the electrospinning nozzle to collect the nanofibers, see Figure 26. The collected nanofibers are then concentrated onto a secondary collector in the shape of a fork. The collected nanofiber bundle is subsequently twisted into a yarn. This motion was achieved by mimicking the cassette tape system invented by Philips in the 1960s, with two reels rotating in the same direction and one long wire that is successively unwound and wound, from and to a reel. The wire forms a loop around the top floor of our prototyping platform. Figure 27 is a set of images of the first working wire driven design, the first operational version of the electrospinning system which produced the first PAN nanofiber yarns.

![Figure 26: Electrospinning system with wire collectors.](image)

[Figure 26: Electrospinning system with wire collectors, [a] shows the collector mechanism where either the fork or the wire can move and [b] the wire path and motor driven collecting reels, features include (1) Silver wire path, (2) Top wire guiding pulley, (3) Platform 14 top floor, (4) Driven reels and (5) Platform 14 bottom floor.]

The design consisted of two DC motors held in place by custom built holders fitted with pulleys. These motors moved the wire through a mechanism consisting of a pulley and a large reel the size of which was made as large as possible to mitigate the bending of the wire at the winding and unwinding points. These custom reels where both placed in the same center shaft and where free to rotate using a ball bearing placed close to their center of mass as shown in Figure 27. The largest pulley held the wire as a reel, and the stacked smaller pulley surface was coated in rubber and was driven using a polyurethane belt. The looping of the wire was achieved using a custom-built pair of two pulley guides that would
allow the wire to cross the second floor with little friction. The wire was chosen to be made of silver and was grounded through a metal ring. The driving units were controlled with an Arduino microcontroller and a simple pair of driving circuits leveraging power with modulation outputs of the Arduino board.

This design was functional and yielded the first PAN nanofiber yarns. However, the great challenge that was faced when using the machine was the catching of the wire in the metal structure that held the pulley guides in place. This problem would result in the wire kinking and electrospinning would never last for more than a few minutes. Despite this issue, this design has proven that the initial concept of using a moving wire as a target was indeed possible. The initial tests also demonstrated that humidity could be controlled and maintained with a dry nitrogen flow to the specification of 20 to 30%, and finally that the machine could be controlled using microcontrollers and motors. It followed that the natural path after this early success was to improve on the design of the pulley guides to achieve smoother and longer operation and reduce the risk of the wire breaking.

Figure 27: Front view and zoom over the first nanofiber yarn produced of the first working electrospinning system presenting the following features: in [a], (1) Fume hood, (2) Syringe pump, (3) Homemade wire guides, (4) Wire reel and pulley, (5) Electric motor coupled with the wire reel via a green belt and (6) Arduino microcontroller; in [b], (1) grounding copper ring, (2) homemade guide system, (3) grounding wire, (4) First nanofiber yarn, (5) silver wire and (6) top floor wire guiding pulley; in [c] engineering drawing of the center pulley-wire reel.
The next design attempted to make a wire guide that would allow for lower friction with the wire and prevent the wire being caught by using a smoother surface. This design is illustrated in Figure 28. The design was made using 3D printed components and fitted with pulleys containing a small ball bearing and securely fitted to the platform. Here the symmetry of the object was used so that the pair on the same side of the sheet could mesh and the minimum distance achieved between the wires was below 30 mm. Finally, a piece of sponge was glued on top and bottom ring so that while passing on top of the pulley it would be cleaned of the nanofibers that would not have been collected by the fork. This design was operational, but a major drawback was the absence of system maintaining the consistent tension of the wire as it goes through the machine.

![Figure 28: 3 pulley guide design with (a), (1) on of the three-pulley guiding the silver wire, (2) base on which cloth can be added to clean the wire, (3) grabbing hole, (4) through holes to prevent rocking](image)
To solve this tensioning issue, the unwinding pulley was rotated and operated at a lower speed than the winding pulley system to create tension. The unwinding pulley system could slip thanks to low friction between the belt and the drive pulley. This slipping of the belt would allow the tension to prevent the bending of the wire and obtain two straight wires as per specifications. Unfortunately, this design also had the side-effect of inconsistent speeds, with the wire speeding up when tension was low and reaching an almost complete stop when the tension was high. It follows that instead of having a continuously fed wire a random stop and go process happened at the same time the electrospinning was performed. This, in turn, meant that yarns could not be made reliably with the machine being stuck for sometimes for up to half a minute and the resulting yarn having diameters ranging from few microns to several hundred microns.

These early prototypes (made with the help of Hussam Hattar) were functional to an extent but lacked the capabilities of making nanofiber yarns reliably. Based on the experience gained through the construction of these prototypes, a decision was made to pursue a new design idea that ultimately became the machine we still use to this day.

**Disk driven nanofiber collection**

The idea behind the disk driven collection prototype was to replace the looped wire by collecting disk pair. These disks would act as the nanofiber collector (shown in violet in Figure 30) and replace the parallel wire collectors used in earlier prototypes. The collecting disk pair protruded through the second floor, and their edges were coated with copper tape and grounded through a slip ring. The slow rotation of the disk pair allowed the collection of sheets of parallel aligned electrospun nanofibers. The unknown parameter was how would a curved grounded surface influence the electrospinning process.
Figure 30: Stable machine configuration with two parallel rotating collector disks with meshing autosampler disks. The machine design consists of (1) copper coated collector electrodes, (2) a main slave pulley that powers (3) a central shaft, a stepper motor (4) that powers a pair of rotary autosamplers (5) through a small shaft (6), a master pulley (7) that drives the main collecting system and is powered by a stepper motor (8) and, finally a slip grounding wire (9) and a grounded shaft (10).

The design was built because of its enormous improvement in simplicity and potential for precision as a competing solution to the wire driven PID controlled collector. In fact, there is only one moving part; the central shaft mounted on ball bearings at its ends. This central shaft is driven by a pulley and timing belt system that transmits power from a stepper motor, which allows the reliable control of both speed and position as shown in Figure 31.

The grounding is achieved by reusing the pulley stack idea. Copper tape was placed on the edge of the electrospinning disk as well as the edge of the stacked pulley and connected by running the tape over the surface of the electrospinning disk. Grounding was achieved by having multistrand bar copper or silver wire run around the grounding pulley of the stack and a stationary grounded shaft placed below.

To take full advantage of the simpler design, an auto-sampling system was added as a pair of disks that meshed inside the two collecting disk (as shown in dark blue in Figure 30). In operation, while the collecting disks were rotated continuously at a constant speed, the autosampler was rotated in a stop and go fashion. This process allowed the nanofibers to be deposited on the disk collectors and automatically collected at the autosampler disks. It follows that once a target time for nanofiber collection was attained the autosampler was then rotated to allow collection of a new bundle of aligned nanofibers. The autosampler rotation could happen several times consecutively allowing for multiple samples to be collected, as shown in Figure 32.
It is interesting to note that as the central shaft is driven with a pulley, the distance between the disks can be adjusted easily from few millimeters to tens of centimeters by releasing the grub screw in the disks and sliding them in opposite directions. Typically, the system was operated with a disk separation distance of 6 cm. This separation allowed for stable electrospinning and produced bundled nanofiber samples that were long enough for characterization and testing.

This new machine design proved to be very successful so that electrospinning could be performed for hours with no perturbation and hundreds of experiments were made over the ensuing years. However, it was observed that electrospinning for long times, such as several minutes per sample usually resulted in fractured samples. It was hypothesized that this fracture was due to the charge buildup as the sample accumulates on the collector so that electrostatic repulsion forces eventually cause the sample to fracture. It was thus decided to add an ionizer fan pointing at the autosampler. Fan ionizers are routinely used in high-speed packing factories to mitigate the electrostatic charge build-up by friction. The ionizer fan is shown in Figure 33.

Figure 31: Engineering drawing of the disk based nanofiber collector design with from top left to bottom right the isometric, top, front and side views.

Figure 32: Principle of operation of the machine nanoyarn synthesis mechanism, on
the left, is shown the first phase of nanofiber collection with the two main collecting
disk and the nanofibers forming between them showing (1) the extrusion syringe, (2)
the parallel disk electrodes and (3) the rotary auto sampling disks. On the right is
shown the late stage of synthesis, the autosampler has concentrated the nanofiber
from the main collector into thin sheets and has rotated to create four samples.

This new collection system resulted in very stable electrospinning with samples made with large
diameters that were deposited on the surface of the disk collectors and then captured by the autosampler
as bundles, which are visible in Figure 34. The first deposited sample was sacrificed to reach a pseudo-
equilibrium and was spun for at least two minutes. A further four samples were then collected by rotating
the autosampler every set time at multiples of 72 degrees consecutively. Once the synthesis of all the
samples was finished the autosampler would place itself over the sacrificed sample, and the experiment
would be stopped or resumed with another polymer to make composites.
Figure 33: Final electrospinning machine placed inside a fume hood (faraday cage and solvent extraction).

These untwisted nanofiber bundles were removed from the autosampler disks for further processing, as shown in Figure 34. To form twisted yarns, the nanofiber bundles were placed vertically hanging from a stepper motor’s shaft and a weight attached to their free end. Operating the stepper motor with a control board would twist the sample to a specified twist density under a controlled tensile load.
Both machine designs that were built had their advantages and disadvantages. Despite the lack of a cleaning feature for the electrodes and the more difficult grounding of the disk edges, the second prototype was superior. The simpler design of the disk machine with only a few moving parts meant that the machine could work longer without maintenance interventions; there were no tension or vibration issues, and both electrode surface speeds and disks position were easy accurately position and control. Using the machine for several weeks, it was noticed that the copper tape on the surface became rough and dark green. We hypothesized that this was the effect of corrosion due to some solvent remaining in the fibers. Fortunately, the disk machine provided the unforeseen advantage the electrodes where cheap while being fast and easily replaced. Thus, electrodes were replaced before every set of experiments.

The design iteration and the pros of cons that led to the synthesis of nanofiber yarns are detailed in Table 1.

<table>
<thead>
<tr>
<th>Element of design</th>
<th>Pros</th>
<th>Cons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Custom prototyping platform with box and three floors</td>
<td>Air tight for humidity control (improvement compared to precedent</td>
<td>Large and bulky</td>
</tr>
<tr>
<td>design</td>
<td>modular designs)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Adaptable to multiple collector</td>
<td></td>
</tr>
</tbody>
</table>
Three floors design allows to isolate electronics and motors from electrospinning area
Fits in fume hood (faraday cage)

<table>
<thead>
<tr>
<th>Designs</th>
<th>Successful synthesis of nanofiber yarns</th>
<th>The wire can get caught in the metal structure surrounding the pulleys and break.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wire driven collector cassette-like system</td>
<td>Successful fabrication of large diameter nanofiber yarns</td>
<td>The slip tensioning system of the wire creates inconsistent wire speeds diminishing reliability.</td>
</tr>
<tr>
<td>Wire driven custom made 3d printed pulleys</td>
<td>Consistent wire speeds</td>
<td>Complex fabrication and maintenance. Expensive as wire corrodes with solvent and requires several meters of silver wire to be replaced frequently.</td>
</tr>
<tr>
<td>PID based wire tensioning system</td>
<td>Consistent surface speeds</td>
<td>Frequent electrode replacement</td>
</tr>
<tr>
<td>Disk driven nanofiber collection</td>
<td></td>
<td>Thick electrodes</td>
</tr>
<tr>
<td></td>
<td>Electrodes are cheap and easily replaceable.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Narrow nanofiber yarn diameter distribution (PAN)</td>
<td></td>
</tr>
</tbody>
</table>

Table 1: Summary of the design iterations during the development of the nanofiber yarn electrospinning machine.

**Synthesis of nanoyarns**

With a now reliable means to synthesize nanofiber yarns the process of making PAN (polyacrylonitrile) and PAA (poly(acrylic acid)), nanofiber yarns were commenced. The following sections describe the methods developed for preparing and characterizing these yarns.

Polyacrylonitrile is known to be an easy material to electrospin since it is tolerant of a wide range of polymer concentrations and chamber humidities. The raw material was sourced from Sigma-Aldrich and
had an average molar mass of 150 kg/mol, a density of 1.184g/mL, a melting temperature at 317°C and a glass transition temperature of 85°C. The purity of the as-purchased PAN was first checked by NMR (Figure 35) which shows that the compounds were pure without any hydrogenated contaminants and ready for use. We then chose dimethylformamide (DMF) as a solvent for our starting solutions as it is relatively harmless, readily available, has excellent solvation properties and temperature stability. The spinning solution was made by carefully weighing the polymer and adding solvent to desired weight concentrations and left to stir overnight at room temperature to yield a slightly yellow stable viscous solution. The process of choosing an electrospinning variable set for this polymer was straightforward. Solutions at different weight concentrations were made, and a set of different feeding rate and voltages were investigated while maintaining a constant 25% chamber humidity and constant electrodes, distances were explored.

![Figure 35: NMR of the different polymers used in this study. The top spectrum is made from diluted polyacrylic acid and the bottom spectrum from diluted polyacrylonitrile both in deuterated DMSO.](image)

Solutions were prepared by placed the correct weight of the polymer in the corresponding weight of solvent. It was then left to stir at room temperature overnight. The light-yellow solution was placed in a syringe then placed in the syringe pump on top of the machine. The needle tip of the syringe was flattened by sanding. A feeding rate was chosen at 1mL/hr, the edge to edge distance between collecting disk was 6cm, and distance from the syringe tip to the collector was 20 cm. The humidity was tweaked by opening the dry nitrogen valve until the humidity was stable for at least 5 minutes.

The machine was started by switching on the microcontroller with the preloaded 3NY program (in Appendix), and the power supply was activated. The presence of effective electrospinning manifested by
the formation of thin sheets (shown in Figure 34) over the autosampler. Also, it was possible to see the nanofiber forming on the edges of the collecting disks with the naked eye.

<table>
<thead>
<tr>
<th>Solutions concentration</th>
<th>0 to 5 kV</th>
<th>5 to 10 kV</th>
<th>10 to 15 kV</th>
<th>15 + kV</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3%</td>
<td>spitting</td>
<td>spitting</td>
<td>spitting</td>
<td>spitting</td>
<td>No nanofibers obtained</td>
</tr>
<tr>
<td>6%</td>
<td>spitting and spinning</td>
<td>spitting and spinning</td>
<td>spitting</td>
<td></td>
<td>No nanofibers obtained</td>
</tr>
<tr>
<td>9%</td>
<td>spitting and spinning</td>
<td>spitting and spinning</td>
<td>spitting</td>
<td></td>
<td>Few nanofibers high defect</td>
</tr>
<tr>
<td>11%</td>
<td>spitting</td>
<td>spinning</td>
<td>spinning</td>
<td>spitting</td>
<td>Nanofibers obtained</td>
</tr>
<tr>
<td>13%</td>
<td>spitting</td>
<td>spinning</td>
<td>spinning</td>
<td>spitting</td>
<td>Nanofibers obtained syringe clogged often</td>
</tr>
</tbody>
</table>

Table 2: Experimental determination of a set of electrospinning variable for different weight concentration of polyacrylonitrile in DMF.

The results of this series of experiments are reported in Table 2. Spinning nanofibers with this machine only appeared to be stable using solvents having a polymer concentration of 11% and when a voltage of 10 to 15 kV was used. Feeding rate could be as high as 2.2 mL/hr. There seemed to be a clear correlation between a higher feed rate and the need to use a high value of the voltage range. This is reminiscent of other reports where the ejection of the nanofibers by the electric field was found to be effectively compensated by a given feed rate.

The result of this optimization step allowed for PAN nanofiber yarn to be spun and then twisted is a nanostructure which was investigated using Scanning Electron Microscopy (SEM) imaging, as shown in Figure 36. From these images, various features can be seen such as the diameter of the yarn, the twist angle of the surface nanofibers to the yarn axis and the overall absence of spitting defects. It is clear from the pictures that some nanofibers are highly aligned and very long so that they extended beyond the
imaged area. In contrast, other nanofibers seem short and less organized. These short nanofibers are potentially due to the spinning over the top of the aligned mat and could be corrected by either decreasing the feed rate or increasing the collector electrode rotation speed.

Figure 36: Low (left) and high (right) magnification of a PAN nanofiber yarn made using optimized conditions (3PANY) at 2000 turns per meter done by SEM on Pt-coated sample.

The diameters of the nanofiber yarns were further investigated using optical microscopy as a function of the set spin time. Spinning used the standard PAN conditions of 10 +/- 2 kV, 25% humidity, 20 +/- 1 cm syringe tip to disk edge distance, 1cm/s collector surface speed and an edge to edge collector distance of 6cm. The results of this study are shown in Figure 37. From this graph, it can be seen that the average diameter of the nanofiber yarn seems to increase monotonically with an increasing collection time and at a given feed rate. With the conditions available, the range of yarn diameters spans from 39µm +/- 13% to 193µm +/-28%. 
Figure 37: Average diameter of PAN nanofiber yarns prepared at different collection times, for a feed rate of 0.4mL/hour. At least four samples were prepared. Error bars represent one standard deviation.

Furthermore, SEM images were used to determine the diameter of individual nanofibers in 5 sheets prepared using the standard PAN electrospinning conditions. A count of 100 nanofibers per sample was analyzed, and the results are reported in Figure 37. The measured values of the nanofiber diameters show a Gaussian distribution centered around a mean of 301nm +/- 25%. The closeness of the diameter distribution for all five samples shows the consistency of the spinning process. An attempt to confirm this result by measuring the metric weight of samples resulted in Figure 39. It is likely that the large distribution of metric weight is the consequence of the small weights.

Figure 38: PAN nanofibers diameter distribution for 100 counts in 5 independent samples. The pooled statistic is an average diameter of 301 nm and a standard deviation of 74 nm.
Further evaluation of the yarn fabrication was conducted by determining the twist angle as a function of the inserted twist (Figure 39). It was observed that on 11 samples the observed angle increased monotonically and nearly linearly with the inserted twist. Twist angle ($\alpha$) has been shown to be geometrically related to inserted twist (T measured in turns per meter of initial yarn length, L) and twisted yarn diameter (d) by:

$$\alpha = \sin^{-1}(\pi d T)$$

This relationship shows that the twist angle is expected to increase with increasing twist insertion. It follows that nanoyarns made using this technique can be readily fabricated with well-controlled twist angle and diameters.

![Figure 39: Physical properties of PAN nanofiber yarns, [a] distribution of metric weight and [b] angle measured by SEM against inserted twist for nanofiber yarns made using PAN standard conditions, 0.4 mL/hr and 3 minutes spin time.](image)

Next, the mechanical properties of the nanoyarns were measured in tension using a Shimatzu mechanical tester. Typical stress and strain curve are shown in Figure 40.A. These PAN nanoyarns typically displayed an initial elastic region (up to ~10%) and then plastic deformation until breakage occurred. In the example shown, the failure occurs at 70% strain and 44 MPa. The measured strengths of various samples were measured and are plotted against the initial angle of yarn. Previous studies have shown that as the helix angle increases the yarn breaking strength decreases (Pan & Brookstein 2001). No strong trend in mechanical properties as a function of twist angle was observed with the PAN nanoyarns as shown in Figure 40. Factors such as electrospinning defects are likely affecting their mechanical properties.
Figure 40: PAN nanofiber yarn mechanical properties against the inserted twist with [a] typical stress and strain curve and [b] the ultimate tensile strength plotted against the yarn helix angle and [c, d] respectively the strain at break and the moduli as a function of the twist angle.

**Synthesis of PAA hydrogel nanofiber yarns**

The main objective of this work is to synthesize highly twisted actuators that will move under stimulation providing a reversible means of control. The method chosen to achieve this end was to use a highly polar hydrogel where the gel water content can be reversibly switched by altering the temperature, pH or ionic strength. This provides an effective means to control the volume of the gel to make a simple actuator. These materials are of interest because hydrogels routinely offer large strains because of the large changes in gel swelling. Large strain actuators are common and offer great possibilities for various applications.

Based on precedent work describing electrospun hydrogel actuators in our lab (Gestos et al. 2010), poly(acrylic acid) (PAA) was chosen as a starting material. PAA is a polymer made by radical
polymerization; it is supplied by Sigma-Aldrich as a white powder of chemical formula \( \text{C}_3\text{H}_4\text{O}_2 \), an average molar mass of 1800 kg.mol\(^{-1}\) and a \( T_g \) of 106 °C. The purity of the as-purchased compound was determined by NMR, as reported in Figure 35.

Here the presence of sharp well defined easily attributable peaks confirms that the compound is pure without any organic contaminants.

Hydrogels are networks of crosslinked polymers that are highly soluble in water in the uncrosslinked state. Crosslinking forms a loose network by attachment of the long molecules that prevent the material from dissolving and affords its high-water absorbency and retention. It follows that to make hydrogel nanofiber yarns, the PAA must be crosslinked. Previous work used ultraviolet (UV) irradiation to crosslink PAA nanofibers. However, due to the potentially low penetration of UV into yarns of several hundred microns in diameter and the risk for a crosslinking gradient throughout the yarn interior based on the diminishing UV intensity from the surface to the center, it was decided to choose a chemical crosslinking method to obtain PAA hydrogels. The crosslinker was chosen to afford a stable chemical bond in water at variable pH, high-temperature stability and its ability to produce crosslinks without the need for a solvated environment. For these reasons an amide bond was chosen since its dry state synthesis is well documented in the literature, the reaction mechanism is self-explanatory, and yields can be as high as 94% (Perreux et al. 2002), (Houlding et al. 2013), (Lanigan & Sheppard 2013), (Wang et al. 2018). To achieve chemical crosslinking a diamine compound is needed to provide a clear chemical pathway to our desired crosslinked product, as shown in Figure 41.

![Figure 41: Expected condensation reaction from a polyacrylic acid polymer and a polyetherdiamine (Jeffamine ED600) under heat treatment.](image-url)
A relatively small polyether amine was chosen was Jeffamine ED600 because of its availability. Initial crosslink tests were performed in an oven at variable temperature. It was found that at 130°C overnight in a mix of PAA in water at 10% w/w, Jeffamine 0.33% v/v in DMF, left to stir overnight, a gel was obtained of a consistency similar to gelatin. Furthermore, the gel was stable in different pH and swelled by absorbing a significant amount of water.

The next challenge was to introduce the Jeffamine crosslinker into the electrospun PAA nanofibers. We first investigated the solubility limits of the mixture with a maximum found at 12% PAA in DMF by weight with Jeffamine up to 1% in volume. Interestingly, we found that humidity was an important factor in the electrospinning of this mixture. It was found that electrospinning only happened when the chamber humidity was below 27%. Other electrospinning parameters were investigated by using a typical full factorial analysis from which the results are summarized in Table 3.

Electrospinning of PAA/Jeffamine mixed in DMF only occurred in a narrow range of concentration at 9% PAA concentration between 5 and 25 kV. The samples showed a large number of defects in the form of large droplets as is shown by SEM in Figure 43. This image was taken for the PAA 9% w/w, Jeffamine 0.33% v/v in DMF at 10.5kV; 0.2mL/hr feed rate; 20 cm distance between the syringe tip and the disk edge; 20% humidity and 6 cm distance between the collector disks. The higher magnification image also shows that the nanofibers of different diameters appear to adhere together and reduce overall yarn porosity.

Any attempt at making the yarn of better quality failed whichever was the set of variables chosen. Furthermore, quality of the nanoyarns formed was observed to be very dependent on ambient humidity (which could range from 20 – 85%). Attempts to adjust the chamber humidity by changing the nitrogen flow rate were only partially successful. It was noted that at high flow rates the Taylor cone would dry quickly and become unstable and causing the solution to spit or even stop altogether. Cleaning the syringe tip during the experiment seemed to prevent the stoppage of electrospinning to, but the structure remained highly defective in humid days no matter the cleaning frequency. A large number of defects means that the diameter of the fiber varies significantly from the zones with small defects to zone with high defects. In the example shown, the diameter varies from 49 µm in the former to 81µm for the latter. Unfortunately, all other investigated conditions did not produce PAA nanofibers. Because of time limitations, it was determined that future work would have to proceed with the PAA nanofibers with droplet defects.

Further studies investigated the ability to vary the PAA nanoyarn diameter and swelling. Attempts at making yarns of small diameters proved unsuccessful since very thin sheets of PAA nanofibers were very fragile preventing any twisting from occurring without breaking. Consequently, the diameter could only be extracted from yarns made at long spinning times, as reported in Figure 42. This figure shows that different spin times in the range 6-12 minutes made no difference to the diameter of the yarns. Experiments performed at longer times than 12 min resulted in the frequent breaking of the yarn due to electrostatic saturation. It was hypothesized that the electrostatic dissipation system was not effective in removing the charge in the PAA-Jeffamine sample at long spinning times, which combined with the low strength of the material led the electrostatic stress to provoke the sample breakage. These limitations...
meant that only a small part of the experimental space was suited to successful electrospinning so that it was not possible to vary the yarn diameter to any significant degree.

<table>
<thead>
<tr>
<th>Solutions concentration</th>
<th>0 to 5 kV</th>
<th>5 to 10 kV</th>
<th>10 to 15 kV</th>
<th>15 + kV</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3%</td>
<td>spitting</td>
<td>spitting</td>
<td>spitting</td>
<td>spitting</td>
<td>No nanofibers obtained</td>
</tr>
<tr>
<td>6%</td>
<td>spitting</td>
<td>spitting</td>
<td>spitting</td>
<td>spitting</td>
<td>No nanofibers obtained</td>
</tr>
<tr>
<td>9%</td>
<td>spitting</td>
<td>spitting</td>
<td>spitting</td>
<td>spitting</td>
<td>Few nanofibers high defect</td>
</tr>
<tr>
<td>11%</td>
<td>spitting</td>
<td>spitting</td>
<td>spitting</td>
<td>spitting</td>
<td>No nanofibers obtained</td>
</tr>
<tr>
<td>13%</td>
<td>insoluble</td>
<td>insoluble</td>
<td>insoluble</td>
<td>insoluble</td>
<td>No nanofibers obtained</td>
</tr>
</tbody>
</table>

Table 3: Experimental determination of a set of electrospinning variable for different weight concentration of polyacrylic acid and Jeffamine in DMF. Jeffamine concentration was kept at 0.33% in all experiments
Figure 42: PAA-Jeffamine nanofiber yarn diameter at different spinning times. Results are reported for the standard PAA-Jeffamine electrospinning conditions.

Figure 43: Low (left) and high (right) magnification SEM images of PAA-Jeffamine nanofiber yarn. A thin 20nm Pt layer was deposited to reduce electrostatic charging during SEM imaging.

Despite the difficulty in the control of the structure of the nanoyarns, it was found that crosslinking and swelling experiments were successful. Figure 44 shows optical micrograph images of PAA-Jeffamine nanoyarns that had been crosslinked by heating overnight in an oven. A large swelling occurred from the dry state when the yarn was immersed in a buffered solution of pH 1.5, and further swelling occurred from pH 1.5 to pH 10. Moreover, it was noted that the twisted sample tended to quickly
unravel during swelling which demonstrates that the yarns were torsionally active. Finally, the structure of the yarns was observed after they were swollen in three cycles in pH 1.5 and 10, then left for three days in large volumes of deionized water and dried for a week in a drying oven at 80 degrees. As shown in Figure 46, the sample has retained its structure with images remarkably similar to the pristine yarns demonstrating that the crosslinking process affords stable yarns both macroscopically and microscopically.

Figure 44: Swelling experiments of a twisted and crosslinked PAA-Jeffamine nanofiber yarn in [a] the dry state, [b] pH 1.5 buffer solution and [c] pH 10 buffer solution.

[a] PAA nanofiber yarn twisted to 1000 tpm
[b] PAA nanofiber yarn twisted to 2000 tpm

Figure 45: SEM images of PAA nanofiber yarns at different twist densities with [a, b] SEM images of the synthesized nanogels and [c] the observed linear density as a function of the inserted linear density in the sample.
Further refinement of the crosslinking process was conducted to investigate swelling ratio as a function of the crosslink times, as shown in Figure 47. The aim was to determine the experimental space that provided a maximum and narrow distribution of swelling ratios for a given crosslink time. Initial tests confirmed that uncrosslinked samples or samples crosslinked at temperatures lower than 100°C quickly and completely dissolved in the presence of water regardless of its pH. Three different crosslinking temperatures were investigated, and samples were crosslinked for different times at each temperature. Multiple repeat samples were prepared for each condition to investigate the reproducibility of the sample swelling. It was noted from these studies that the variability of the results was reduced when crosslinking temperature increased from 110°C to 130°C or 160°C. Swellability of the gels is directly related to the concentration of crosslinks, and the lower crosslinking temperature decreases the probability of an effective crosslink forming leading to high variability in swelling ratios. All samples prepared at 110°C showed excessive swelling and were fragile. The swelling was reduced by crosslinking the samples at higher temperatures. However, at 160°C the sample had substantially changed in color showing a dark yellow color instead of the light yellow seen in all the other conditions. The darkening suggested a form of chemical degradation that was thought to be undesirable. It was decided that 130°C was the optimal crosslinking temperature giving reproducible and controllable swelling through the control of the crosslinking time. The standard crosslinking condition was set at 130°C for 6 hours of crosslinking time. This condition afforded up to 509% swelling in volume and gave yarns with sufficient strength allowing for their handling.
An important parameter in preparing twisted yarn actuators is the ability to insert variable twist. PAA nanoyarns were prepared by inserting different twist and then imaged by SEM to evaluate the retained nanofiber twist. As shown in Figure 45, twisted samples displayed the expected helically oriented nanofiber orientation at the yarn surface. Also, yarns prepared with increasing inserted twist displayed higher helix bias angles (taken relative the yarn long axis). The measured twist is plotted against the inserted twist (measured by counting the number of turns inserted during twisting of the yarn). As shown in Figure 45, there is a correlation between measured and inserted twist with a slope close to 1. However, the intercept is far from 0 at ~400 turns/meter. This discrepancy suggests that there is a consistent loss of inserted twist that was retained in the final structure for all yarns. This loss of twist is potentially a consequence of the handling of the nanofiber yarn as the sample to untwist when detached from the sample holder. The untwist may be due to elastic recovery of the inserted twist or could be due to the sample swelling when exposed to ambient humidity.

**Conclusion**

In conclusion, we were able to make a machine that follows our design requirements. We were set to make nanofiber yarns that would be as strong as possible independent of the material chosen and would...
accommodate the maximum amount of twist independent of its diameter. We established that filament yarn is the strongest type of yarn because they are not held by friction between the fiber but by molecular interaction between the polymer molecules and that to accommodate the maximum amount twist was to obtain the smallest fiber diameter. To obtain the minimum fiber diameter we made one dimensional fibers using electrospinning and using the gap alignment technique we were able to form nanofiber diameter fibers that are centimeters assembling them into yarn by twisting thin sheets. To make our synthesis practical, we used a novel two-disk design that allows for electrospun fibers to be collected and their electrostatic charge to be neutralized using an industrial ion blower allowing for yarns of different diameters to be made with polyacrylonitrile. Yarn made of polyacrylonitrile were well behaved, and statistical analysis of their size was achieved as well as characterization of their mechanical strength.

We then proceeded to making actuators by electrospinning poly(acrylic acid) with a diamine crosslinker. We showed that we can obtain nanofiber yarns but that the presence of defects made it difficult to obtain clear differences diameters. Moreover, the shape of the nanofiber which appears to resemble ribbons more than cylinders and melting of the nanofibers made their characterization difficult. Crosslinking the nanofiber yarns into a hydrogel in the dry using heat was successful and allowed us to demonstrate control over a wide range of diameter changes in response to pH from 1.6 to 2.6 times. Finally, hydrogel nanofiber yarns where twisted and it was shown that their angle was slightly lower when inferred from the twisting process than the true angle measured by SEM. Twisted hydrogel nanofiber yarns were torsionally responsive and were placed in a water bath provoking an untwist of the yarn while the material was stable in these conditions for several weeks.

It follows that we will attempt to characterize the torsional actuation of our samples in different pH solution and results will be presented in the following chapter.

III. Hydrogel nanofiber yarn torsional actuators

Introduction to torsional artificial muscles

High output torsional actuators are an emerging branch of artificial muscles that differ to bending actuators in that they can rotate over a full turn per millimeter of their length in response to stimulation. They are of interest as they are an excellent candidate for miniaturization where conventional piston driven combustion engine or electric motors have proven difficult to engineer and control at small scales. Torsional actuators, not unlike bending actuators, rely on the deformation of the actuator to create motion. The torsional motion is achieved in helically shape actuators made from twisted fibers or yarns and is due to a change in helix angle. Torsional actuation can reach rotation speeds of $10^5$ revolutions per minute and torsional strokes can be several hundred degrees per millimeter of length. This change in helix angle is achieved by relying on different chemistries but has the net effect of producing an internal torque inside the actuator provoking a change in twist density. Moreover, the change in twist density can subsequently be harnessed to create a rotational actuator (Javad Foroughi et al. 2011) or translational actuators (Lima, Li, Jung de Andrade, et al. 2012). The mechanisms operating in torsional actuators are reviewed below as are their potential applications in a variety of fields.
**Mechanism of torsional actuation**

Torsional actuators leverage a variety of different mechanisms to provide torsional motion. The most important contributions occur in torsional actuators that use a deformation of their crystalline or semi-crystalline structure, a change in volume or a combination of the two.

**Change in volume**

**Pneumatic driven change in volume**

A change in volume as a source for torsional actuation is of special interest in the context of pneumatic actuators. Here a pneumatic pump inflates an airtight bladder which in a helical shape as shown in Figure 48. The deformation of the bladder is reminiscent of that observed in McKibben muscles with the difference that the filaments are arranged asymmetrically provoking the torsion and ultimately rotation at its end.

![Figure 48: Pneumatic torsional actuator (a) before and (b) after the bladder is inflated. Reproduced from (Sanan et al. 2014).](image)

The pneumatic actuator described by Sanan *et al.* can rotate its ends up to 40 degrees for a 200mm long actuator placing this actuator at the lowest torsional output of this review. However, they possess interesting potential application in soft robotics and allow for the introduction of volume change as the main input parameter to torsional actuators.

**Chemically driven change in volume**

Torsional actuators relying on the change in volume of the helically shaped sample are the most recent and yet the most common. The change in volume drives the change in helix angle which is responsible for the torsional motion.

The first high stroke torsional actuators were made from twisted carbon nanotube (CNT) yarns. These torsional actuators were made by twist spinning CNT forests made by chemical vapor deposition...
into yarn with high twist densities (up to 20000 turns/m). The torsional actuators, originally invented by leveraging their conductivity in an electrochemical configuration where the yarn was placed in an electrolyte solution of tetra butyl ammonium perchlorate, providing a large cation, and is charged negatively using a potentiostat (J Foroughi et al. 2011). The injection of the large cation into the electrochemical double layer to balance the surface charge results in the change in volume of the yarn. Experimental results are reproduced in Figure 49, which shows the actuators morphology and actuation under electrostimulation. Here the yarns are made of very thin filaments that are bundled and highly twisted. When partially immersed in the electrolyte and with the electrochemical cycling of the immersed part in the so-called ‘two ends tethered’ configuration (detailed in Figure 56) the torsional actuation is seen by the rotation of a paddle attached to the yarn. Torsional actuation of up to 41 full turns for a 6 cm long CNT yarn at speeds up 590 turns/min were reported for the electrochemically actuated samples.

![Figure 49](image)

Figure 49: Torsional actuation of CNT nanofiber yarn, scanning electron microscopy and geometry presented in [a] and resulting actuation under electrochemical stimulation in [b].

Reproduced from (J Foroughi et al. 2011).

A whole range of different composite yarns has successfully been made that are derived from the electrochemically driven CNT torsional actuators. The composite yarns retain a highly twisted multifilament structure and incorporate some element to control the actuator’s volume. Using an infiltrated guest during yarn spinning allowed the actuator’s volume to be controlled by heating relying on the thermal volume expansion of the guest. Paraffin wax (Lima, Li, Jung de Andrade, et al. 2012) was the first such guest material. As the temperature increased the paraffin first melted and then further heating of the liquid paraffin guest increases in volume creating an internal pressure that acts against the filaments of the CNT yarn consequently expanding the diameter of the yarn and increasing its helix angle. Subsequently, when tethered at both ends and coupled with return spring made of an inactive (not paraffin infiltrated) actuator section, this increase in helix angle creates an internal torque that provokes
an untwist in the actuating region and an increase in twist in the return spring. At the junction between the two where a paddle is placed and is observed its rotation is concomitant with the yarn’s torsional actuation, which can reach up to 5 turns at 12K turns/min for the wax infiltrated yarns. When the heat is removed, the return spring untwists and re-twists the actuating part of yarn to provide reversibility to the torsional actuator. This is shown by the million actuation cycles the wax infiltrated yarn was able to undergo without appreciable loss of speed or range of motion. Compiled results are reproduced in Figure 50 where CNT yarns are actuated by Joule heating leveraging their conductivity which provokes the wax expansion.

![Figure 50: Torsional actuation of two ends tethered CNT yarn with half the actuator infiltrated with wax and the other half used as a return spring. Actuation is the result of Joule heating, [a] shows the remarkable cycling stability and [b] the torsional actuation behavior at different stress against the input power. Reproduced from (Lima, Li, Jung de Andrade, et al. 2012).](image)

More generally it was shown that phase change materials could trigger a yarn change in volume irrespective of the such as icosane (Suh et al. 2016) the shortest compound found in paraffin waxes, could be used to drive the active part of the actuator change in twist density

More exotic examples of chemically driven volume changes have been shown in the context of CNT torsional actuators, such as by hydrogen absorption on palladium coated CNT yarns. The sample with its two-ends tethered comprising non-actuating return spring was placed in a chamber where 0.05 ATM of H₂ was fed which adsorption is provocuing the volume change in the yarn. The actuator was then able to recover its original shape when hydrogen was removed thanks to the return spring. Furthermore, actuation can be triggered by the adsorption of water on PEDOT-PSS infiltrated CNT yarn (Gu et al. 2016) that also could be triggered by changing humidity in the actuator’s surrounding. This lead to a reversible torsional actuation of 106 revolutions for a 25 mm sample. In both, these precedent examples adsorption is responsible for large volume changes due to the large surface area of nanometric structures which is responsible for the macroscopic change in the actuating part of yarn twist density.
Interestingly, chemically driven torsional actuation was not restricted to CNT yarns and was shown in another type of fibers. All these actuators have in common a high twist density and a fiber acting as a stiff matrix. It was shown that graphene oxide hydrogels based highly twisted fibers could actuate up to 588 degrees per mm (Cheng et al. 2014) by absorbing water reversibly.

**Deformation in crystalline or semi-crystalline structure**

The first reports of torsional actuators emerged almost 20 years ago (Keefe & Carman 2000; Kim & Kang 2001; Paik et al. 2010; Rodrigue et al. 2015). These actuators were made from shape memory materials that rely on a change in their crystalline or pseudo-crystalline structure to change shape and create motion. Among such actuators are shape memory alloys which torsional actuation mechanism and metrics are detailed below.

**Shape memory alloys based torsional artificial muscle**

These artificial muscles were among the first demonstrating torsion whereby a change in the internal structure drove a significant torsional motion of the actuator. Driven by solid-state phase transition in the crystalline structure of the material industrially developed shape memory alloys comprise a wide range of crystals among which nitinol (Ni-Ti) is the most common. The shape memory is shown by bending a sample past its elastic limit then by heating the deformed sample past its critical temperature when the process is done the material recovers its initial shape and can undergo a wide number of these deformation-recovery cycles which makes it an excellent candidate artificial muscles. This simple memory can further be exploited to show reversible memory by complex training process. This is due to the martensitic solid state crystal phase transformation which transforms the martensite composition of the alloy into austenite crystals (Humbeeck et al. 1991). This memory effect can be reset by annealing resulting in a new permanent shape of the austenite crystalline structure.

Furthermore, progress into harnessing these deformation patterns to make high throughput torsional actuator have been met with success. Using a 25 µm nitinol wire speeds up to 10K rpm where achieved with a torsional stroke of 46 degrees per mm yielding 12.5 turns for a 25 cm actuator (Mirvakili et al. 2018). The nitinol microwire was twisted into a loop and a paddle was attached at the junction (as shown inFigure 51), torsional motion was observed as the sample were heated and the paddle rotated.

![Figure 51: Twisted nitinol heat activated torsional actuator reproduced from (Mirvakili et al. 2018).](image-url)
The nitinol wire’s permanent shape is unbent so after the microwire is deformed into a twisted structure and heated, the actuator untwists to recover its initial shape. Consequently, it develops an internal torque rotating the paddle that is eventually balanced by the rest of the yarn’s twist which acts as a return spring. When the heat is removed, the sample retwists and a new cycle can begin.

Interestingly a new wave of polymer-based shape memory material has recently been discovered which have allowed a leap in torsional actuation scale. These plastic actuators have attracted the attention and focus of intense research in past years and represent a viable alternative to shape memory alloys as they are cheaper, easier to manufacture and readily available.

**Semi-crystalline polymer torsional artificial muscle**

In the recent years, a breakthrough in torsional actuators came in the form of highly twisted carbon nanotube yarn actuated by electrochemistry, detailed above. It was quickly followed by the use twisted highly oriented polymer fibers such as nylon and high-density polyethylene (Haines et al. 2014) as torsional actuator leveraging two interesting phenomena, their negative thermal expansion in the fiber length and an increase in the fiber diameter when heated. This anisotropic thermal expansion on heating contributed to the partial untwist of these fibers when they were heated.

The interesting and uncommon thermal properties are usual in highly drawn semi-crystalline polymer fibers (Choy et al. 1981) and appears to be a consequence of the alignment of the crystal chain axis in the fiber direction due to the drawing of the fiber during its processing and the incomplete crystallization leading to the presence of an oriented amorphous phase. The latter is a blend of several different types of polymer chains structure detailed in Figure 52. Of particular interest are tie molecules which are thought to be at the origin of the negative thermal expansion (Choy 1981). Due to their freedom to move outside of their anchor points, they could show the entropic effect found in rubbers, with the crystalline part forming the crosslinks. The actual length of the inter-crystalline region is determined by the resulting internal stress balance between the moduli of the two phases that make up this region: the amorphous tie molecules contracting and exerting a compressive force on the crystalline bridge region. Consequently, as explained by rubber elasticity theory the modulus of the rubbery amorphous phase increase with temperature [see “The Origin of the Elastic Retractive Force” from (Mark 1981)] and results in a shortening of the fiber as the force exerted by the amorphous region increases to further compress the crystalline regions.
Figure 52: Schematic view of the inter-crystalline (B, A and TM) and crystalline (C) regions of a highly drawn semi-crystalline polymer fiber. The former appears as a blend of (B) crystalline bridge molecules, (A) folded polymer chains and oriented tie molecules. Reproduced from (Choy et al. 1981).

This shortening of the fiber in the axial direction in a twisted helical fiber results in a higher twist density in the sample leading to an increase in the bias angle of the fiber. Furthermore, heating of highly drawn crystalline fiber causes an increase in their diameter as a response concomitant with the reduction of their length. An increase of diameter also provokes an increase in the bias angle of the fiber at constant twist density. As a result, these two processes are at the origin of an increase in the helix angle of the fiber. It follows that when coupled to a return spring the increase in twist density in the actuating fiber can be released in the spring making their junction point turn.

Interestingly torsional actuation is repeatable and stable when cycled multiple time through heating and cooling (shown in Figure 53). Here the twisted sample is free to move thanks to a low friction air bearing system, and it is heated in cycles to provoke an untwisting of the fiber.
Figure 53: Untwisting due to the torsional actuation of a twisted 70mm nylon fiber reproduced from (Aziz et al. 2015).

It follows that these heats driven actuators show a combination of volume change and change in the semi-crystalline structure which allows for a large motion to be obtained. Interestingly change in volume can be leveraged to make torsional actuators that show interesting properties such as actuation provoke using chemistry or pneumatics.

**Potential applications of torsional actuators**

The compactness and lightweightness of these new actuators make them a compelling alternative to traditional rotary engines such as electric motors or piston driven crankshaft in the microscopic application. Proposed opportunities are in the development of microfluidic mixers and autonomous microbots in which the actuator would mimic the bacterial flagella (Javad Foroughi et al. 2011).

Active micromixers are an important requirement for lab on chip application to achieve their anticipated ease of use and widespread deployment (Janasek et al. 2006) as they potentially can allow for controlled mixing without the need for vortex mixers and passive micromixing using complex channels that consume chip space. Torsional actuators have been shown to be applicable as a micro stirrer, which was obtained with CNT nanoyarns in the two-end tethered configuration with a return spring and controlled by electrochemistry. This system allows in-channel mixing of fluids and makes torsional actuators an interesting alternative to regular mixing techniques.

Moreover, with its ability to react to chemical changes torsional actuators make for interesting sensors. By producing a nanogel MWNT composite yarn and using boronic acid as a sensing chemical, it was shown that a change in volume could be obtained by exposing the yarn to glucose. The change in volume in the twisted yarn structure allowed for a torsional motion that could be detected allowing for the estimation of glucose concentrations from 4 to 20mM. This glucose sensor is an important step towards implantable, self-powered actuating sensor for controlled drug delivery (Lee et al. 2016).

Leveraging the change in volume in twisted structure can also be done with the aim of energy harvesting. It was shown that was half infiltrated CNT yarn could actuate using the guest expansion upon...
heating and were demonstrated to be able to produce enough torque to act as passive blinds (Suh et al. 2016) that can open on close as a function of temperature which could harness the difference of temperature between day and night. Ultimately this change in temperature is transformed into mechanical energy. Furthermore, CNT yarns have been shown to produce up to 250 W/kg of electrical energy when the yarns are twisted and coiled and operated as an electrochemical capacitor. The coiled structure deforms under stress which changes its areal capacitance: when the tensile stress increases it creates radial compressive stresses on the carbon nanotubes bundles that decrease the porosity of the yarn effectively decreasing the capacitance of the twisted structure. Consequently when the yarn is subjected to a cyclic loading this change in capacitance can be harnessed as electrical energy (Kim et al. 2017) and can be used in an electrolyte solution or air by having yarns of opposite chirality act as a two-electrode system while tension is maintained by a rubber filament. Harnessing mechanical energy was also shown using the triboelectric effect with a complex assembly of a silver coated nylon coiled around a polyurethane fiber enclosed in a multi-layer assembly of piezoelectric PVDF-TRFE and CNT sheet. This multilevel filament was able to harness mechanical energy from the friction between the PDVF-TRFE and the silver coated nylon using the triboelectric effect and also act as a bend and stress sensor (Sim et al. 2016).

Lastly, one of the most important applications of torsional actuators is in the development of artificial muscles. When twisted into coils CNT yarns have been shown, when infiltrated with guests such as wax, to transform the torsional actuation triggered by heat into linear actuation of the coiled structure. Here when the wax infiltrated coiled CNT yarn is heated the actuator changes in volume which subsequently decreases the distance between each coil reducing the overall length of this actuator. The geometry effectively transforms the torsional strain in the twisted fiber to a length change in the coil (Lima, Li, Jung de Andrade, et al. 2012). Furthermore, similar processes occur in twisted and coiled polymer fibers, such as nylon. Here the nylon filaments are highly twisted and coiled to form an actuator that can contract and expand as a function of the temperature.

Hydrogel torsional actuators

This study aims to make torsional actuators by leveraging the capabilities of the nanofiber yarn making machine. Hydrogel nanofiber yarns were prepared by electrospinning a poly(acrylic acid)-jeffamine in DMF solution and subsequently using heat treatment to crosslink this material into a gel. This method can provide a wide range of volume changes as well as helix angles to provide a comprehensive description of the potential of this novel material and its interesting geometrical properties.

It was expected that the small diameters of the electrospun fibers would be suitable for preparing yarns with large twist densities. The high inserted twist is considered important for making high stroke torsional actuators. As the object swells, and the volume is increased it would consequently rotate as the helix angle increases and, since hydrogel are highly-swellable materials, they may generate higher torsional actuation than previously reported. Moreover, the high length to diameter ratios of this material, with sub-millimetre diameters and several centimeters in length, may result in increased actuation speed compared to bulk gels. To shape this study, the starting point was to model the potential outcomes using
the existing knowledge hinging on the single helix theory and the dimension of the samples fabricated using the methods described in Chapter 2.

**Modeling**

The single helix theory attempts to capture the torsional motion of yarns by describing these materials as a string wrapped helically around a cylinder. This approach allows for the description of the system as a set of triangles as shown in Figure 54. The triangles represent a 2D projection on a plane done by unraveling the helix. This model is first used to derive expectations on the hydrogel nanofiber yarns’ actuation. To simplify this preliminary analysis, the results of the precedent studies will be used. In these studies, the invariants were the string length (the length of the helically wrapped ‘string’ or the long side of the triangle) and the swelling ratios and yarn initial dimensions.

Using this model, the following equations are derived based on the set of the following variables $L_s$ and $L_{s0}$ respectively represent the length of the wrapping string after swelling and the initial string length. It follows the swelling ratio of the string is $\lambda_{Ls} = \frac{L_s}{L_{s0}}$. The other variable follows the same nomenclature and describe the swelling ratio in the diameter direction $\lambda_D$ and in the yarn’s length $\lambda_L$. Furthermore, $n$ represents the number of turns with which the string wraps itself around the cylinder. From this nomenclature and the single helix model it can be shown that,

\[
(L_{s0}\lambda_{Ls})^2 = (n\pi D_0\lambda_D)^2 + (L_0\lambda_L)^2
\]

\[
(L_{s0})^2 = (n_0\pi D_0)^2 + (L_0)^2
\]

And then,
\[ \lambda_{n}^{2} = \left( \frac{n}{n_0} \right)^2 = \frac{(S)^2 - (L)^2}{(\pi D_0)^2} \times \frac{(\pi D_0)^2}{[S^2_0 - L^2_0]^2} \]

Simplifying and rearranging,

\[ \lambda_{n} = \frac{1}{\lambda_D} \left[ \frac{S^2 - L^2}{S^2_0 - L^2_0} \right]^{1/2} \]

It follows that,

\[ \Delta \frac{T}{T_0} = \frac{1}{\lambda_D} \left[ \frac{(S_0^2 - L_0^2)^2 - L_0^2}{S_0^2 - L_0^2} \right]^{1/2} \]

The advantages offered by both the high twist densities and large swelling ratios in the hydrogel nanofiber yarns can now be explored using the above relations. As a first approximation, the string length will be assumed to be constant (\( \lambda_L = 1 \)) and equation 3 solved for a given sample geometry and isotropic swelling. This approach is used to model the impact of a change in volume swelling ratios (\( \lambda_V = \lambda_D^2 \lambda_L \)) and its effects on the torsional actuation at different initial twist densities, as shown in Figure 55. The results show that under the precedent conditions the model predicts high torsional actuation (\( \Delta T \)), here a large untwist, when the swelling ratio in volume and the initial twist density are increased. It can also be seen that under these assumptions the model predicts complete untwisting of the twisted yarns for larger volume changes. This result may be due to the assumption that the string length does not change and will have to be considered in further experimental modeling.

In conclusion, this early stage modeling constitutes a solid base which predicts interesting properties for the hydrogel nanofiber yarn that eventually could rival the best performing torsional actuators made to date especially in the region of interest where the swelling approach the swelling ratios of \( \sim 2 \).
Results and Discussion

Study layout

To characterize this new material and its geometry several experiments were performed. Firstly, the torsional actuation was evaluated in the one-end-tethered configuration with the sample exposed to different pH solutions. The samples were fully immersed in the different pH solutions and free to untwist. Subsequent experiments involved the samples being tethered from both ends. These experiments allowed for the characterization of the torsional and linear actuation of half immersed samples. Moreover, the experimental data was used to undertake a modeling effort and predict the behavior of hydrogel nanofiber's yarn torsional performance. Finally, samples were fully immersed in a bath with their two ends tethered to prevent both rotation and translation and discovered a new type of motion that has never been reported in the literature to our knowledge. The schematic illustration of the two modes of characterization, one end tethered and two ends tethered are shown in Figure 56.
Figure 56: Drawing of the nanofiber yarns characterization techniques with [a] the one end tethered configuration with (1) a steady holding surface, (2) the free to untwist nanofiber yarn and (3) an attached weight allowing to count the turns and indicating the rotation direction. And [b] the two end tethered configuration with (1) A lever arm system to apply constant force and measure length changes, (2) a hook system to hold the sample, (3) a highly twisted nanofiber yarn sample and (4) a steady surface. Note: in this test the sample was only partially immersed in the pH solutions.

One end tethered experiments

Hydrogel nanofiber yarns were prepared according to methods and their volume transition was obtained by immersion in different buffered pH solutions. The swelling ratios in diameter were determined independently using a microscope to be up to 2.16 times. The untwisting and the change in length of the sample was monitored using a camera and interpreted with the Tracker opensource software by making a vector. This 2D object allowed for the encoding of both the length and torsional change occurring in the sample while the pH was varied.

In one typical one end tethered experiment (in Figure 57), it can be seen that a sample, initially with a twist density of 1448 turns/m loses up to half its inserted twist when the weight of a small paddle (up to 100 mg) was attached to one end in air. It was found that this weight was an imperative requirement to prevent the yarn sample from floating during the subsequent immersions. This initial untwist of the sample is represented by black dots at time t=0 in Figure 57 In the first immersions in pH 1.5, it is seen that the actuator untwists abruptly and loses all its remaining twist and eventually stabilize rotation around -200 turns/m.

It should be noted that any negative twist values are likely due to variations in the initially inserted twist of each sample. The initial twist was calculated from the length of the sample and the twist per length inserted into the full yarn length during fabrication. Any error in sample length measurement, any inhomogeneity in twist insertion or sample’s diameter, or any loss of sample twist during handling would result in an incorrect determination of the initial twist. These factors could account for the apparent ‘negative twist’ for the samples immersed in pH 1.5 solution.
To provide grounds for further analysis, the tests were repeated eight times on fresh samples and the data analyzed with a routine statistical analysis using OriginPro statistics package. The combined results were plotted using one standard deviation as error bars and obtain the data shown in Figure 58. As shown, the average twist in the samples settles around 0 after the first immersion at pH 1.5. It is hypothesized that this complete untwisting is a consequence of the crosslinking method and the geometry of the samples. It is noted that the load induced untwisting was not reversed upon the removal of the stress. This inelastic torsional deformation indicates that the highly aligned multifilament nanofibers act independently with little inter-fiber adhesion and few physical entanglements that would impart strain recovery during unloading. During the synthesis, the crosslinker was mixed with the PAA polymer solution to electrospin into nanofibers for bundling and twisting into the yarn. The crosslinker was then activated by heat but appears to remain inside the nanofibers and did not promote adhesion between fibers. Thus, the yarn is free to untwist since there no crosslinking at the bundle of nanofibers scale.
Figure 58: Untwisting of a set of hydrogel nanofiber yarn torsional component

The samples’ changes in length were also determined by video recording for all eight samples. The statistical analysis results are represented in Figure 59. Although again there was considerable variability, a consistent trend was observed for the average length increasing in pH 10 solutions compared to the length in pH 1.5 solution. Based on the initial (dry) length of the samples (20 mm), the average increase in sample length was 113% when the object was first immersed in pH 1.5. When the pH was changed from 1.5 to 10 the length increased to 125% based on the initial dry length. The change in length was reversible when the pH was switched back to 1.5 from 10.

Figure 59: Average length (with one standard deviation as error bars) of PAA hydrogel nanofiber yarns when exposed to different pH solutions. The initial dry length of the yarns was 20 mm.
This preliminary study has shown that hydrogel nanofiber yarns are sufficiently robust for pH actuation. The samples are torsionally active under load and that their length change is reversible. At pH 1.5 swelling was shown to provoke a large untwist, up to 100% of the initially inserted twist when the sample was free to untwist. It follows that the samples are indeed pH-responsive under load and that the twist in the sample is affected by the swelling degree. Furthermore, the samples were able to expand in the diameter direction up to 2.03 times and an average length expansion of 1.13 times when the sample was immersed in the pH=1.5 solution and when compared to the dry state length and diameter. These values yielded a volume change of 4.66 times. These results show that the change in volume is anisotropic with an anisotropy ratio of \( \rho = \frac{\lambda_L}{\lambda_D} = 0.56 \) illustrating twice the amount of swelling in the diameter direction than in the length direction.

To conclude, the PAA twisted yarns were shown to be torsionally active, here the large swelling caused complete untwisting in the one-end-tethered condition. It follows that attempts were made to obtain reversible torsional actuator by adding a spring element consisting of a non immersed nanofiber yarn part and are shown below.

Two ends tethered experiments

Effect of twist density

In the previous set of experiments, the sample would completely untwist and was unsuitable for reversible, pH driven actuation. As in previous studies, the reversibility of the torsional actuator was improved by adding a return spring to the experimental setup. This was done by tethering the yarns at both ends and immersing only half of the sample length in the pH solution. In addition, a paddle was attached to the yarn near its center to measure the torsional actuation. In this two-end-tethered configuration, it was also possible to control the tension applied to the yarn and simultaneously measuring the length of the yarn using a force/distance transducer (Lever Arm system). The minimum tensile force that could be provided by this system was \( 6.10^{-3} N \). With this experimental set up it was possible to obtain a reversible torsional actuation when cycling the sample from pH=1.5 to pH=10. Examples of the obtained actuation results for several pH cycles are reported in Figure 60 using PAA yarns crosslinked to give diameters swelling ratio of 2.16 times from pH 1.5 to 10. The figure compares the torsional actuation obtained from PAA yarns prepared with different amounts of inserted twist. All samples showed an initial loss of twist during the first immersion in pH=1.5. This untwisting was considered irreversible, as no attempt was made to dry the samples. This irreversible torsional actuation represents up to 25% of the initial twist density. Subsequent immersions in pH=1.5 and pH=10 were then reversible and the torsional actuation was on an average approximately 50% of the twist density remaining at pH 1.5.
Figure 60: Actuation of two end tethered hydrogel nanofiber yarns with different twist inserted and half-immersed in pH 1.5 or pH 10 and at a constant tension of 8 mN. Each point represents a half turn of a paddle attached to the yarn center and the torsional stroke is given as the twist density by normalizing to the immersed length of yarn.

Repeat tests on different samples gave similar results, as shown in Figure 9. The overall torsional actuation for the highly twisted 2000 turns/m samples cycles between ~80% and ~55% of the initially inserted twist when equilibrated in pH 1.5 and pH 10 solutions, respectively. This leads to an average reversible torsional stroke of ~500 turns/m, or 180°/mm, for the most highly twisted yarn. The torsional strokes compared with values 50 turns/m, 222 turns/m and 683 turns/m reported for two-end-tethered, half active fibres prepared from niobium nanowires infiltrated with paraffin wax; CNT yarns infiltrated with a mixture of paraffin and an elastomer; and neat CNT yarns electrochemically charged in an organic electrolyte, respectively. The hydrogel nanofiber yarns generate close to the highest recorded torsional strokes in the two-end-tethered configuration and as stimulated by a change in solution pH.

As expected, the two-end-tethered torsional actuation was smaller in magnitude that the free rotation that occurred in the one-end-tethered case. In the latter, the yarn samples were observed to fully untwist after first immersion in pH 1.5 solution. In contrast, the immersed part of the two-end-tethered yarn lost approximately 20% of the initially inserted twist when first immersed in pH 1.5. This fivefold reduction in actuation stroke is due to the constraining effects of the non-immersed yarn in the two-end-tethered case. In previous analysis (J Foroughi et al. 2011) has shown that the constraining effect of the non-actuating, return spring fiber is to reduce the torsional stroke by $\beta/(\beta+\gamma)$compared to the one-end-tethered configuration where $\beta$ is the ratio of the torsional moduli and $\gamma$ is the ratio of the lengths of the actuating
and non-actuating fibers. Direct measurement of the torsional moduli of the hydrogel nanofiber yarns was not possible. However, the observed four-fold torsional stroke reduction for the two-end-tethered compared with the one-end-tethered experiment suggests a maximum value of $\beta$ of around 0.27. This value would be consistent with a measured diameter ratio of ~2 and a modulus ratio of 0.017 for the wet to dry yarn, since torsional moduli can be determined using $\pi Gd^4/32$ where $G$ is the fiber shear modulus and $d$ is the fiber diameter. This sixtyfold reduction in shear modulus when the dry gel is swollen in pH 1.5 is thus reasonable.

![Fractional torsional actuation](image)

**Figure 61:** Relative torsional actuation of a two-end tethered hydrogel nanofiber yarns crosslinked at 130 degrees for 6 hours with an initially inserted twist of 2000 turns/m.

A further consideration in understanding the torsional actuation in the PAA nanoyarns is their length change that accompanies the swelling and de-swelling transitions. These experiments involved using a lever arm transducer to apply a fixed tensile force to the two-end-tethered sample and to measure the length change of the combined immersed and non-immersed parts of the sample. Example results showing the measured change in length against time for a PAA yarn sample during several part immersions in pH 1.5 and pH 10 solutions is shown in Figure 62 a). Some disturbances in the measured length change occurred when the pH solution was changed leading to drift in the baseline values. However, the results indicate that the sample length decreases when first immersed in pH 1.5 from dry, increases when subsequently immersed in pH 10 and decreases again when re-immersed in pH 1.5. Taking a moving average approach and normalizing the length change to the previous equilibrium length, the results of Figure 62 b) show a consistent pattern for three samples prepared using the same conditions. All samples show a consistently shorter length in pH 1.5 and longer length in pH 10, settling at -1.15% at pH=1.5, 2.3% at pH=10 for an overall change of 3.4%. It is also noted that the variability in sample length tended to decrease with subsequent immersions. The standard deviation starts high at 1.75 for the first immersion in pH=1.5 and 0.14 for the last immersion.
This change in standard deviation can be explained by the synthesis process. When the nanofibers were first prepared in a low and controlled humidity environment (under nitrogen) they are then twisted in a variable humidity environment (highly variable uncontrolled laboratory atmosphere) to form nanoyarns. This sudden change in humidity can cause a volume change that may form crimps in the yarn’s structure. Attempts at using large weight to unravel these crimps was difficult due to the low breaking strength of the hydrated or partially hydrated specimens. Successive immersions in pH=1.5 and pH=10 under load tends toward what appears to be a stable equilibrium length.

Using these two stable length states and assuming that the non-immersed part of the yarn shows a negligible length change, the twist density in the active part of the samples was determined and the change in twist density was calculated using equation 4.

These values are summarized in Table 4 with the relative dimensional changes for yarns prepared with different initial twist. The absolute magnitude of untwist in each swelling condition increased with increasing inserted twist, however, it was found that the relative twist loss seemed to be independent of the twist inserted. For all samples investigated an average of 26% of change in twist density was observed during the transition between the dry state and pH 1.5 and 40% of change in twist density from pH 1.5 to pH 10 relative to the active length (Table 5). Interestingly, it was noted that as the sample twist density is increased the change in volume during the pH transitions does not change (shown in Figure 63).

<table>
<thead>
<tr>
<th>T0</th>
<th>500</th>
<th>1000</th>
<th>1500</th>
<th>2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>1.5</td>
<td>10</td>
<td>1.5</td>
<td>10</td>
</tr>
<tr>
<td>$\lambda_D$</td>
<td>1.45</td>
<td>2.03</td>
<td>1.45</td>
<td>2.03</td>
</tr>
<tr>
<td>$\lambda_V$</td>
<td>1.71</td>
<td>4.50</td>
<td>2.63</td>
<td>4.49</td>
</tr>
<tr>
<td>------------</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>$\lambda_L$</td>
<td>1.24</td>
<td>1.09</td>
<td>1.25</td>
<td>1.09</td>
</tr>
<tr>
<td>$\lambda_n$</td>
<td>0.90</td>
<td>0.67</td>
<td>0.83</td>
<td>0.61</td>
</tr>
<tr>
<td>$\frac{\Delta T}{T_0}$</td>
<td>-0.27</td>
<td>-0.39</td>
<td>-0.34</td>
<td>-0.44</td>
</tr>
</tbody>
</table>

Table 4: Result of the two end tethered experiment with different twist densities of PAA nanofiber yarns made at 130 degrees 6H. $T_0$ and all $\lambda$ ratios refer to the starting state for the transition from the dry condition to immersion in pH 1.5 and to transition from pH 1.5 to pH 10 condition.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Average $\frac{\Delta T}{T_0}$</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry $\rightarrow$ pH 1.5</td>
<td>-0.26</td>
<td>0.06</td>
</tr>
<tr>
<td>pH 1.5 $\rightarrow$ pH 10</td>
<td>-0.40</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Table 5: Average change in twist density from dry to pH 1.5 and pH 1.5 to 10 where $T_0$ is the twist density at the start of each transition.

It must also be noted that the fact that the experimental results summarized above represent only a small fraction of the experiments carried out with a survival rate at three pH cycles estimated below 40%. This high failure rate was interpreted as the consequence of the large proportion of defects in the structure of the nanoyarn in the forms of beads. These large beads may have created localized regions where swelling may have been significantly higher than in the remainder of the sample. This discontinuous swelling in conjunction with the low breaking strength of the samples may have led to the frequent breaking under stress.
Figure 63: Relative change in volume as a function of the twist density, the red points represent the transition between dry to pH 1.5 and the blue point between pH 1.5 to pH 10.

**Effect of Swelling ratio**

Next experiments investigated the torsional actuation output of the PAA nanoyarn samples by changing the swelling ratio of the PAA. To achieve this, samples at the same starting twist density of 2000 turns/m were exposed to different amounts of heat to vary the extent of the crosslinking reaction. The three crosslinking conditions were 130 degrees Celsius for 4 hours, 130 degrees Celsius for 15 hours and 160 degrees Celsius for 15 hours.

These different crosslinking conditions lead to varying swelling ratios characterized by microscopy by measuring the diameter change depending on the pH ($\lambda_D$). Also, the length change in the one end tethered condition (full untwist) and then in the two-end tethered configuration (half immersed) were determined.

$$\rho = \frac{\lambda_L}{\lambda_D}$$  \hspace{5cm} 5

The results are summarized in the Table 6. Here, it was observed that as the samples were exposed to increased heat during crosslinking, the swelling ratio and the swollen volume decreased. These changes are the consequence of the heat driven crosslinking reaction. As the temperature is increased the chemical equilibrium is shifted toward the formation of effective crosslinks in between the polymer molecules. It follows that the ability of the gel to swell is hindered as the number of free carboxylate moieties decreases and the crosslink network density increases. Furthermore, it was observed that this change in swelling did not have a significant impact on the torsional actuation of the samples at the dry to pH 1.5 transition. However, the extent of swelling influenced the torsional actuation at the pH 1.5 to 10 transition with a net decrease of the torsional actuation as the sample was further crosslinked. It is likely that this
difference is due to the relative importance of the two effects with a comparatively small generated untwist as the dry to pH 1.5 condition compared to the pH 1.5 to pH 10 condition.

Lastly, it was found that the anisotropy of the sample characterized at 0 twist decreased with increasing crosslinking temperature. It is hypothesized that the anisotropic swelling of our samples is due to the alignment of the backbone of the polymer chains with the fiber axis which is a known side effect of electrospinning. This is further corroborated by the decrease in anisotropy as a function of the crosslinking temperature as an increase in temperature is likely to reduce the alignment of the polymer backbone with the fiber axis as it induces a random motion of the polymer molecules.

<table>
<thead>
<tr>
<th>Crosslinking conditions</th>
<th>130-6H</th>
<th>130-15H</th>
<th>160-4H</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>1.50</td>
<td>1.50</td>
<td>1.50</td>
</tr>
<tr>
<td>$\lambda_n$</td>
<td>0.80</td>
<td>0.91</td>
<td>0.92</td>
</tr>
<tr>
<td>$\lambda_v$</td>
<td>2.08</td>
<td>1.68</td>
<td>1.40</td>
</tr>
<tr>
<td>$\lambda_{L2}$</td>
<td>1.10</td>
<td>1.09</td>
<td>1.03</td>
</tr>
<tr>
<td>$\lambda_D$</td>
<td>1.45</td>
<td>1.36</td>
<td>1.08</td>
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<tr>
<td>$\lambda_L$</td>
<td>1.01</td>
<td>1.10</td>
<td>1.20</td>
</tr>
<tr>
<td>DT/T0</td>
<td>-0.21</td>
<td>-0.17</td>
<td>-0.24</td>
</tr>
<tr>
<td>$\rho$</td>
<td>0.76</td>
<td>0.80</td>
<td>0.96</td>
</tr>
</tbody>
</table>

Table 6: Change in swelling and twist for samples prepared at a constant twist density (2000 turns/m). $T_0$ and all $\lambda$ ratios refer to the starting state for the transition from the dry condition to immersion in pH 1.5 and to transition from pH 1.5 to pH 10 condition.

**Single Helix Modelling**

The results of both the one-end-tethered and two-end-tethered experiments clearly show a tendency of the twisted PAA nanoyarns to untwist due to swelling when immersed in pH 1.5 from dry and further when immersed in pH 10 solution. Previous studies have also shown that twisted fibers and yarns show a
torsional untwist during volume expansion. The common feature in all these previous studies was the presence of a stiff, helically oriented element, such as carbon nanotube bundles or oriented polymer chains. This stiff ‘reinforcing’ element is believed to cause the untwist of such systems as it resists extension during the fiber volume expansion and drives an untwist of the fiber to accommodate its fixed length. The twisted PAA nanoyarns do not contain any such stiff reinforcing material. Each individual nanofiber in the yarn would be expected to swell in both the length and diameter direction when immersed in the different pH solutions. The question of why these yarns also untwist during volume expansion is considered by applying the single helix model.

Figure 64: Schema of a filament yarn with filament helicoidal path changing from the center to edge of twisted structure [A] and geometrical interpretation [B] of the center and middle filaments with D₀, S₀ and L₀ respectively the diameter, string length and actuator length prior and D, S and L after swelling.

The PAA nanoyarns are considered by a greatly simplified model consisting of two nanofibers: one straight fiber representing a nanofiber at the centre of the yarn; and a helically oriented fiber located at some radius away from the centre. The two fibers are connected at both ends, as shown in Figure 18. Swelling of the straight central nanofiber causes a length change of \( \lambda_L = L/L_0 \) which is the same as the change in the end-to-end length of the helix. If it assumed that the ‘string length’ of the helically wrapped nanofiber (ie. the length of the helical path, S) changes in the same ratio as that of the straight fiber, then \( \lambda_S = S/S_0 = \lambda_L \). By substituting this condition into equation 2, the ratio of final twist in the yarn to the initial twist is given simply by:

\[
\lambda_n = \frac{n}{n_o} = \frac{\lambda_L}{\lambda_D}
\]
All of the experimental results reported for the PAA nanoyarns shows that the yarns preferentially swell in the diameter direction compared with the length direction. In such cases \( \lambda_L < \lambda_D \) and the single helix model predicts that \( \lambda_n < 1 \) which corresponds to a sample untwist. It is therefore concluded that the untwist of PAA yarns occurs due the anisotropic swelling occurring in the yarns and is derived from similar anisotropic swelling in the individual nanofibers. If the yarns swelling was isotropic, then equation 2 is solved to show that \( \lambda_n = 1 \) and there would be no change in yarn twist.

Anisotropic swelling of the nanofibers likely results from a degree of molecular alignment induced by the electrospinning. This process is known to generate highly oriented polymer chains in the fiber direction. In this study, this orientation may be locked into the fibers by the crosslinking reaction. Absorption of water during immersion in the pH solution is then likely to swell the fibers more in the direction perpendicular to the chain orientation (diameter direction) than parallel to the chains.

 Attempts were made to further apply the single helix model to quantitatively predict the amount of untwisting that was experimentally observed. The total expected untwist \( \frac{\Delta T}{T_0} \) at the different studied transitions can be calculated using equation 4. These results are given in Table 7. Two different calculations were performed that provided a solution to the problem of how to determine the string length change during each transition. The change in string length could not be independently measured so in the first case it is assumed that the string length does not change either during the transition from dry to pH 1.5 or during the change from pH 1.5 to pH 10. With this assumption, equation 4 becomes:

\[
\frac{\Delta T}{T_0} = \frac{1}{\lambda_L \lambda_D} \left[ \frac{S_o^2 - L^2}{S_o^2 - L_0^2} \right]^{1/2} - 1
\]

Secondly, the degree of untwist was also calculated using the assumption that the change in string length is the same as the change in the twisted yarn length, as described above. In this case the change in twist is given by:

\[
\frac{\Delta T}{T_0} = \frac{1}{\lambda_D} - 1
\]

<table>
<thead>
<tr>
<th>Twist (tpm)</th>
<th>( \frac{\Delta T}{T_{DRY}} )</th>
<th>( \frac{\Delta T}{T_{1.5}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>Calculation 1</td>
<td>Calculation 2</td>
</tr>
<tr>
<td>Experimental</td>
<td>Calculation 1</td>
<td>Calculation 2</td>
</tr>
</tbody>
</table>
Table 7: Comparison of the experimental and predicted values for fractional change in twist using the single helix theory. Calculation 1 refers to the results obtained assuming the ‘string length’ remains constant during each transition. Calculation 2 is based on the assumption that the change in string length is the same as the change in the overall yarn length during each transition.

<p>| | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>-0.27</td>
<td>&lt;0</td>
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<td>-0.39</td>
<td>NA</td>
</tr>
<tr>
<td>1000</td>
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<td>-0.44</td>
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<tr>
<td>2000</td>
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<td>-0.34</td>
<td>-0.31</td>
<td>-0.37</td>
<td>-0.54</td>
</tr>
</tbody>
</table>

The results summarized in Table 7 show that the single helix theory predicts an untwist for all samples, which is due to their anisotropic swelling. Interestingly, the single helix theory predicts unreasonably large degrees of untwisting if the assumption is made that the string length does not change during the transitions. For small degrees of inserted twist, the single helix model predicts a complete untwist during the first immersion in pH 1.5 if the string length does not change. In fact, experiments showed that the loss of twist was only ~20% to 30% based on the initially inserted twist. In previous studies, it has been shown that the ‘constant string length’ assumption was valid since those studies involved twisted fibers and yarns that included a stiff, helically oriented reinforcing fiber. However, the PAA nanoyarns do not contain any such inextensible helical reinforcement.

The second assumption that the string length ratio is the same as the twisted yarn length ratio gives single helix model predictions that appear to be in reasonably good agreement with the experimental values for both transitions. The single helix predicted values were on average 28% higher than the experimental values for both transitions. This error can be due to multiple factors, including the experimental difficulty in accurately determining the sample dimensional changes and assumptions based on the string length change. Also, it is expected that the return spring (non-immersed part of the sample) will exert a torque on the sample at high untwist preventing further untwist and reducing the observed torsional actuation.

**Nanofiber yarn snarling and coiling**

An incidental observation made of yarns held in the two-end-tethered configuration and when the yarn was fully immersed in the pH solutions was the occasional formation of coiled superstructures. Unfortunately, in these situations the yarn would almost immediately break thereby releasing its inserted twist abruptly. To further investigate this intriguing transition, a new experiment was designed to decrease the amount of stress applied to the sample, while maintaining its twist density by tethering at
both ends. These conditions were achieved by vertically suspending the yarn sample with a long plastic fiber attached to the free end. This yarn and attached fiber were fixed between two vertical glass slides so that the yarn end was free to move vertically but could not rotate.

A typical result is shown in Figure 65, when the high swelling PAA yarn of 2000 turns/m was completely immersed in pH 1.5 solution. The torsionally active PAA nanofiber yarn end started to rotate but the rotation was limited by the attached fiber contacting the glass slide. The yarn then started folding with the sample formed a tightly bent snarled and coiled superstructure. Consequently, the overall yarn length reduced substantially as the sample snarled giving a final contraction of well over 50% of its initial length. Furthermore, when subsequently immersed in a pH 10 solution the sample clearly showed signs of forming more superstructures with further shortening in length. Returning the sample to pH 1.5 with the application of a small tension force on the yarn end it was possible to unravel the sample. Placing in pH 10 again would provoke a similar shortening sequence of events.

![Figure 65: PAA nanofiber yarn sledge experiment forming superstructures and shortening as a result. Scale can be deduced from the 0.5mm nylon fiber.](image)

Constant length tests were next performed in a horizontal bath to further investigate the reversibility of the samples’ superstructure formation. A custom-made bath was fabricated so that the nanofiber yarn’s ends would be tethered, and the sample would be fully immersed in pH solutions. The small receptacle was made by welding layers of laser cut Perspex and is shown in Figure 66.
Figure 66: Custom design immersion box for the horizontal two end tethered full immersion experiment showing [a] the isometric view and [b] the longitudinal section with (1) the water line, (2) the sample and (3) the glue points.

Full immersion, constant length tests were performed on the low-swelling yarns prepared by crosslinking at 160°C for 4H. Spectacular behavior such as illustrated in Figure 67. Here when the two-end-tethered, fully immersed PAA nanofiber yarn was exposed to pH 1.5 solution it swelled substantially in both diameter and length. The latter caused the yarn to progressively bend and then formed a spiral shape followed by a “snap-in” transition to a large bend resembling a coil.

Figure 67: Coil forming in a PAA nanofiber yarn immersed in pH 1.5 solution. Fiber is ~100μm in the dry state.

Subsequent immersion of the same sample in the pH 10 solution caused a second coil on top of the first, shown in Figure 68. This motion appeared to be due to the tip of the snarl rotating and curving on itself driving the propagation of the deformation as the sample swelled. Eventually, the sample stopped moving after 4 minutes and finished with a large snarl, a few millimeters long that was static and appeared stable. After having reached this steady state the sample was again immersed in the pH 1.5 solution and it simultaneously deswelled and unsnarled. The latter provoked a wide motion whereby the entire snarl rotated round the sample’s main axis until only one coil remained. This was remarkably similar to the starting point when the sample was originally immersed in pH 1.5.
Figure 68: Progressive reversible snarling of a PAA nanofiber yarn sample micrographs that show the snarl expanding (image a) at pH 10 solutions with the steady state at pH 10 (image b) and reversed state (image c) at pH 1.5. Fiber is ~100\(\mu\)m in the dry state.

When the same experiment was repeated on another sample, the same general behaviour was observed but the shape of the coiled structures differed. In Figure 69, it can be seen that the immersion in pH 1.5 lead to a similar outcome, with the sample showing the formation of one coil out of the sample’s main axis. However, when placed in pH 10 solution the sample continued forming tight coils instead of a snarl forming radially until it reached a steady state shown in Figure 70. This steady state is particularly interesting because it appears to be formed of a knotted structure where a coil formed by wrapping around another coil forcing it to bend even more perpendicularly to itself. This knotted structure was surprisingly reversible to the pH 1.5 state when in its environment.

Figure 69: Formation of coiled structure in the sample immersed at pH 1.5. Image [a] shows the formation of the first coil and [b] the steady state showing a zoom over the three meshing coils. Fiber is ~100\(\mu\)m in the dry state.
These processes are highly reminiscent of the commonly observed phenomenon whereby a flexible elastic string is twisted while held under some tension and then the string ends are moved closer together. Loop formation occurs at a critical twist insertion, or torque, which depends on the applied fiber axial tension (Zajac 1962). As analyzed by Ricca (Zajac 1962) and Goss (Goss et al. 2005) the elastic energy due to twisting of a stretched fiber can relax by bending, loop formation and snarling.

The prerequisite conditions for loop formation and snarling are fiber slack and the existence of a torque acting on the fiber. Both conditions occur during the swelling of the PAA nanofiber yarns. Firstly, the untwist in the yarn is thwarted by the clamped fiber ends, so an internal torque develops within the yarn. Swelling the yarn with its ends clamped is entirely analogous to the situation where one end of the yarn is free to rotate on yarn swelling and then that fiber end is rotated back to the starting point by an externally applied torque. Consequently, the yarn that was swollen with both ends clamped can be thought of as being acted on by an external torque. Secondly, the yarn length increases so that the initially taut fiber becomes slack. The degree to which snarling occurs in the PAA nanofiber yarns depends upon the untwisting torsional stroke and the length change, both of which depend upon the extent of swelling.

This series of experiments have unequivocally shown that the formation of the superstructure as a consequence of swelling in the PAA nanofiber yarns can induce a change in the sample’s size as well as be reversible in two different swollen states.

**Conclusion**

In conclusion, the PAA hydrogel nanofiber yarns have been shown to be torsionally active when swollen with aqueous solutions. Their large change in volumes of over 400% provokes a total untwist under load for a fully immersed yarn that was free to rotate. This torsional actuation was not reversible. However, reversible actuation was achieved by operating the nanoyarn against a return spring. Yarn untwist was shown to be due to the anisotropic swelling of the yarns and this anisotropy was likely induced by the molecularly aligned structure formed by electrospinning. No significant differences regarding the change in twist density due to pH swelling for yarns prepared with different twist densities
whereas the change in twist density decreased with increased degree of crosslinking. However, the single helix model suggests that small changes in sample swelling in the diameter or length directions could lead to large variations in the expected yarn untwist. This observation may account for the large variation in experimental results. Finally, an interesting new actuation mechanism was observed in some fibers whereby the fiber untwist due to swelling was converted into coils and snarls.
IV. Composite nanofiber yarn linear actuator

Snap-buckling artificial muscles

In the precedent chapter, while investigating our hydrogel nanofiber yarns, we discovered an interesting new property where our sample would reversibly buckle into snarls when the pH was changed. Attempts at using this phase transition in a linear actuation were unsuccessful because of the fragility of the yarn, but insights that this may occur were obtained. As a result, we hypothesized that if we were to increase the toughness of our yarns, we might obtain a linear buckling actuator of high stroke.

Nature has always been a strong source of inspiration in material engineering and recently mimicking these properties as led to the synthesis of new functional materials relying on buckling and bending as a source of motion. As reviewed below, the torsion-driven buckling of fiber systems is known in nature and provides a basis for developing and analyzing the composite yarn linear actuators.

Biomimetism a source of inspiration

The buckling and warping of plants as inspiration

Plants have evolved interesting, intricate structures to allow for a wide range of motion (Suyi & Wang 2017) allowing to spread seed, open vents and trap prey. One of such specialized structure is the Venus fly trap; it is a bistable leaf-like structure that undergoes an osmotically driven snap-through actuation under stimulation. The purpose is to catch animals which require the structure’s movement to be swift making this type of motion of special interest due to its rapidity and responsiveness. Here, the stimulation of the fibril on the edge of the trap triggers an electrical signal that is transmitted through the plant via voltage-gated ion channels allowing for fast signal transmission and provokes the closing of the trap through hydrostatically driven motility relying on mechanical instabilities (Volkov et al. 2009).

Mechanical instabilities in plants have been shown to arise from the composite nature of some actuating structures involving stiff cellulose microfibrils dispersed and oriented in preferred directions in the extracellular matrix of seedpods (Reyssat & Mahadevan 2009). In this study, the orientation of the stiff structure within the actuators and its effect were artificially replicated by dispersing and magnetically aligning anisotropic nanoparticles within a thermally-responsive hydrogel matrix (Erb et al. 2013). Among the results of the study, the synthesized composite ribbons were shown to exhibit twisting and warping properties as shown in Figure 71. Interestingly, in these experiments when the sample swells, the increase in twist is accompanied by an increase in length. Here the orientation of the stiff regions constricts the swelling of the material to the preferred direction of alignment provoking a programmable swelling anisotropy depending on the starting angle of the reinforcing nanoparticles and the layer thicknesses.

This first attempt to create responsive material that folds and bend led (Jeon & Hayward 2017) to synthesize responsive self-folding helices that show complex warping in response to stimulation (Fig. 1). An interesting range of motion was made possible by micropatterning and multilayer synthesis of a ribbon made with a layer of distinct elastic modulus and a thermo-responsive swellable material. Furthermore, this helix chirality was determined by the orientation of the striped structure during the
processing step allowing for chirality control and the synthesis of complex shape-shifting objects.

Figure 71: From left to right, micro-patterned PNIPAM ribbon twisting upon swelling, from (Erb et al. 2013), and actuation of a microscale ribbon warping in differently angled helices from (Jeon & Hayward 2017).

The bio-inspired approach has consisted here to mimic the microscopic composite structure in the natural actuator and replicate their function to achieve complex motion. Actuators that show bending and warping are also naturally occurring in the animal realm suggesting a new source of inspiration to potentially develop a new type of motion in artificial muscles.

The spasmoneme as inspiration

In reaction to vibration in their environment, microscopic unicellular animals such as Vorticellid ciliates include a long stalk that can contract by collapsing from a straight rod into a helically coiled structure thereby reducing the end to end distance. This stalk contraction occurs at significantly high rates and can reach 1800 times the cell’s length per second (Moriyama et al. 1998). Still, images and a model for the stalk contraction are reproduced from (Misra et al. 2010) showing the “head” or cell body and the tethered rod-shaped contractile stalk shown in Figure 72. Interestingly, contrary to the skeletal muscle, the stalk shows ATP independent contraction where the helically-wrapped spasmoneme located inside the cell body and responsible for the motion, generates a tensile force responsible for the coiling collapse of the stalk. This large contraction, up to 72% its initial stalk length, is the consequence of the release of Ca\(^{2+}\) ions from the sarcoplasmic reticulum that causes the spasmoneme to contract in length. This Ca\(^{2+}\) signal is then propagated as a calcium wave by calcium-induced calcium release along the spasmoneme provoking further stalk coiling until it reaches full contraction.
Figure 72: (a and b) Images of V. convallaria in extended and contracted states (22), (c and d) The model in extended and contracted states. The head is modeled by an incompressible sphere, the stalk by an elastic rod (in gray), and the spasmoneme by a thin fiber (in black) winding helically around the stalk.

Reproduced from (Misra et al. 2010)

Asai et al. (Moriyama et al. 1999) have reported an isotropic change in volume of the spasmoneme, decreasing up to 81% in volume from the relaxed to the contracted states. This study was conducted by isolating the spasmoneme from the stalk by dissection and exposing the separated spasmoneme to solutions of calcium ions. Exposure to calcium ions caused a near-isotropic contraction of ~50% in the length and diameter of the spasmoneme. Moreover, the divalent calcium ions released during stimulation were shown to act as a bridge in the contractile macromolecules, organized in filaments of 2-4 nm diameter spanning along the spasmoneme length. This contractile material was identified to be a polymer of the Ca$^{2+}$ binding protein spasmin. Furthermore, in the same study, using rubber elasticity theory, the authors have shown that the spasmin nanofilaments are in a straight conformation when the spasmoneme is in the expanded state and form intramolecular bonds with the divalent ion in the contracted state yielding to a random yet shorter end to end structure. The exact mechanism of spasmoneme contraction, specifically originating from the entropically driven polymer collapse or the excretion of water is not yet fully elucidated. The main hypothesis is that the change of conformation of the spasmin protein when bound to the calcium ions exposes hydrophobic structures and provokes the excretion of water or saline yielding that may lead to a synergy of the two effects during the contraction phase.

A model of the macroscopic behavior of the stalk-spasmoneme contraction is reproduced in Figure 73. It is proposed that in reaction to calcium wave progression the spasmoneme contracts in length changing in shape from a helix wrapped around the stalk to a straight rod (2 ms) and provoking the collapse of the stalk from straight to a helix of opposing chirality. This change in shape allows for the
explanation of the recovery and the ability of this contractile system to undergo several contraction extension cycles without fracture by modeling the recovery as a passive process due to the elastic energy stored into the helically shaped stalk transitioning to a straight structure and winding the spasmoneme back to its initial position.

Figure 73: Contraction model is showing the mechanics of buckling of the spasmoneme in black and stalk in grey. Reproduced from (Misra et al. 2010).

As we have seen in preceedently we were able to demonstrate the snarling behavior of our highly twisted PAA nanofiber yarn at a constant length. Inspired by the litterature, we thus hypothesize that a composite structure may allow us to block the change in dimension occurring in length. The placement of a stiff material in the yarn with a microstructure aligned with the length of the sample may constrict swelling to the diameter direction. This would thus provoke the end to end shortening of the composite as it bends to form snarls.

**Theoretical analysis of the bending of filaments**

Cable kinking and snarling is a well described phenomenon that has been a recurrent problem in the textile and power transmission industries, in the latter particularly in the oceanic application of undersea cables. Due to varying tension and torsion during the manufacturing process or due to environmental change cables can form loops or kinks and lead to damage or eventually the fracture of the cable.

When a coil or kink is formed the torsional energy of the object is transferred to a bending elastic energy and work is done against the axial load as the cable shortens. Ross (Ross 1977) has performed an equilibrium analysis of such behavior using the idealized case of a single perfect loop forming. Ross derived the minimum required torque to first obtain a coil (equation 9). Where \( \tau_c \) is the critical torque, \( E \) the Young’s modulus of the cable, \( I \) the second moment of area and \( P \) the tensile force applied to the end of the cable.
This analysis provided a lower bound to the formation of a loop in a cable and led the author to the conclusion that to prevent loop from forming in cables the torsion should be maintained below the value afforded by equation 10.

This model of the critical torque at the origin of different buckling processes in fibers has been the object of experimental studies (Belov et al. 1999) in an attempt to predict the occurrence of snarling. They used the Ross and Greenhill criterion as their models to evaluate their respective predictive value. Greenhill estimate of the critical torque is reported in equation 10.

\[ M_c = \sqrt{4PEI} + \frac{\pi^2EI^2}{L^2} \]

Fibers of different mechanical properties were twisted at different tensions and observations were made reporting the onset of transformation from the twisted to the deformed state. The study found that for monofilament fibers the experimental values fell in good qualitative agreement with the models with experimental values for the critical torque falling between the Greenhill (upper boundary) and Ross criterion with Ross criterion providing a better quantitative predicate. It was found however that the predictive value of the model for reinforced fibers was low due to high non-linearity of the twisting curves and theoretical shortcoming was identified as the linear dependence of the torque on the twist of both models. This departure from the predicted values was found to be prominent at high tensions.

Furthermore, after these first analyses, researchers have continued studying the phase transition in cables, wires, and fibers deriving models where the formations of kinks are reversible, and their secondary structures are varied. Figure 74 shows different phases in twisted rubber filaments as described by (Ghatak & Mahadevan 2005). In this experimental series, rubber filaments were subjected to a constant load and progressively twisted. The authors then remarked the formation of different secondary structures depending on the applied extensions. At high strains (Figure 74. Inset e.) they observed the formation of meshing solenoid coils as samples were twisted beyond a threshold value. As they continued twisting the object the coiled region extended to the entire filament (Figure 74. Inset f.) and eventually to the formation of tertiary higher order structures (Figure 74. Inset h.). At smaller initial extensions the twisting induced snarls (or ‘plectonemes’) as shown in Figure 74 d and i.
The rubber filament can transition between these secondary structures depending on the applied load such as shown in the stretch-relaxation experiments reproduced in Figure 75. Here is shown the response of the sample with different secondary structure to an extension cycle and shows different patterns depending on the type of secondary structures formed. A sawtooth response was observed in both extension and contraction for solenoidal coiled samples (curve 2 in Fig. 4). A sawtooth pattern was present only in the extension phase of a sample with multiple plectonemes to a smoother response for a sample with just one plectoneme secondary structure. This transition in between secondary structures in response to experimental variables and more specifically its dependency on the starting load has been captured by mathematical modeling allowing for the description of the phase transition between the straight fiber and plectoneme or helicoidal structures to be rationalized as reproduced in Figure 76.
Summary

In conclusion, this literature review has allowed us to design a new set of actuators based on our preliminary results reported in the preceding chapter and mimicking the naturally occurring Vorticella stalk contraction mechanism. In addition, the literature details various approaches to modeling the mechanics of coil and snarl formation by twisting and highlights the important material properties and loading conditions that favor the formation of snarls or coils. The materials described in the previous chapter were limited by the low mechanical strength and were unable to sustain even relatively small external loads without fracture. The present chapter aims to develop stronger composite twisted nanofiber yarns and explore their actuation behavior. The aim is to use the torsional actuation during swelling of highly twisted hydrogel nanofiber yarn to induce a phase transition from straight to helically coiled or snarled and to provoke a shortening of the sample’s end to end distance. In contrast to the naturally occurring contraction of the Vorticella stalk where the contraction of the spasmoneme organelle generates the coiling of the stalk, in the present study we will explore the use an expanding hydrogel yarn co-twisted with an inextensible fiber to generate torque and coiling.

Results and Discussion

The electrospinning machine’s design was leveraged to synthesize two-ply composite nanofiber yarns made of PAN and PAA and was achieved by collecting the two materials sequentially on the secondary collector. Here in addition to our general method, once the desired amount of nanofiber bundles was successfully deposited on the rotary autosampler, the machine was loaded with a different polymer solution and spinning resumed. The result was a bicomponent nanofiber sheet that was subsequently twisted into a two-ply nanocomposite yarn. The resultant plied structure is evident in Figure 80 where the two layers of the plied structure appear as semi-transparent in the case the dry PAA and opaque white in the case the dry PAN. To further our understanding of the obtained structure we report the SEM images of the composite nanofiber yarn in Figure 77. We observe that the nanofiber yarn is constituted of well-defined phases, one appears to contain defects and the other a defect free nanofibrils structure. Using chapter 2 conclusions we can deduce that the former is the PAA and latter PAN components of the yarn. It is interesting to note that the two visible PAA parts in this picture of the surface of the yarn are separated by 540 µm, which is close to the 2000 turn per meter initially present in the sample. However, it has to be noted that most samples did not show such high degree of organization and mixing between the two phases was very frequent.
Figure 77: Image of a composite nanofiber yarn in the dry state made by electrospinning the two component PAN (fine fibers) and PAA (fibers with defects) one and six minutes and twisting the resulting sheet into a yarn at 2000 turns per meter.

With this interesting insight in the microstructure of our samples we attempted a swelling experiment and obtained optical microscopy images of our samples in the pH 1.5 and pH 10 environments respectively reported in Figure 78 and Figure 79. In this picture of a yarn free to untwist we observe, in both images, the composite structure in the swollen state. From this micrograph and the SEM pictures we can deduce that the samples behave similarly to PAA nanofiber yarns by swelling when exposed to different pH solutions with the largest diameter obtained in pH 10 followed by pH 1.5 and finally in the dry state, respectively representing a swelling ratio of 172% and 112%. Moreover, it is clear from the picture that a swollen sample free to untwist retains a certain amount of twist upon swelling. The exact degree of retained twist could not be accurately measured from this micrograph due to the uncertainty over the spatial separation of the two phases and the difficulty of establishing baseline from which deduce an angle.
We were thus successful in the synthesis of torsionally-active and swellable composite nanofiber yarns. We then next proceeded to perform experiments to explore the composite yarn structure and its resilience to repeated swelling and de-swelling in response to pH changes. First experiments used a composite structure prepared by depositing PAN for one minute and PAA for six minutes which became the standard for our study.

**Nanocomposite diameters and crosslinking**

Initial characterization of the plied bicomponent yarns investigated the effect of the new sequential deposition method on the overall diameter of the yarn. For comparison, the components were also deposited individually, and their diameter measured. The results are summarized in Table 8. The PAN yarn prepared by electrospinning for 60 seconds and twisting to 2000 turns/m had a diameter of 34 ± 13 μm. Electrospinning the PAA for 360 seconds and twisting to 2000 turns/m gave a yarn diameter of 83 ± 7 μm. Given the uncertainty on the diameters, the bicomponent yarn diameters of 126 ± 14 μm are well within the expected range for the sum of the two parts (with a minimum of four experiments per data point). This observation is important because it allows us to explore dimensions at which the characterization of the diameter of individual components would be made difficult by their small size.

First actuation results aimed to determine a set of experimental parameters that are most likely to consistently yield a stable and reversible linear actuator. Of interest is the case where PAA gel swelling induced coiling or snarling that could be observed and reversed by PAA de-swelling. The actuation experiments used the two-end tethered fully immersed experiments against the lever arm to measure displacement against time while controlling for the applied force. Moreover, optical microscopy was performed simultaneously to characterize the samples’ responses to changing pH in the diameter direction. Microscopic observation also identified failure types to guide further experimental design.
Table 8: Comparison of diameters in pristine and composite nanofiber yarns

Table 9, Table 10 and Table 20 compile the experimental conditions trialed and actuation behavior observed. All samples in these initial tests had the same component ratio (1 - 6 minutes for PAN and PAA components) but were prepared with different crosslink densities for the hydrogel. The twist density was 2000 turns/m in most cases with one set of samples prepared at 1500 turns/m. As shown in Table 9, when first immersed from the dry state to the pH 1.5 solution, most samples survived without failure. However, only one sample displayed snarling / coiling behavior. This observation was the first time that coiling was shown to occur against a constant external force, in this case, applied by the lever arm. Attempts to conduct such experiments with the PAA nanofiber yarns were not successful as the PAA yarns would always fracture. It was noted that the phase transition between the dry state and pH 1.5 was considered irreversible because of the hydration and swelling of ions in the PAA component could not be fully reversed by simply drying the samples. No attempt was made to reverse the immersion in pH 1.5 by first neutralizing the acid and then drying. As such, the reversibility of the experiments is identified as NA for “Not Applicable.”

<table>
<thead>
<tr>
<th>Crosslinking time</th>
<th>PAN spin time</th>
<th>PAA spin time</th>
<th>Twist density</th>
<th>buckling</th>
<th>reversibility</th>
<th>n</th>
<th>n_{tot}</th>
<th>comment</th>
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<td>s</td>
<td>turns/m</td>
<td>type</td>
<td>type</td>
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<td></td>
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<tr>
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<td>60</td>
<td>360</td>
<td>2000</td>
<td>no buckling</td>
<td>NA</td>
<td>5</td>
<td>5</td>
<td>stable</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>360</td>
<td>1500</td>
<td>no buckling</td>
<td>NA</td>
<td>2</td>
<td>2</td>
<td>stable</td>
</tr>
<tr>
<td>5</td>
<td>60</td>
<td>360</td>
<td>2000</td>
<td>no buckling</td>
<td>NA</td>
<td>4</td>
<td>4</td>
<td>stable</td>
</tr>
</tbody>
</table>
Table 9: Actuation results of composite nanofiber yarns at constant components ratio. Transition between dry to pH 1.5 for $n_{\text{tot}}$ samples and $n$ samples showing the buckling and reversibility properties.

PAA spin time was always 6 times the PAN spin time.

Coiling of a composite nanofiber yarn by the immersion from dry to pH 1.5 solution was demonstrated as an unlikely yet possible outcome. To further enhance the likelihood of coil formation, the pH was increased from 1.5 to 10 to cause further swelling of the samples. The sample details and observations from the cyclic immersion in pH 1.5 and pH 10 solutions are given in Table 10. It followed that all sample types showed the formation of various type of buckling, from coiling to snarling and a combination of the two.

<table>
<thead>
<tr>
<th>Crosslinking time</th>
<th>PAN spin time</th>
<th>Twist density</th>
<th>buckling</th>
<th>reversibility</th>
<th>n</th>
<th>$n_{\text{tot}}$</th>
<th>comment</th>
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<tbody>
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<td>hour s</td>
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<td>tpm</td>
<td>type</td>
<td>type</td>
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<tr>
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<td>60</td>
<td>2000</td>
<td>NA</td>
<td>NA</td>
<td>1</td>
<td>5</td>
<td>Coiled and suddenly broke</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>1500</td>
<td>snarl</td>
<td>no (1 cycle max)</td>
<td>2</td>
<td>2</td>
<td>mixed coils and snarls</td>
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<tr>
<td>5</td>
<td>60</td>
<td>2000</td>
<td>snarl and coils</td>
<td>no (1 cycle max)</td>
<td>2</td>
<td>4</td>
<td>1 Snarls and 1 coils</td>
</tr>
<tr>
<td>6</td>
<td>60</td>
<td>2000</td>
<td>snarl and coils</td>
<td>YES (up to 3 cycles)</td>
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<td>4</td>
<td>3 snarls and 1 coils</td>
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<tr>
<td>8</td>
<td>60</td>
<td>2000</td>
<td>coils</td>
<td>Yes (up to 2 cycles)</td>
<td>1</td>
<td>1</td>
<td>Snarls</td>
</tr>
</tbody>
</table>
Table 10: Samples actuation characteristics at different crosslinking times. Transition between 1.5 and pH 10. PAA spin time was always 6 times the PAN spin time.

These results demonstrate that this buckling mechanism is ubiquitous in the PAA-PAN bicomponent plied yarns when subjected to a high degree of swelling of the PAA in pH 10 solution. This success was moderated by the poor reversibility and frequent sample fracture. Most experiments resulted in a fractured sample for what seems to be a form of delamination whereby the PAA hydrogel component breaks away from the PAN component, but the PAN component remains intact. This type of delamination provokes a catastrophic failure event, where all the twist present in the sample is released rapidly and the sample is either ruptured or stops being pH-responsive. When looking carefully at the fraction of experiments that showed delamination we see that a lower crosslinking times seem to correlate with a higher probability of delamination. Another experimental difficulty occurred when the large length contraction caused by snarl or coil formation is responsible for the lever arm to fall out of its measurement range. When this happens the lever arm starts vibrating significantly and may be responsible for the failure of these samples.

Figure 81: Displacement against time of a reversible pH responsive plectoneme actuator.
A decrease in length represents a shortening of the actuator.

Improved stability against failure during repeated switching between pH 1.5 and 10 solutions was achieved by limiting the PAA swelling and by careful monitoring of the lever arm position to keep it in range. Preparing composite yarns with a crosslinking time of 6 hours meant that 50% of the samples have shown reversibility and one sample has shown no sign of failure after 3 actuation pH cycles (Figure 81). To correct for the limited displacement range of the lever arm, the sample end clamp was manually moved as the sample contracted to maintain the lever arm within its measurement range. This process
meant a loss in precision of the displacement measurement, but this was instrumental in circumventing the lever arm's induced sample failures. Furthermore, the higher crosslinking and reduced swelling at pH 10 increased the sample's resistance to fracture or delamination. Based on these observations, the preferred method for making samples with a high probability of giving reversible coiling / uncoiling actuation were made with a components ratio given by the 1-6 spinning time, with a twist density of 2000 turns per meter and crosslinking time of 6 hours at 130 °C under 60 kPa vacuum.

This reversible experiment shown in Figure 2 illustrates several interesting characteristics of a coiling type artificial muscle. Firstly, a slow shortening occurred during the first immersion in pH 10 solution followed by a typical staircase signal. The latter clearly captures the snap-coiling behavior of this actuator leading to large and sudden length contractions. Elongation at pH 1.5 occurs rapidly and without discontinuities. The displacement does not always recover to its initial length implying that some coils remain trapped in the sample.

These two phenomena of snap-coiling and smooth recovery have been described by Mahadevan (Ghatak & Mahadevan 2005) in the context of a rubber string that is mechanically twisted at a constant applied load. The authors describes the seesaw length contraction signal that occurs during twist insertion with sudden contraction jumps occurring due to coil formation.

**Nanocomposite linear actuation**

An intriguing detail of the mechanism of linear actuation due to coil or snarl formation is provided from the microscopic images captured during pH switching of the bicomponent fibers held in the two-end-tethered condition. A set of actuations still images at the same magnification is reported in Figure 82. In the first frame, the seemingly straight dry composite nanofiber yarn that is highly twisted (2000 tpm) is shown. The plied structure illustrated in Figure 1 is just noticeable at the low magnification used in Figure 3. When the sample was immersed in the pH solutions a lensing effect occurred due to the refractive properties of water giving a higher overall magnification. The swelling due to immersion of the dry sample in pH 1.5 solution is evident by comparing the relative fiber diameters in the first and third frames, which were both captured in air. The third frame was obtained during the pH switching when the pH 1.5 solution had been removed from the sample bath and before the pH 10 solution had been added. The image was acquired immediately after the pH 1.5 solution was removed so that drying would be negligible. Here, there is a clear difference in diameter and the swelling ratio was estimated at approximately 1.5 times the dry diameter by comparing microscopes images at constant magnification. This swelling ratio appears to be lower than the 2 times previously reported for the neat PAA nanofiber yarns with similar crosslinking. A reduced swelling is expected for the bicomponent yarn in comparison to the neat PAA yarns, since the PAN component is unaffected by the pH solutions. Further sample swelling is evident when the sample was immersed in pH 10 by comparison of the relative fiber diameters in frame 2 (immersed in pH 1.5) and frame 4 (immersed in pH 10). The swelling ratio in diameter was estimated to be 2.9 times the dry diameter.

The most significant observation from these experiments is the very large length contractions (Figure 2) that accompany the fiber swelling when the sample was switched from pH 1.5 to pH 10. The microscopic images of Figure 3 confirm that the length contractions are caused by the formation of coiled structures, and other samples formed snarls and/or combined snarl and coil structures (described below).
It follows that the contractile phase appears to be forming a tightly meshed structure of well-defined non-coiled and coiled parts. In the example shown in Figure 3, coiling occurs during the swelling transition from dry to swollen in pH 1.5, although as mentioned above the occurrence of coil formation at this stage was unusual. Successive immersion in pH 10 results in further coiling by adding additional coils to the previous coiled region. As time passes and the gel continues to swell it is noted that both the fiber and the newly formed coils have larger diameters. Interestingly, the coils that were formed previously did not change in diameter although they were also exposed to the swelling pH 10 solution. This is an unexpected result and it may be due to the compressive forces acting on the gel in the coiled phase that formed in pH 1.5.

Figure 82: Optical microscopy images of a 126 ± 14 µm composite nanofiber yarn during the contraction events at the condition indicated.

Close examination of the immersed gels provides further detail of the twisted and coiled fiber structures. When immersed in the pH solutions the PAA portion becomes translucent and the plied PAN nanoyarn is mostly visible in the twisted and non-coiled sections. The coiled sections are wound in a tight and stable structure. The coils form almost perpendicularly to the sample’s main axis and successive coil turns pack tightly. Coil formation follows a nucleation and growth pattern such that subsequent coiling extends an already coiled region.

A close-up focus on the nucleation process in Figure 83 illustrates the snap-coiling motion. A helicoidal structure is shown in the boxed region of frames 2 and 3. No particularly discerning feature is seen in frame 1 that would suggest the location of the coil nucleation, so the process may be a random event or may be triggered by undetectable structural features. Over a time period of 14 seconds, the yarn forms a bend that distorts the helix out of the fiber’s main axis into an "E" shaped formation (frame 3). This series of images suggests that a length of bicomponent yarn of approximately two initial ply pitch lengths are deformed into one coil turn. The coil outer diameter is approximately equivalent to twice the
bicomponent yarn diameter. It is not possible to establish whether the yarn within the coil is still twisted, however frames 2 and 3 indicate a degree of untwisting as the coil begins to form. These observations suggest that as the bicomponent yarns swell they develop an internal torque since the two-end-tethering prevents any untwisting of the ply. The torque can be released by the formation of a coil since the coiling converts yarn twist to writhe (Haines et al. 2014). Consequently, this deformation would allow the sample to maintain its structural integrity, acting as a torque release mechanism. In addition, significant shortening of the fiber end-to-end length occurs since the coil diameter is larger than the non-coiled diameter.

Figure 83: Close-up characterization of the snap-coiling motion.

Other similarly prepared and tested samples have shown snarling rather than coiling and is analogous to the previously observed snarling of the single component PAA nanofiber yarn torsional actuator. An example of snarl formation and release in the bicomponent yarn is shown Figure 84 where all images were taken at the same magnification. The transition from the dry sample to the partially swollen state at pH 1.5, is responsible for the formation of one short snarl or coil. The inset shows details of the snarl initiation. When subsequently exposed to the pH 10 solution, the snarl grows radially into a longer structure producing a large net shortening of the end-to-end length of the actuator. The snarl is formed by a double helix of two distant parts of the actuator wrapping around the other. In the example shown the snarl consists of 6.5 turns. The actuator reverts to its original, non-snarled shape when immersed again in the pH 1.5 solution.
The snarl seems to follow a similar nucleation-growth pattern to the coil nucleation process whereby the object initially bends out of the main axis and then snaps into the deformed state. In this case the initial bend forms symmetrically to an "S-shaped" structure (frame 2 in inset). The bent section then rotates progressively until it reaches a 90 degrees angle to the actuator's main axis and snaps into a snarl (frame 3). The snarl length then grows subsequently in a similar fashion in a bend-rotate-tumble motion as additional turns are added to the snarl.

Lastly, some samples have shown a mixture of coils and snarls and higher order ‘knotted’ structures. An example is reported in Figure 85. This sample was robust enough to survive three actuation pH cycles without failure. The still images show that the shortening region of the actuator assumes a three-dimensional staircase clover leaf shape in pH 10 solution which is formed of both coils and snarls. This deformed structure does not appear to fully revert to its initial state when immersed again in pH 1.5. A few coils are retained at pH 1.5 but mostly the knotted structure has reverted to a straight fiber.
Figure 85: Optical microscopy image of the first cycle of composite nanofiber yarn plectoneme actuator in different pH solutions

In this series of experiments, we have seen that the actuator’s complex motion is the consequence of the change in pH of the solution. The crosslinked PAA component of the highly twisted structure in the composite nanoyarn swells by absorbing water and increasing its diameter. The swelling would initiate uncoiling if at least one yarn end was free to rotate, but in the two-end-tethered arrangement, the swelling exerts a torque on the held ends of the sample. This phenomenon is likely accompanied by a change in the composite nanofiber yarn’s modulus as the gel component modulus decrease while swelling and the contribution of the gel to the overall diameter increase with swelling.

To investigate the relation between the critical torque and the formation of deformed structures we have evaluated the twist released by the yarn swelling from dry to pH 1.5. In this test, a 10mm composite nanofiber yarn was loaded with a weight to generate 26 kPa of tension. The weight was free to rotate, and the yarn was observed to untwist 15 turns when immersed in pH 1.5. Thus, the maximum amount of untwisting is 75% of the initial 2000 turns per meter present in the sample. The Ross criterion can be used to evaluate the number of turns needed to form a coil in the yarn sample. The torque generated by our sample can be expressed as,

\[ T_b = \Delta n J G \]

Here \( T_b \) is the blocking torque, defined as the torque needed to prevent the object of rotating. \( \Delta n \) is the change in turns per metre caused by the yarn swelling, \( J \) is the polar moment of area, \( G \) is the cylinder shear modulus. And by expressing change in twist with torque deduced from the Ross criterion (equation 9) we obtain,
$$\Delta n = \frac{\sqrt{2PEI}}{JG}$$

Here $E$ represents the Young’s modulus of the material idealized as a single component yarn and $I$ is the second moment of area of the yarn. And by approximating our system with a cylinder we have,

$$J = \frac{\pi D^4}{32}, \quad I = \frac{\pi D^4}{64}, \quad \text{and} \quad \sigma = \frac{P}{\pi d^4}$$

With $\sigma$ the applied stress. Finally, by solving for $\Delta n$,

$$\Delta n = 2 \frac{\sqrt{2\sigma E}}{DG}$$

Equation 13 can now be used to obtain an order of magnitude estimate of the change in turns needed to obtain first deformed structures (snarl of coil) in the swollen yarns in the pH 10 solution. This analysis requires knowledge of the mechanical properties of the yarns in the two pH solutions. To this end we designed the following experiment series presented in Figure 86. A sample’s initial twist angle and swelling ratios are obtained independently from a small part of the prepared sample by using SEM and a free swelling experiment under the optical microscope.

Figure 86: Experiment design to obtain the mechanical properties of our composite
nanofiber yarns (s-s is the short for stress and strain curves)

Figure 87: Characterization setup to extract the mechanical properties from immersed nanofiber yarns consisting of (1) A microscope, (2) an horizontal lever arm and (3) a syringe body containing swelling solution and the sample which end can be turned to change the latter's twist density.

The remaining pristine part of the yarn sample was then characterized by a two-end tethered swelling experiment in a specially designed apparatus represented in Figure 87. This apparatus allows twist to be inserted or extracted from the sample while the tension is held constant using the lever arm system. The sample of 2000 turns/m inserted twist was first immersed in the pH 1.5 solution and twist density was progressively released. The stress and strain curves were obtained at each twist density by small stretching of the sample within its elastic region. To do so, stress was applied and removed three consecutive times to the sample to prevent any destruction and resulted in a strain up to 2% relative to the initial swollen length, as shown in Figure 88 and Figure 89. The stress and strain curves show close to a complete recovery and excellent cycling ability demonstrating that this indeed is the elastic domain of strains. The engineering stress was used in all cases and based on the diameter obtained from an untethered sample in the swollen state as measured by optical microscopy. Engineering strain was obtained relative to the length of the sample when swollen in the respective solutions under 0.35 MPa. It can also be seen that the sample decreases in length when it was exposed to the pH 1.5 solution. This contraction is consistent with our hypothesis that the sample’s helix angle increases relative to the main axis at constant twist when the diameter is increased provoking an overall shortening.
Figure 88: Axial strain of composite nanofiber yarn swelling in pH 1.5 solution where time was recorded after the addition.

Figure 89: Typical set of stress and strain curves obtained from a composite nanofiber yarn swollen in pH 1.5 with an unaltered 2000 turns per meter twist density.

Repeating the stress and strain experiments at decreasing twist resulted in the following compiled set of curves presented in Figure 90. The modulus as a function of the inserted twist was obtained by fitting the unloading part of the curves to linear function and extracting the slope as shown in Figure 91.

Figure 90: Stress and stress curves at decreasing twist for a sample immersed in pH 1.5 solution.

Figure 91: Linear fit of the unloading curve of a sample in a pH 1.5 solution.

The aggregate results of all the moduli obtained by this method are reported in Figure 92 and Figure 93, respectively, for pH 1.5 and pH 10 solutions. The absolute number of turns contained in the sample was monitored throughout the experiment and the nominal twist angle was obtained from equation 14. Here $D$ represents the swollen diameter, $L$ the length of the swollen sample and $n$ the absolute number of turns present in the sample.
\[
\alpha = \arctan\left(\frac{\pi D}{L}ight)
\]

The results obtained show that in both pH solutions the modulus of the sample depends on the helix angle of the composite nanofiber yarn. Specifically, the modulus of the sample decreased in a non-linear fashion as the twist density increased, which is similar behavior to that reported in the literature (Rao & Farris 2000). These modulus values were next used in the modelling of coil formation.

The formation of coils was investigated experimentally by adding twist to the sample until one coil was observed in pH 10 solution. This coil formed with a twist of 36 net turns in the sample. Untwisting from this point demonstrated that the coil was released at 28 turns. By allowing \( E = 3G \) (Naficy et al. 2013) and using equation 13 we can build the table (Table 11) predicting the minimum twist density to obtain coils in the composite nanofiber sample.

**Table 11: Ross criterion estimate of the twist density needed to form a coil in the swollen**
This analysis provides an estimated twist of 1327 turns per meter for the formation of coils at pH 10, or 41 turns for a sample of 30 mm in length. This estimate is certainly within the same order of magnitude of the experimentally observed 28-32 turns needed to obtain coil under stress for this length sample. The Ross criterion illustrates that the twist needed to generate coiling is very sensitive to the yarn diameter.

Equation (3) expressed in terms of the load (rather than stress) shows that the critical twist needed for coiling is proportional to $1/D^2$. Small variations in yarn diameter will shift the critical twist value to a large extent. Given the experimental errors involved in determining the input parameters of yarn modulus and yarn diameter, the Ross criterion can be concluded as providing a good estimate for the formation of coils and snarls in the nanofiber yarns.

Figure 94: Modelling of a coil in a twisted structure with [a] a three-dimensional view and [b] the schematic geometrical interpretation.

Previous experiments had shown that multiple coils or snarls commonly occur when nanofiber yarns were end-clamped and immersed successively in pH 1.5 and pH 10 solutions while held at constant tensile load. Multiple coiling/snarling would be expected when the sample untwist exceeds that necessary for the first coil formation. One additional coil or snarl turn could be expected for each torsional rotation above the critical value. Taking the complete untwist of the sample as the upper limit, a sample of 2000 turns/m has the capacity to generate a maximum of 60 turns in a 30mm long sample. Considering a critical value of 41 turns for initial coil formation, it is seen that the nanoyarns prepared at 2000 turns/m likely have the capacity to generate multiple coil or snarl formation when fully swollen at pH 10.

The Ross criterion has been shown to reasonably predict the onset of coil/snarl formation in the nanocomposite yarns. The Ross criterion was developed for the situation where an external torque is applied to a fiber to induce coiling/snarling. For the nanocomposite yarns, the coil/snarl formation is due
to swelling by pH solutions, which suggests that an internal torque is developed during swelling. This situation would occur if the nanocomposite yarns are torsionally active during pH immersion.

Torsional actuation experiments were performed to assess the extent of untwisting that occurred during immersion in pH 1.5 and pH 10 solutions. Experiments to characterize the maximum possible actuation in the samples were carried out by immersing a sample free to untwist in each pH solution. It was found that the sample untwisted 29.5% for the dry to pH 1.5 transition and further untwisted at 56.3% of its initial twist density at the pH 1.5 to pH 10 transition. For the coiling experiments it follows that the sample can untwist 33.8 turns in a 30 mm sample prepared at 2000 turns per meter. This available torsional stroke is indeed more than the 30 +/- 2 turns experimentally observed to initiate coil formation. The additional untwisting capacity above the minimum needed to initiate the first coil equates to 3.8 +/- 2 turns left to form coils and snarls. When the coils are meshing and assumed to be oriented perpendicular to the fiber axis, the single helix theory can be used to predict that the length of the coiled region, presented in Figure 94, should be $S^2 = (n\pi^2D^2) + D^2$ before a coiled is formed and $D$ after it is formed. It follows that the change in length due to the transition between pH 1.5 and pH 10 is $\Delta S = D - [(n\pi^2D^2) + D^2]^{1/2}$ and can be calculated to be -4.6 +/- 2.4 mm yielding a stroke of -15 +/- 8%. This calculated stroke is the much lower of magnitude than the reported repeatable 49 +/- 9% stroke shown in Table 18. This discrepancy may be due to the samples presenting a combination of coils and snarls as shown in Figure 101. Attempt at modelling the formation of this complex superstructures or segregating them by increasing the stress, which was unavailable due to low strength of our samples, should be the object of further work.

**Effect of Bicomponent Yarn Diameter on Coil/Snarl Formation**

To further characterize this new actuation phenomenon, the effect of the composite nanofiber yarn diameter was investigated by reducing the spinning time and attempting to keep both the crosslinking and the component ratio constant. As shown in Figure 95, the overall bicomponent composite yarn diameter was reduced from ~130 \(\mu\)m to ~20 \(\mu\)m in the dry state by reducing the spinning time for each component by a factor of 10 (Table 2). The Ross criterion predicts that the critical twist needed to form coils increases as the fiber diameter decreases. To compensate for this effect, the smaller diameter yarns were given additional twist. The bicomponent yarns were twisted to an extent such that the final twist angle was between 28 and 38 degrees relative to the long axis of the yarn, as shown in Table 12.
Figure 95: Composite nanofiber yarns dry diameters at constant components ratio, represented by their total spin time (sum of spin time for both PAA and PAN components).

<table>
<thead>
<tr>
<th>PAN - PAA</th>
<th>Diameters</th>
<th>SD</th>
<th>Twist density</th>
<th>Twist angle relative to the main axis</th>
<th>Actuation stress</th>
</tr>
</thead>
<tbody>
<tr>
<td>type</td>
<td>µm</td>
<td>µm</td>
<td>tpm</td>
<td>degrees</td>
<td>MPa</td>
</tr>
<tr>
<td>60-360</td>
<td>129.0</td>
<td>12.0</td>
<td>2000</td>
<td>38.9</td>
<td>0.48</td>
</tr>
<tr>
<td>20-120</td>
<td>43.4</td>
<td>4.2</td>
<td>4000</td>
<td>28.6</td>
<td>0.97</td>
</tr>
<tr>
<td>15-100</td>
<td>53.5</td>
<td>3.6</td>
<td>4000</td>
<td>33.9</td>
<td>0.10</td>
</tr>
<tr>
<td>5s - 30s</td>
<td>16.7</td>
<td>4.3</td>
<td>8000</td>
<td>31.1</td>
<td>0.39</td>
</tr>
</tbody>
</table>

Table 12: Characterization of remarkable nanofiber composite actuators at different spinning times.

To characterize the actuation of the bicomponent composite yarns the same isotonic, fully immersed, two-end-tethered configuration as described above was used. However, with a minimum stable force of 6mN from the lever arm it was not possible to directly test the smaller diameter yarns at the same tensile...
stress as the larger diameter yarns. To reduce the stress on the small diameter yarns, attempts were made to prepare samples with multiple parallel strands of the bicomponent yarns. The first multi-strands samples were prepared by using two meshing pairs of helical hooks and looping one long length of yarn between the end hooks to make a 5-parallel strand sample (Figure 8). The yarn ends were adhered to the hooks using superglue.

The results of the new series of experiments are reported in Table 13. The multi-strand experiments were conducted using samples prepared with the 20-120 spin times and with 3, 4 or 5 parallel strands. The results showed that samples with less than 5 strands have shown buckling but were unable to significantly move the lever arm (set at its minimum force of 6 mN) and delamination typically occurred causing failure of the actuator. However, the samples with 5 strands has shown reversible onset of coiling and uncoiling without any failures. This improved stability is likely due to the decrease in stress applied per strand as the number of strands is increased.

This multi-strand strategy became impractical with yarns of smaller diameter. For example, the 6.75 times smaller cross-sectional area of the thinnest yarns would require 34 parallel strands to reduce the tensile stress to the same level as the larger diameter yarns. The current limitation of our manufacturing process allows for a maximum nanocomposite yarn length of 6cm and looping this length 34 times would consequently make the parallel yarn segment length too small to be characterized reliably. It was noted that below a length of 6 mm the nanofiber yarns would not bend but mostly break. This was reminiscent of the observation of (Belov et al. 1999) which noted that small yarn lengths have significant effect on the generated torque.

A new test method was devised to investigate the actuation of the smallest diameter yarns. Instead of using the lever arm to detect both displacement and to control the tensile force, the samples were simply suspended vertically with a known weight attached to their free end. The weight could be adjusted to control the tension and the displacement of the sample was detected using optical microscopy. One problem with this test method, however, was rotation of the suspended weight when the multi-strand samples were immersed in the pH solution. To counter the rotation, new samples were prepared using identical yarns that were twisted in opposite directions. Samples were made using two yarns of opposing chirality and attached in parallel to a single weight (Figure 82). This design allowed the testing of sample having a dry diameter down to 16.7 µm while maintaining stress under 0.3 MPa.
The torque balanced samples have been shown to exhibit very frequent buckling with more than 50% of the samples showing a buckling transition between pH 1.5 and pH 10. Moreover, the samples were robust enough for repeat switching between the pH solutions and these results are reported in Table 14. The most prevalent buckling mechanism in these experiments was the formation of a mixed coil and snarl contractile phase. Further characterization of these torque balanced experiments involved counting the samples showing at least two actuation cycles as a function of their composition. The results showed that this repeatability occurred in over 60% in PAN-PAA 15-100 samples and over 38% for PAN 5-30 samples. As the diameter was reduced it seems that the stability of the samples decrease and their fracture under stress was more likely. This susceptibility to mechanical failure was attributed to the relative importance of defects in the structure of the samples. As the diameter is reduced the defect size contribution relative to the total diameter of samples increases. Several samples of reduced diameter showed clear inhomogeneities with localized large swellings observed at certain points along the strand length. This observation strongly suggests that the low reversibility is due to the samples’ structure as the localized high swelling is likely responsible for delamination in the samples and consequently the low observed reversibility.

Interestingly, the appearance of a new type of contractile phase in the 5-30 samples series was noted. An imperfect balance of the torques generated by the two opposing chirality actuators resulted in a net rotation of the free-hanging end of the sample and the plying of the two strands. Further plying and contraction led to the appearance of a super-plectoneme phase consisting of the two untangled actuators in a spiral shape. This behavior was observed in 5 of the 10 actuating samples and, a detailed view is reported in Figure 98. This new contractile phase usually materialized shortly before the samples failure and we observed that it was only reversible in rare occurrences and was responsible for significant shortening of the samples.

<table>
<thead>
<tr>
<th>PAN-PAA spin times (s)</th>
<th>20-120 (multistrand)</th>
<th>15-100 (torque balanced)</th>
<th>5-30 (torque balanced)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Occurrences of buckling</td>
<td>Number of Comments</td>
<td>Twist density</td>
<td>Relative occurrence</td>
</tr>
<tr>
<td>Table 13: Small diameters exploration of composite nanofiber yarn actuation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>3</td>
<td>Buckling and breaking</td>
<td>Tpm</td>
<td>type</td>
</tr>
<tr>
<td>4000</td>
<td>6/7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5000</td>
<td>6/8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Buckling and breaking</td>
<td>Tpm</td>
<td>type</td>
</tr>
<tr>
<td>8000</td>
<td>7/8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9000</td>
<td>3/9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Reversible coiling</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Table 14: Torque balance experiments reversibility and buckling type of the subset of experiments showing a characteristic buckling actuation |
|---|---|---|---|
| PAN-PAA spin time | twist angle | Buckling type | Reversibility |
| (s) | Degrees | Type | Over 3 cycles/sample |
| 15-100 | 33.9 | 1 snarls 7 coils and snarls | 78% of 18 cycles |
| 15-100 | 40.0 | 6 coils and snarls | 61% of 18 cycles |
| 5-30 | 31 | 3 coils and snarls | 38% of 21 cycles |
| 5-30 | 34.0 | 2 coils and snarls | 44% of 9 cycles |
Figure 98: Newly observed plied phase transition in imperfectly torque balanced experiment.

A result set of typical tensile strains at different pH are reported in Figure 95. In each case one cycle of switching from pH 1.5 to pH 10 and back to pH 1.5 is shown. For all samples the length contraction that occurs when immersed in pH 10 results in a staircase shaped signal. The sudden decreases in sample length were due to the aforementioned snap-buckling process. The formation of a snarl or coil happens in two phases: first deformation which appears as the formation of a bend out of the actuator axis and a sudden snapping motion to form a coil or snarl. Notably, the number of steps seems to be dependent on the actuator's diameter with an overall smoother signal noted as the diameter is decreased. In contrast to the step-wise contraction, only a smooth expansion process was observed during de-swelling by immersion in pH 1.5. Furthermore, it was noted that the extension phase was several orders of magnitude faster than the contraction. The speed of actuation is considered in the following section.
Table 15: Typical composite nanofiber yarns actuation one cycle strain for different compositions.

The contractile strain, defined as the ratio of the actuator’s end to end length at pH 1.5 and pH 10, varied significantly depending on the experiment. Strains varied from 37.5% in the case of the 43 µm diameter bicomponent yarn to 61% for the 129 µm diameter yarn.

Composite nanofiber yarns of different diameters were produced by leveraging the capabilities of the electrospinning machine. These samples have shown that actuation by forming deformed superstructures was possible in diameters as low as 16.7 µm if the test environment was adapted for small loads. Furthermore, a new contractile phase was discovered consisting of a two-ply of yarns of opposing chirality forming coils. Furthermore, it is interesting to note that there was a clear dependency on the amount of torsion present in the sample prior to the experiment and the resulting strains observed.

Nanocomposites actuation speed

To analyze the actuation speeds generated by different diameter bicomponent yarns in more detail the actuation results are compiled together in Table 16. The average actuation speed for both the expansion and contraction phases were calculated by dividing the maximum strain by the time needed to complete the transitions. As shown in Table 4, the expansion speeds of the actuators were increased significantly as their diameters were reduced. The contraction speeds also increased for the smaller
diameter fibers, but the effect of diameter on contraction speed is less strong than on the expansion speed. Comparing the 129 µm and the 43 µm diameter fibers, the ~3-fold reduction in diameter caused a 4.7-fold increase in expansion speed and ~1.6 times increase in contraction speed. Further comparison of the 43 µm diameter fibers and the 17 µm diameters showed a similar trend. The diameter ratio of 2.5 times generated an increase in expansion rate of 4.3 times. However, the contraction speed was slightly slower in the case of the 17 µm diameter fiber in comparison with the 43 µm fiber.

<table>
<thead>
<tr>
<th>PAN - PAA type</th>
<th>Pressure per strand (MPa)</th>
<th>Max strain (%)</th>
<th>Contraction at max strain (%/s)</th>
<th>Extension at max strain (%/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60-360</td>
<td>0.49</td>
<td>61.00</td>
<td>0.13</td>
<td>0.14</td>
</tr>
<tr>
<td>20-120</td>
<td>0.97</td>
<td>37.5</td>
<td>0.21</td>
<td>0.66</td>
</tr>
<tr>
<td>15-100</td>
<td>0.1</td>
<td>57</td>
<td>0.22</td>
<td>1.84</td>
</tr>
<tr>
<td>5s - 30s</td>
<td>0.39</td>
<td>52.73</td>
<td>0.18</td>
<td>2.83</td>
</tr>
</tbody>
</table>

Table 16: Actuation results of the best performing composite nanofiber yarns at different diameters constant components ratio

The observed contraction speeds appear to be inconsistent with gel swelling kinetics from which, we can derive the expected change in speeds if the actuator motion is assumed to be the sole consequence of the diffusion of water in and out of the gel as pH is varied. According to Tanaka et al. (Tanaka & Fillmore 2004) the dependency of the swelling time in an osmotic pressure driven swelling process is inversely proportional to the square of the diffusion length. In the present case, the fiber samples can be approximated as a cylinder with a length significantly greater than its diameter. Here the diffusion of the water in the gel is then inversely proportional to the square of the gel diameter. The actuation speeds are presented as a function of the yarn diameters in Figure 99. The extension speeds seem to vary almost linearly with yarn diameter, rather than as a squared dependency. Furthermore, the contraction speeds are almost independent of the yarn diameter.
This conflicting result is likely due to the complexity of the motion of the actuator during actuation and the experimental conditions.

For example, the contraction speed was found to vary for samples tested against different external loads, as reported in Figure 100. These differences reflect the complexity arising from the fact that the contraction step involves the actuator doing work against the load to form the secondary structures. The mechanism of contraction is therefore not only diffusion controlled but also controlled by the speed at which the bending occurs at different load. The formation of snarls and coils is dependent on a number of factors including the hydrogel modulus, yarn diameter and torque generated as the hydrogel swells. Snap buckling occurs when conditions reach a critical value at which bending deformation is preferred over storing twist along the structure.

Figure 99 Actuation plotted against the yarn diameter.

Figure 100: Contraction speeds as a function of the applied stress
Effect of External Load on Actuation Behavior

To further our understanding of the dependency of the actuation properties of our sample on the applied stress we attempt to capture our samples’ ability to actuate under varying load. This study mimicked the Mahadevan loading experiment for twisted rubbers, as reviewed in the introduction section above. The results of the series of experiment are reported in Table 17. At increasing load, we can see that the extent of the contraction at pH 1.5 decreases and that the extent of extension at pH 10 increases. This indicates that some of the plectoneme contractile structure has remained trapped in the sample at small loads and that it is released as load is increased. Moreover, it also indicates that the amount of contraction is dependent on the stress applied to the sample reaching a maximum between 20 and 25% of the starting actuator’s length. Consequently, the actuation cycle strain developed by the sample increases as load is increased until the actuator fails at 0.95 MPa. Such an observation was made by Mahadevan as he observed that the unwinding of the secondary structure happened at a higher load than the winding. Furthermore, no change in phase transition was observed as the load was increased, the contractile phase remained composed of a plectoneme secondary structure. This result is interesting as it demonstrates the stability of the response to different loading condition and compels further research to be done to better understand the cause of such a phase transition and eventually how to control it. To achieve it it is important to obtain samples with repeatable actuation properties, with thus repeated the experiments in an attempt to analyze the actuation properties in the context of an experiment cohort leveraging our previous experience in experimental design.

<table>
<thead>
<tr>
<th>Stress</th>
<th>pH 1.5</th>
<th>pH 10</th>
<th>Strain</th>
<th>Contractile phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPa</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>type</td>
</tr>
<tr>
<td>0.24</td>
<td>9.55</td>
<td>19.15</td>
<td>9.6</td>
<td>Plectoneme</td>
</tr>
<tr>
<td>0.51</td>
<td>25.01</td>
<td>66.77</td>
<td>41.76</td>
<td>Plectoneme</td>
</tr>
<tr>
<td>0.80</td>
<td>20.36</td>
<td>94.54</td>
<td>74.18</td>
<td>Plectoneme</td>
</tr>
</tbody>
</table>

Table 17: Actuation of a composite nanofiber yarn in response to different applied stress.

Nanocomposite actuation repeatability

To further our research and access the potential underlying these interesting new mechanical properties we attempt to repeat the first series of experiment to explore this design’s repeatability in stroke and speeds. To increase the probability of success we used a new experimental strategy. The sample is suspended by a hook and immersed in the different solutions and tension was applied using a weight. The sample was prevented to unravel by using two glass slides. Samples were made in the same
fashion as presented previously (PAN 1 min PAA 6 min) and the actuator’s movement was followed using a camera.

This repeat experiment series was done several months after the original experiments and was designed to quantify the repeatability of the samples actuation properties and access the reproducibility of the previous results. It resulted in similar outcomes as the original one. The comparison of the original obtained diameters and repeat experiments diameters shows that the first have a significantly greater average diameter than the seconds. This appears to imply that there are some experimental variables that are still uncontrolled, it is likely that a small change in the conductivity of the grounding surfaces, contacts and wires in our electrospinning system could be responsible for different number of nanofibers forming on the secondary collector yielding varying results as time passes. Future electrospinning machine designs should account for this potential shortcoming during their engineering.

<table>
<thead>
<tr>
<th>PAN-PAA type</th>
<th>diameter</th>
<th>SD</th>
<th>Metric weight</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Repeat experiment</td>
<td>105.5</td>
<td>17.4</td>
<td>0.0116</td>
<td>0.00254</td>
</tr>
</tbody>
</table>

Table 18: Repeat experiment metrics (6 experiments per data point)

Similarly, to the original experiments the samples underwent large shortening in the pH 10 solution (Figure 101). Interestingly, we can see that here the bending of the sample seems to involve a larger part of the sample and does not appear to be as localized as in Figure 84. We hypothesize that this different bending mechanism is the consequence of the smaller diameters of the yarns and that they might act as stress spreading mechanism and allow for better repeatability of the experiments.
Figure 101: Still image showing the change in actuation mechanism to a long range buckling in the formation of snarls

A detailed cycle experiment is reported in Figure 102. We can see that the sample shortens as expected during its first immersion in pH 1.5, during the dry to pH 1.5 transition and shortens reversibly in the pH 1.5 to pH 10 cycles. Moreover, we observe that at pH 1.5 the sample appear to be extremely short. This is due to the surface tension of water, that, during the filling of the beaker, that pushes against the weight relieving tension and allowing it to proceed shortening. This shortening is an experimental artifact that undergoes correction when the weight overcomes the surface tension of water and sinks.

Repeating this experiments with different samples for several cycles allows to create a data base for statistical analysis. A statistical analysis of the pooled dataset of all experimental results for the stroke of the actuator independent of the cycles is reported in Table 19. We observe the large stroke of the actuator is repeatable at respectively 49% and 48% for the contraction and extension parts of the actuation cycle, for over 10 different cycles. This is a very promising result as it shows that beyond the ubiquity of the samples bending during the actuation cycle the extent and reversibility of the stroke is an important parameter in assessing the performance of a new potential actuator technology. Furthermore, speeds are an important parameter of an actuator’s operation and here the speeds in the contraction and extension cycles show a wide standard deviation. Consequently, our experiments were repeatable in their stroke but not in their speed.
Figure 102: Representative snarling repeat experiment with PAN 1min (0.4mL/hrs) and PAA 6min at 2000tpm.

<table>
<thead>
<tr>
<th>Actuation</th>
<th>Mean stroke</th>
<th>SD</th>
<th>Mean speed</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>%</td>
<td>%</td>
<td>%/s</td>
<td>%/s</td>
</tr>
<tr>
<td>Contraction</td>
<td>49.5</td>
<td>9.6</td>
<td>0.04518</td>
<td>0.04121</td>
</tr>
<tr>
<td>Extension</td>
<td>48.8</td>
<td>8.9</td>
<td>0.07328</td>
<td>0.0584</td>
</tr>
</tbody>
</table>

Table 19: Repeatability experiments pooled dataset of 10 different pH cycles at 0.5MPa.

**Conclusion**

In this chapter we have reported the synthesis and characterization of a novel type of linear actuator leveraging mechanical instabilities to achieve chemically induced motion.

To our knowledge this phase transition allowing for the reversible shortening from a straight or partially coiled object to an object containing a significant plectoneme phase as never been shown in the literature. If so this would make these experiment the first chemically induced reversible self-snarling and coiling artificial muscles ever demonstrated.
We subsequently attempted to gather insights on the mechanics of the bending process and showed that the contractile secondary structures where the result of a nucleation and growth process whereby as the sample swell and internal torque develop and reach a critical value the sample bends and forms a coil or a snarl that then propagates along the structure.

Moreover, we have investigated the possible correlation between the speed of the actuator and the samples’ diameter and shown that other snap buckling dependent mechanical properties play a role in the dynamics of actuation.

Lastly, we were able to produce repeatable stroke in several cycles and samples showing promise in the potential application of such a technology.

<table>
<thead>
<tr>
<th>Crosslinking time</th>
<th>PAN spin time</th>
<th>Twist density</th>
<th>Failure likelyhood and type</th>
<th>comment</th>
<th>force</th>
</tr>
</thead>
<tbody>
<tr>
<td>hours</td>
<td>s</td>
<td>tpm</td>
<td>n ntot</td>
<td></td>
<td>mN</td>
</tr>
<tr>
<td>4 60</td>
<td>2000</td>
<td>5 5</td>
<td>5 Delamination / 1 fracture</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>4 60</td>
<td>1500</td>
<td>2 2</td>
<td>2 Delamination / 1 out of range</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>5 60</td>
<td>2000</td>
<td>2 4</td>
<td>2 Delamination / 1 out of range</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>6 60</td>
<td>2000</td>
<td>2 4</td>
<td>1 Delamination / 1 fracture / 2 out of range</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>8 60</td>
<td>2000</td>
<td>1 1</td>
<td>1 Delamination</td>
<td>6</td>
<td></td>
</tr>
</tbody>
</table>

Table 20: Samples failure types at different crosslinking times. Transition between pH 1,5 and pH 10.
V. Conclusion and suggestions for further work

The thesis aim has been to explore the functionality of nanostructured pH responsive hydrogels twisted into yarns. In particular, the application of these hydrogel yarns as torsional artificial muscles has been the main focus. The thesis project was motivated by recent literature reports of giant torsional actuation from various twisted fibers and yarns. These studies had concluded that volume swelling of such twisted structures could induce torsion through a partial untwisting mechanism. No previous work had been reported on the use of hydrogels to form twisted fiber torsional actuators, although these materials are well known for generating very large volume transitions. The project involved three main sections: the synthesis of the twisted yarn actuators using a novel approach to nanofiber yarn electrospinning; the characterization of the torsional actuation of the twisted structure in response to pH; and the synthesis of nanocomposite yarns and their application as both torsional and tensile linear actuators.

The last part of the work arose from the observation that when fully immersed the nanofiber hydrogel yarns exhibited an unexpected actuation behavior. A never shown before transition from twisted to coiled fiber was observed that suggested the possibility of developing a new type of tensile actuator. Following work attempted to control the formation of coiled superstructures to create linear actuators by making composite that could withstand the forces needed for characterization.

Fabrication of Twisted Hydrogel Nanoyarns

Making nanostructured yarn is an area of research in its infancy, with few available technologies and rare all-in-one solutions. One example is represented by the Nanoyarn Spinner, which is a commercially-available machine that uses double conjugate electrospinning to manufacture nanofiber yarn. This machine in its first versions can make continuous lengths of twisted polyacrylonitrile nanoyarns but its drawbacks were that it was very complex to use and application to humidity sensitive polymer solutions was compromised due to the absence of weather proof sealing. Moreover, the double conjugate electrospinning is composed of two set of electrodes that are oppositely charged. This means that the optimization of conditions is extremely difficult as the ability of liquid to store electrostatic charges changes with the polarity of the field. The consequence is that the optimization function depends on the relative flow rate and electric field for two solutions and that in the case of polymers that are difficult to electrospin it is very likely that it cannot easily be used. This thesis was concerned with the production of nanofibers from poly(acrylic acid). The inherent polarity of PAA due to the COOH moiety makes this polymer very difficult to electrospin. In particular, the need for low humidity and the extreme sensitivity to the applied potential made it a bad candidate for double conjugate electrospinning using the Nanoyarn Spinner.

It was thus decided to make a new electrospinning setup. Inspired by various literature, the apparatus was based on the Hall effect that allowed for collection of nanofibers as aligned sheets. The original aim was to build a collector that allowed for the bundling of aligned nanofibers and their subsequent transfer to a yarn spinning system to allow for continuous lengths of twisted yarn to be prepared. Retrospectively the difficulty of the task was considerably underestimated, and this endeavor consumed many months.
The process involved many design/build/test iterations that first required the construction of an air tight enclosure for atmosphere control, in particular humidity.

Another major challenge was to build a collector for making aligned bundles of nanofibers. First, the gap electrospinning method was used to make aligned structures that could be rolled by hand into hollow cylinders that would collapse when twisted into yarns. The major issue was that the control over the twist angle was difficult and the method gave poor repeatability and reproducibility. The next iteration used two moving parallel wires for the collector. Practical difficulties associated with wire tensioning and breakage made this method unusable. The final solution for making a nanofiber yarn prototype involving a set of two grounded disks collecting nanofibers on their edges. This method allowed for the nanofibers be collected on a forked structure and then twisted into a yarn. The method was restricted to just short lengths of nanoyarn. Further testing showed it was possible to make different diameter yarns from polyacrylonitrile and that the quality of sample and the alignment of nanofibers in the direction of the fiber axis was excellent.

Furthermore, the disk-based electrospinning system has proven to be both a practical and reliable means to make short nanofiber yarns. The same system has been used for several years without the need for any repairs besides simple and cost-effective electrode replacements. The system was used successfully to make poly(acrylic acid) nanofiber yarns. Because of the sensitivity to humidity it was observed that most of the preparation time and sample variability was due to the humidity control process. As the apparatus was opened to retrieve a sample the ambient air in the lab with uncontrolled humidity would infiltrate into the system and the humidity control optimization process had to be carried away again. To reduce down times, the system was upgraded by addition of an autosampler in the form of a meshing disk pair which allowed for up to six samples to be manufactured without opening the box and thereby reducing the time spent in making samples by up to 60%. This process allowed for hundreds of samples to be made during the next years. An ion blower was also subsequently added to the system to mitigate the detrimental effect the electrostatic charge remaining on the samples which allowed us to make twisted polyacrylonitrile and poly(acrylic acid) nanofiber composite yarns of up to 100 microns.

Poly(acrylic acid) was selected for this project since it is a polyelectrolyte polymer that can be switched reversibly with pH between charged and neutral ionization states. Some optimization work was required to develop a method for crosslinking the PAA to prevent its dissolution in water. A convenient means for crosslinking into a hydrogel was by using a diamine crosslinker that was incorporated into the electrospinning solution and activated by heat after spinning and yarn twisting. The crosslinked yarns were shown to swell several times compared to its dry volume at low pH and swell further at high pH due to the osmotic pressure created by carboxylate ions moiety in solution. Despite best efforts, these nanofiber yarns did still present numerous defects that impeded further characterization of their diameter and may have led to mechanical failure during pH swelling experiments. Nevertheless, the yarn diameters could be varied to a reasonable degree and the swelling properties of the yarn could be modified by the amount of heat the sample was exposed to during crosslinking. Furthermore, it was shown that hydrogel nanostructure where stable after several cycles of pH change.

With the successful synthesis of hydrogel nanofiber yarns, this novel fabrication technology was then leveraged to make composite nanofiber yarns. This process involved the electrospinning of
polyacrylonitrile and forming the nanofibers into thin sheets over the autosampler. Next, the electrospinning solution was changed to produce a thin layer of poly(acrylic acid) nanofibers over the autosampler adjacent to the previously spun polyacrylonitrile. The co-twisting of the two bundles produced composite yarns that were strong enough for actuation testing. The composite yarns behaved differently to the pristine poly(acrylic acid) nanofiber yarns and were able to fabricate linear actuators.

Time limitations prevented the further development of the electrospinning apparatus into a system capable of producing long lengths of twisted yarns. However, preliminary studies showed that by continuously rotating the autosampler produced thick layers of polyacrylonitrile nanofiber to deposited at the edges between the disks. It was seen that by collecting the mat on a shaft and drawing it away from the disks it was possible to make meters long twisted yarns. A new design was developed that used a brushless dc motor to provide a method for automating the process. This design was not implemented due to time constraints, but further work could be carried to establish a method to obtain nanostructured stapled yarns of infinite length.

Exploration of the potential designs to automate the process for making long lengths of twisted yarn showed that a simple approach could be derived from pre-existing yarn spinning technologies. The proposed twisting and winding units, shown in Figure 103, are composed of two spinning shafts, one that rotates a mandrel (in blue) and a collecting spool (in green). By spin twisting the nanofiber from the continuously spinning autosampler and mounting the resulting yarn in the proposed yarn spinner it is likely that nanofiber yarns may be formed. Control over the nanostructure would then be a function of the relative speeds of the mandrel and the spool as well the amount of nanofibers collected on the autosampler. Interestingly, the autosampler can also act as a buffer that may be able to collect several different nanofibers on its edges, as shown in the nanocomposite synthesis, and thus afford the continuous synthesis of complex composite staple nanofiber yarns.
Figure 103: Section and full preview of the proposed twisting and winding units for making continuous lengths of nanofiber yarn.

**Actuation of Twisted Hydrogel Nanoyarns**

The preparation of hydrogel nanofiber yarns and composite nanofiber yarns provided the means for investigating their pH induced actuation behavior. In particular, the focus of this project was the torsional actuation properties of hydrogel nanofiber yarns. Experimental studies demonstrated that poly(acrylic acid) nanofiber yarns were torsionally active. Dry twisted nanofiber yarn swelled when immersed in pH 1.5 yielding a net untwist. This untwist was found to be statistically equal to the inserted twist and irreversible so that the first immersion of the nanoyarns in pH 1.5 caused the yarns to totally untwist. The single helix model of torsional actuation showed that full untwist was possible for the large diameter swelling and smaller length swelling encountered during immersion in pH 1.5 from dry.

The full untwisting of the yarns prevented any further exploration of the torsional actuation induced by a change in pH. However, the use of a return spring by immersing only half of the yarn in the pH solution prevented full untwist and provided a means for reversible actuation. This setup demonstrated that the hydrogel nanofiber yarn untwisted at pH 1.5 and further untwisted at pH 10. The reversibility of the change in twist density was shown for cycles of pH 1.5 and pH 10. Even when operated against a return spring, the torsional stroke of the PAA yarns was high. The hydrogel nanofiber yarns generate close to the highest recorded torsional strokes in the two-end-tethered configuration of ~500 turns/m for a yarn of initially inserted twist of 2000 turns/m.

The single helix theory was used to understand why the PAA twisted yarns tended to untwist when their volume was increased. By simplifying the twisted yarn structure to an assembly represented by one central straight fiber and a second helically wrapped fiber, the analysis concluded that yarn untwist would occur only if the volume expansion was anisotropic with the diameter change greater than the length change. Experiments supported this conclusion. Further quantitative analysis using the single helix model and based on the assumption that the string length ratio was the same as the ratio of the twisted fiber length during a volume transition yielded reasonable estimates of the measured torsional strokes. However further work should be focused in providing an experimental method to quantify the change in string length represented by $S = \lambda S_0$ as the actuator swells.
A key feature identified by the single helix modelling was the importance of volume expansion anisotropy. The anisotropy was experimentally verified and interpreted as the result of the alignment of the polymer backbone with the fiber axis during the electrospinning process.

It was thus shown that the torsional activity of the PAA twisted nanoyarns is the consequence of the anisotropy of the swelling. Further work could investigate in more detail the impact of anisotropy over the torsional actuation of the sample. Recent work has shown how to control the swelling anisotropy of hydrogel fibers made be wet spinning (Nakajima et al. 2017). Adoption of such fabrication methods would provide a means for exploring the link between swelling anisotropy and torsional stroke.

During the exploration of the torsional actuation properties of the PAA nanoyarn samples it was observed in some occurrences the actuator bent and formed superstructures promptly followed by the actuator’s rupture. Interestingly, it was observed that samples made with higher crosslinking densities where able to form large superstructures consisting of coils and snarls without rupture and with the superstructures controlled by the pH of the solution. In controlled experiments with such samples it was possible to reversibly produce these superstructure in fully immersed samples. The formation of superstructures became the focus of the last phase of this project using composite yarns of higher strength.

The study of neat PAA hydrogel nanoyarns was made difficult by the mechanical properties of the yarn which were intrinsically weak especially at low crosslink densities. This low strength conflicted with the desire to obtain the largest possible torsional actuation which required the largest swelling possible of the samples and thus the lowest crosslink densities. Consequently, many samples failed mechanically, and reproducibility issues were encountered as the sample quality varied significantly depending on the lab humidity even with the best efforts to control humidity in the electrospinning machine. Further work on hydrogel nanoyarn actuators would greatly benefit from methods to make nanoyarns more reproducibly and to use gel toughening strategies to make more robust samples.

**Actuation of Twisted Composite Hydrogel Nanoyarns**

This twisted PAA-PAN composite nanofiber yarns have shown interesting novel properties when fully immersed and swollen in different pH solutions. In particular, the actuator was found to bend into different superstructures such as snarls and coils. This phenomenon was highly repeatable and seen in many composite samples prepared with different diameters and with different degrees of PAA swelling. This superstructure formation was due to the untwist of the yarn and was accompanied with a large shortening of the overall length of the actuator. Moreover, it was found that the superstructure formation was reversible in different pH conditions.

The mechanism of the formation of the superstructures was investigated and it was shown that the mode of symmetry breaking during swelling was at the origin of the formation of coils or snarls. Furthermore, it was shown that the first formation of coiled superstructures could be predicted reasonably by the Ross criterion which attempts to capture the torque induced formation of coils in twisted fibers.

A major potential benefit arising from the formation of superstructures is the large length change which offers the potential of generating large stroke tensile artificial muscles. In some examples, the stroke was observed to be up to 80% of the initial sample length. Despite this interesting outcome, the prediction and control of the stroke of these artificial muscles was hindered by the different kinds of
superstructure that could be formed. In the repeatable experiments it was observed that superstructures where formed by a combination of coils and snarls. In all experiments conducted only two experiments showed a clear segregation of superstructure with one sample showing only coils and another only snarls induced by the pH transition.

Previous investigations of the mechanics of superstructure formation by twisting of fibers, ropes or cables has shown that the type of structure formed is load dependent: snarls form at low tensile loads and coils form above a certain load threshold (Ghatak & Mahadevan 2005). It follows that it should then be possible to obtain a segregation of the superstructures with sample that would exhibit either snarls or coils depending on the initial tension applied to the samples. Attempts in the present study to obtain different superstructures by varying the load applied were unsuccessful as under excessive stress the composite yarn would delaminate. Delamination was observed to be the consequence of hydrogel part of the composite breaking which resulted in a total loss in twist of the actuator. It is suggested that the use of stronger, tougher hydrogels would mean that experiments could be conducted at higher stresses. Possible modifications include increasing the PAA crosslinking; synthesis of stronger gels; and the change of the ratio between the polyacrylic acid and the polyacrylonitrile in the composite yarns.

To guide future endeavors to develop twist-to-coil high-stroke artificial muscles, an overarching model is outlined here. The model draws together the single helix theory and the Ross criterion and applies to samples that can be induced to only containing coils (by surviving actuation at high tensile stress). The model is developed that could predict the stroke of these actuators. The contraction stroke comes from the change in overall length due to the formation of coils and is determined by the number of coil turns that form, the diameter of each coil turn and the angle with respect to the tensile direction. Each of these elements is considered below.

\[
\nonumber n_{SH} = \frac{n_0}{\lambda D} \left( \frac{S_D^2 - L^2}{S_0^2 - L_0^2} \right)^{1/2}
\]

Equation 15: Resulting equation from the single helix theory

The number of coil turns that form will be determined by the difference between the total torsional stroke generated by the twisted yarn and the threshold torsional stroke needed to induce coiling. Using the results obtained in Chapter 3, the change output number of turns \(n_{SH}\) due to the swelling of hydrogel part of nanocomposite can be written as

Equation 15. (Note here the string length is assumed not to change because the string is formed by the inextensible PAN helix in the twisted composite fiber). At the present time, the input variables of the diameter and length expansion ratios must be experimentally determined. However, further studies into the origin of anisotropic volume expansion may provide a means for calculating these parameters from first principles.

It follows that by using the Ross criterion to determine the threshold untwist \(n_R\) in the sample provides a reasonable estimate for the onset of coil formation. The following equation is derived by
subtracting the threshold untwist from the expect untwist obtained from the single helix model to obtain the amount of untwist left for further coiling \( n_c \), as shown in Equation 16.

\[
n_c = n_n - n_R = n_0\left(1 + \frac{1}{\lambda_D} \left[ \frac{S^2 - L^2}{S_0^2 - L_0^2} \right]^{1/2} \right) - \frac{2\sqrt{2GE}}{DGn_0}
\]

Equation 16: Resulting number of coils from the untwist modelled by the single helix theory

Finally, this change in the number of coils can be modelled by applying the single helix theory to the coil geometry and yielding the net stroke which is the ratio of the change in the overall \( \Delta L_c \) over the starting length \( L_c \). As described in Chapter 4, the special case of meshing coils gives a change in length of

\[
\Delta L_c = D - [(\pi n D)^2 + D^2]^{1/2}
\]

However, the more general case includes coils that can form at any bias angle \( \alpha_c \) and any coil diameter \( (D_c) \) as:

\[
\Delta L_c = \pi n_c D_c \frac{\sin \alpha_c - 1}{\cos \alpha_c}
\]

\[
\frac{\Delta L_c}{L_c} = \frac{\pi D_c}{L} \left[ \frac{\sin \alpha_c - 1}{\cos \alpha_c} \right] \left[ n_0\left(1 + \frac{1}{\lambda_D} \left[ \frac{S^2 - L^2}{S_0^2 - L_0^2} \right]^{1/2} \right) - \frac{2\sqrt{2GE}}{DGn_0} \right]
\]

Equation 17: Resulting stroke of a coiled modelled from the untwist due the swelling snap buckling actuator

This last equation attempts to capture the change in length due to snap buckling at the swelling transition of the actuator. Further investigations of the mechanics governing coil formation should provide means for estimating the coil diameter and coil bias angle. This overall equation provides guidance for the future development of large stroke tensile artificial muscles that exploit the twist to coil transition. Important material properties that will govern the extent of the stroke generated will include the swelling extent (and its anisotropy) and the material elastic properties.
Literature


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VI. Appendix microcontroller program

Program for the disk collectors

The programming of the microcontroller (shown in Figure 104) was done by reusing the sample codes given by the manufacturer of the Arduino board and the stepper motor shield. This sample code leverages the provided motorshield library and AccelStepper library that allows for precise and simultaneous control of several stepper motors. Mostly the code wraps the I2C control features of the motor shield inside Accelstepper objects allowing the user to set all the required properties of the motors such as the speed, stepping type to the precision desired and a method of the wrapper is called that creates the stepping pattern (stepper.run()).

The actual code to control the two different machine stepper motors, the one that controls the collecting disk and the autosampler are contained in the microcontroller loop. The code is very simple, the user sets the number of experiments he wants to obtain (XP), the time for sacrificed experiments (WAITTIME) and the time for the other experiments (INTERVAL).

After the program is loaded and the microcontroller’s power supply is switched on the program starts, it starts the rotation of the collection disks (stepper2.run()) and computes the specified speed from the primitive (float rpm2 = 1) and the microcontrollers constants and desired precision. The interval between experiments of the auto sampler was then corrected by summing to the time the stepper motor took to rotate from a give position to the next set position. Finally, the stepping method was called as many time as needed to complete one full rotation which was deduced from the set number of desired sample (XP) by a conditional statement (rev <= 1 + 1 / xp) leveraging the angle increment variable (rev).

// Requires the Adafruit_Motorshield v2 library
// https://github.com/adafruit/Adafruit_Motor_Shield_V2_Library
// and AccelStepper with AFMotor support
// https://github.com/adafruit/AccelStepper

// This tutorial is for Adafruit Motorshield v2 only!
// Will not work with v1 shields

#include <AccelStepper.h>
#include <Wire.h>
#include <Adafruit_MotorShield.h>
#include "utility/Adafruit_MS_PWMServoDriver.h"
ADAFRUIT_MotorShield AFMSbot(0x61); // RIGHTMOST JUMPER CLOSED
ADAFRUIT_MotorShield AFMStop(0x60); // DEFAULT ADDRESS, NO JUMPERS

// Connect two steppers with 200 steps per revolution (1.8 DEGREE)
// TO THE TOP SHIELD
ADAFRUIT_StepperMotor *myStepper1 = AFMS_top.getStepper(200, 1);
ADAFRUIT_StepperMotor *myStepper2 = AFMS_top.getStepper(200, 2);

// Connect one stepper with 200 steps per revolution (1.8 DEGREE)
// TO THE BOTTOM SHIELD
ADAFRUIT_StepperMotor *myStepper3 = AFMS_bot.getStepper(200, 2);

// You can change these to DOUBLE or INTERLEAVE or MICROSTEP!
// Wrappers for the first motor!
void forwardStep1() {
    myStepper1->onestep(FORWARD, MICROSTEP);
}
void backwardStep1() {
    myStepper1->onestep(BACKWARD, MICROSTEP);
}

// Wrappers for the second motor!
void forwardStep2() {
    myStepper2->onestep(FORWARD, MICROSTEP);
}
void backwardStep2() {
    myStepper2->onestep(BACKWARD, MICROSTEP);
}

// Wrappers for the third motor!
void forwardStep3() {
    myStepper3->onestep(FORWARD, INTERLEAVE);
}
void backwardStep3() {
    myStepper3->onestep(BACKWARD, INTERLEAVE);
}

// Now we'll wrap the steppers in an AccelStepper object
AccelStepper stepper1(forwardStep1, backwardStep1);
AccelStepper stepper2(forwardStep2, backwardStep2);
FLOAT STEPPERREV = 200;
FLOAT RPM = 100;
FLOAT RPM2 = 1;
FLOAT MICROSTEP = 16;
FLOAT MICROSTEP2 = 16;
FLOAT XP = 6;
UNSIGNED LONG WAIT
TIME = 2 * 60L * 1000L; // FIRST XP IS ALWAYS SACRIFICED
LONG INTERVAL = 6 * 60L * 1000L;
LONG LASTLAP = 0;
LONG TRAVELTIME = 0;
INT SWITCH1 = 0;
FLOAT REV;
FLOAT STEPPERSECOND = RPM * MICROSTEP * STEPPERREV / 60;
FLOAT STEPPERSECOND2 = RPM2 * MICROSTEP2 * STEPPERREV / 60;
VOID SETUP()
{
    //AFMSbot.begin(); // START THE BOTTOM SHIELD
    AFMStop.begin(); // START THE TOP SHIELD
    SERIAL.begin(9600);
    STEPPER1.setMaxSpeed(STEPPERSECOND);
    STEPPER1.setAcceleration(20000.0);
    STEPPER2.setMaxSpeed(STEPPERSECOND2);
    STEPPER2.setAcceleration(2000.0);
    STEPPER2.moveTo(2000000);
}
VOID LOOP()
{
    STEPPER2.run(); // FIRST COLLECTOR
    IF (MILLIS() > WAIT
TIME) { // PREP BEFORE XPS
        IF (STEPPER1.distanceToGo() == 0) {
            // SECOND COLLECTOR IS DONE MOVING (NO SENSOR)
            // SWITCH ALLOWS FOR ONE CALL TO CORRECTEDINTERVAL COMPUTATION PER
            CORRECTEDINTERVAL
            IF (SWITCH1) {
                CORRECTEDINTERVAL = INTERVAL + (MILLIS() - TRAVEL
TIME);
                SWITCH1 = FALSE;
            }
        }
    }
}
} IF (MILLIS() - LASTLAP > CORRECTEDINTERVAL) {
  // Serial.println((waitTime));
  rev = rev + 1 / xp;
  stepper1.moveTo((long)(-rev * stepperrev * microstep));
  Serial.println(rev);
  Serial.println((-rev * stepperrev * microstep));
  lastlap = millis();
  traveltime = millis();
  switch1 = true;
}
}

IF (rev <= 1 + 1 / xp)
  stepper1.run();

Figure 104: Code used in the nanoyarn collection apparatus

Program for the winding unit

The objective of the winding unit is to transform the synthesized nanofibrous objects that resembles sheets into nanofiber yarn by twisting them. Because of the simpler task we used a simple PWD driven motor controller hook on an Arduino Uno.

The code relies on the accelstepper library thus leveraging the high precision Arduino timer. It calculates the require amount of turns the stepper needs to make (turns) from the sample size (SAMPLESIZE) and the desired twist desity (TPM) and then invokes the accelstepper wrapper by allocating the stepping schema (stepper.moveTo) and starting the movement process by invoking the run method (stepper.run).

// HTTPS://GITHUB.COM/ADAFRUIT/AccelStepper
#include <AccelStepper.h>
// Define a stepper and the pins it will use
// Defaults to 4 pins on 2, 3, 4, 5
// Step 3 Dir 4 AccelStepper stepper1(1, step, dir);
accelstep stepper1(1, 3, 4); //150
const int microstep = 8;
const int stepsPerRevolution = 200 * microstep;
float tpm = 2000;
float samplesize = 5.0; //cm
FLOAT TURNS = TPM * SAMPLESIZE * 0.01;
FLOAT DIR = 1; // -1 CCW 1 CW
VOID SETUP()
{
    STEPPER.setMaxSpeed(1500);
    STEPPER.setAcceleration(2000);
}
VOID LOOP()
{
    STEPPER.moveTo(DIR * TURNS * STEPSPERREVOLUTION);
    STEPPER.run();
}
VII. Appendix Machine’s Engineering drawing

Engineering drawing of the box and prototyping platform

![Box design drawing](image)

Figure 105: Front view of the box and the prototyping platform.

**Box design**

<table>
<thead>
<tr>
<th>Design (lengths in mm)</th>
<th>Quantity</th>
<th>Role</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Box design image" /></td>
<td>1</td>
<td>Top part the box fitted with a hole for the syringe pump</td>
</tr>
<tr>
<td><img src="image" alt="Box design image" /></td>
<td>2</td>
<td>Side part of the box fitted with holes for the wiring and the dry nitrogen gaz inlet.</td>
</tr>
<tr>
<td>Design (lengths in mm)</td>
<td>Quantity</td>
<td>Role</td>
</tr>
<tr>
<td>------------------------</td>
<td>----------</td>
<td>------</td>
</tr>
<tr>
<td>1 Bottom floor, held by the lab jack, hold the upper floor through pillars, the electronics, the autosampler and the stepper motors.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 Pillars that hold the upper floor, the grounded shaft and the collecting apparatus.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Top floor, insulate the electrospinning from the yarn making, fits the collecting apparatus.

**Disk driven collecting apparatus**

Figure 106: View of the collecting apparatus with the collection disks and the autosampler.

<table>
<thead>
<tr>
<th>Design (lengths in mm)</th>
<th>Quantity</th>
<th>Role</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Collection disks, collects the nanofibers on its copper coated edge. Grounds the edge with a slip ring.</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Center shaft, holds the collection disks and is held by the prototyping platform pillars.</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Autosampler disks, mesh with the collection disk, are held by the autosampler shaft.</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Autosampler shaft, holds the autosampler disks.</td>
<td></td>
</tr>
</tbody>
</table>
Autosampler holder, holds the autosampler shaft and disk assembly as well as the stepper motor that drives it. Is held on the bottom floor of the prototyping platform by screws allowing it to slide.