GENERALIZATION AND EXTENSIONS OF CAPILLARY THINNING DRIVEN SELF ASSEMBLY OF NANOSTRUCTURED AIR-BRIDGES

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M.S., University of Louisville, USA 2005
B.Tech., Jawaharlal Nehru Technological University, INDIA 2003

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SELF ASSEMBLY

AUTOMATIC OR SELF-GUIDED FORMATION OF STRUCTURES FROM PRE-EXISTING ENTITIES

SELF ASSEMBLY OFFERS THE POSSIBILITY OF FABRICATING MATERIALS/STRUCTURES/DEVICES WITH EASE

SPHERICAL WATER DROPLET ON LEAF

NANO/MICRO FIBRILS IN A BLOOD CLOT
BRUSH-ON OF NANOFIBER AIR-BRIDGES FROM LIQUID POLYMERS

FIBRIN: 1D FIBER ARRAYS
GENERALIZATION AND EXTENSIONS OF BRUSH-ON

Different structures other than fiber air-bridges with increased complexity

Different solidification mechanisms other than evaporation

Different procedures other than brushing
FUNCTIONAL AND STRUCTURAL ROLES FOR SELF ASSEMBLED AIR-BRIDGES IN MEMS/NEMS

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- ✓ Demonstrated in this dissertation
- ☐ Extended in this dissertation
- X Proposed future work
FUNCTIONAL AND STRUCTURAL ROLES FOR SELF ASSEMBLED AIR-BRIDGES IN MEMS/NEMS

**AIR-BRIDGE STRUCTURES**
- 1D fiber air-bridges
- 2D fiber air-bridges
- Horizontal membranes
- Trampolines
- Vertical membranes
- Single ended free standing 1D fibers
- Beads on a string
- Bifurcated fibers

**MATERIAL MORPHOLOGY**
- Solid
- Block or blends
- Permeable
- Porous

**ORGANIZATION OF ARRAYS OF AIR-BRIDGES**
- Periodic arrays
- Chaotically switching
- Multilevel
- Skewed planar

**MATERIAL COMPOSITION**
- Polymers
- Biopolymers
- Nano composites
- Metallic alloys
- Salts
- Colloidal solutions

**TEMPLATING**
- Multilayering
- Sacrificial removal of polymer from multilayered structures
- Sacrificial removal of polymer from nanocomposite fibers
- Insulated conductive wires by reflow of polymer

**TRANSFER OF AIR-BRIDGES ONTO OTHER SUBSTRATES**
- Direct write
- Selective melt-on

☑ Demonstrated in this dissertation
☒ Extended in this dissertation
☒ Proposed future work
FIBRIN: 2D FIBER ARRAYS

10 µm
SUSPENDED MEMBRANES

Brush-on of large volumes of concentrated polymer solution

BIFURCATED FIBERS

Vertical retraction with blunt tips from a pool of solvated polymer

FIBRIN: TRAMPOLINE ARRAYS
FIBRIN VERTICAL MEMBRANES
Direct-write of 2 wt % PEO (5000 Kg/mol) in chloroform
Beads on a string

A

Brush-on

2 wt % PEO

(5,000 Kg/mol)
in water
Brush-on of 2 wt % PEO (5,000 Kg/mol) in water
SINGLE END SUPPORTED PMMA FIBERS

Brush-on of 25 wt % PMMA (996 Kg/mol) in chloroform

THESE ARE POSSIBLY OBTAINED DUE TO A CHANGE IN BRUSHING SPEED OR DUE TO LESS SOLUTION BEING APPLIED ONTO THE PILLARS
FIBRIN: TRANSITION ZONE
Thermal annealing (140 °C) of amphiphilic PLLA-PEO-PLLA polymer followed by gradual cooling and then soaking in water (2 min) induces porous morphology.

Polymer samples provided by J.M. Rathfon and G.N. Tew (Univ. of Massachusetts-Amherst)
CAPILLARIES TEMPLATED ON POLYMER FIBERS

Overcoat with metal, glass or parylene

Dissolve polymer leaving capillary

Gold
20 nm film

1 μm Chrome
Parylene

2 μm

Glass

10 μm

CNT FIBERS AFTER DISSOLVING PMMA IN ACETONE

Single fiber

Close-up of similar fiber
COMPOSITE POLYMER FIBERS USED TO PREPATTERN NANOMATERIAL AIR-BRIDGES

Bridges as narrow as 10 nm have been made.
ARRAY OF 2D MULTI WALLED NANOTUBE AIR-BRIDGES

Pabba et al. ACS Nano. 2007
DIRECT-WRITE OF AIR-BRIDGES

Polymer Solution

Syringe

Separation between the surface and the syringe tip

Micro-textured surface

SCHEMATIC

VIDEO
FUNCTIONAL AND STRUCTURAL ROLES FOR SELF ASSEMBLED AIR-BRIDGES IN MEMS/NEMS

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SELECTIVE PATTERNING OF AIR-BRIDGES

☑ Demonstrated in this dissertation
☒ Extended in this dissertation
☒ Proposed future work
GENERALIZATION AND EXTENSIONS OF BRUSH-ON

Different structures other than fiber air-bridges that increase the complexity of air-bridges

Different solidification mechanisms other than evaporation

Different procedures other than brushing
BRUSH-ON OF NANOFIBER AIR-BRIDGES FROM LIQUID POLYMERS
POLYMER FIBER AIR-BRIDGES OF LONG RANGE ORDER

POLY(VINYL ACETATE) (50 Kg/mol) IN ACETONE
MODEL FOR FORMATION OF ORIENTED NANOFIBER AIR-BRIDGES

DEWETTING RESULTS IN BREAKUP OF POLYMER MEMBRANE INTO LIQUID BRIDGES

MODEL WAS DEVELOPED BASED ON OBSERVATION OF FIBER FORMATION IMMEDIATELY FOLLOWING BRUSH-ON UNDER AN OPTICAL MICROSCOPE
CONDITIONS FOR STABLE FIBER FORMATION

Measured capillary thinning rates for 7% to 17% wt. PMMA (950,000 MW) in chlorobenzene

Theory (McKinley-MIT)

\[ P = \frac{h \eta}{\sigma} \]

Processing Parameter
GENERALIZATION AND EXTENSIONS OF BRUSH-ON

Different structures other than fiber air-bridges that increase the complexity of air-bridges

Different solidification mechanisms other than evaporation

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**POTENTIAL METHODS TO SELF ASSEMBLE AIR-BRIDGES DRIVEN BY CAPILLARY FORCES**

### Brush-on

- **Liquid polymer solidifies as solvent dries**
  - Marked with a checkmark. *Demonstrated in this dissertation*

- **Barely dissolved polymer precipitates at high strain rate**
  - Marked with a checkmark. *Extended in this dissertation*

- **Liquid monomer polymerizes to solidify during brushing**
  - Marked with a checkmark. *Proposed future work*

- **Liquid to gel transformation of sol-gel material systems**
  - Marked with an asterisk. *Elements that support the possibility of a successful demonstration*

- **Salt solution solidifies as it dries**
  - Marked with a cross. *Preliminary positive result but additional improvements are required*

- **Precipitation of intermetallic crystals from alloy melts**
  - Marked with an asterisk. *Completely demonstrated*

### Methods

- **By tilting an array from liquid**
- **Point to point electrostatic interconnection**
- **Melting of polymer films**
EVALUATION OF BRUSH-ON METHOD

With concentrated polymer solutions driven by evaporation

With dilute high MW polymer solutions driven by strain hardening
ARRAYS OF POLYMER FIBER AIR-BRIDGES

A. 23 wt % PMMA in chlorobenzene

B. 15 wt % PLLA in chloroform

C. 15 wt % PMMA-MWNT- chlorobenzene
EFFECT OF EVAPORATION RATE

For PMMA (996 Kg/mol) solutions with three different solvents

- Dichloromethane
- Acetone
- Chlorobenzene

No fiber

Vapor Pressure (mmHg) vs. Concentration (wt%)
Identifying regions of minimal polymer chain overlap to highly entangled overlap of chains in solution and melts.
CONCENTRATION - MOLECULAR WEIGHT DIAGRAM FOR PMMA IN ACETONE

FIBER AIR-BRIDGES FORM IN CONCENTRATED ENTANGLED REGION
CONCENTRATION - MOLECULAR WEIGHT DIAGRAM FOR POLY(ETHYLENE OXIDE) IN WATER

FIBER AIR-BRIDGES FORM IN SEMI-DILUTE ENTANGLED REGION
POLY(ETHYLENE OXIDE) NANOFIBER AIR-BRIDGES

Diameter ~ 45 nm
PEO (8000 Kg/mol) in DI water
CaBER ANALYSIS: PEO (1 M Da) IN WATER
CaBER ANALYSIS: PEO (5 M Da) IN WATER

Non-uniform thinning

Drastic increase in extensional viscosity as the noted
POLYMERIZATION DRIVEN SELF ASSEMBLY OF NANOFIBER AIR-BRIDGES
Let’s replace solvent evaporation with bio-polymerization and see if stable fibers can still form due to capillary thinning.
BIOPOLYMERIZED FIBER AIR BRIDGES
MADE FROM PURE PROTEIN EXTRACTS

Suggests initiated polymerization with organic monomers

LONG RANGE ORDER OF HAND-BRUSHED FIBRIN

At least 48 x 62 µm

36 nm fibers
SD: 6.82 nm
FIBRIN VERTICAL MEMBRANES

No vertical membranes in this region

550 x 400 µm area
SMALLEST BIOPOLYMERIZED FIBERS

Fibrinogen

Fibrin fiber

Actin fiber

MgCl₂

16 nm

X

1460 nm

22 nm
MONOMER BRUSH-ON AND POLYMERIZATION

NORBORNYLENE POLYMERIZED WITH GRUBBS’ CATALYST
SELF ASSEMBLY OF AIR-BRIDGES BY MELTING OF POLYMER FILMS

Polyester film heated at 250 ºC for 15 min

Teflon tape heated at 385 ºC for 6 hrs
TIME LAPSE IMAGES OF MELT-ON

65 nm thick polystyrene film heated at 110, 120, 130, 140 °C each for 30 min

Developed in collaboration with J.R. Rathfon and G.N. Tew
University of Massachusetts Amherst
MELT-ON FABRICATION WITH LOCAL HEATING
SUMMARY OF MAJOR FINDINGS

Brush-on with
Concentrated polymeric solutions
Dilute high MW polymer solutions
Monomer solutions

Driving Force
Evaporation
Strain hardening
Polymerization

Melting of polymer films

Brush-on and subsequent processes produced a wide variety of structures

Structure
Nanotrampolines arrays
Membrane septums
Nanomaterial air-bridges
Nanoporous air-bridges

Material System
Fibrin
Fibrin, PEO, Norbornylene
Nanotubes, Nanowires, graphene sheets*
Block copolymers*

* Process includes templating
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THANK YOU
Fiber diameter depends on as well as droplet diameter (Tripathi and McKinley)

\[ P = \frac{\text{Evaporation rate} \times \text{viscosity}}{\text{Surface tension}} \]

as well as droplet diameter

(Tripathi and McKinley)
DESCRIPTION OF BOS STRUCTURE BY ITERATIVE STRETCHING MODEL
Fibrin is very sticky and elastomeric with an extensibility of ~350 %. Movie shows a broken fiber on probe tip after it was adhered to a two-point fibrin bridge and stretched 38 %.
AVERAGE FIBER DIAMETER AS FUNCTION OF BRUSHING SPEED

(•) 25 wt % PMMA-chlorobenzene and (*) 15 wt % PMMA-acetone solutions. A constant pressure of 16.61 psi was applied for pressurizing the polymer solution.
PLLA (137.7 g/mol) film

Thickness ~ 200nm

Heated at 130 °C for 5 min
<table>
<thead>
<tr>
<th>Sample</th>
<th>Polymer name</th>
<th>Molecular weight (kg/mol)</th>
<th>Solvents</th>
<th>Concentration (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PMMA</td>
<td>996</td>
<td>CB MEK Chloroform Acetone DCM</td>
<td>20,23,25,30 35 18,20,25,30 35 15,20,25,30 35 15,20,25,30,35 10,15,20,25,30</td>
</tr>
<tr>
<td>2</td>
<td>PVAc</td>
<td>50</td>
<td>Acetone</td>
<td>25,35 20,30</td>
</tr>
<tr>
<td>3</td>
<td>PLLA</td>
<td>137.7</td>
<td>Chloroform</td>
<td>20,30,35</td>
</tr>
<tr>
<td>4</td>
<td>P(S-b-MMA)</td>
<td>138</td>
<td>Toluene</td>
<td>30,35,40</td>
</tr>
<tr>
<td>5</td>
<td>P (LLA-b-EO-b-LLA)</td>
<td>136.4</td>
<td>Chloroform</td>
<td>15,20,25</td>
</tr>
<tr>
<td>6</td>
<td>P(α-MS)</td>
<td>400</td>
<td>Toluene, tetrahydrofuran</td>
<td>25</td>
</tr>
<tr>
<td>7</td>
<td>PS</td>
<td>280</td>
<td>Chloroform (ChCl₃)</td>
<td>25,30</td>
</tr>
<tr>
<td>8</td>
<td>PVDF</td>
<td>400</td>
<td>Acetone and DMF (V/V:50/50)</td>
<td>10,15</td>
</tr>
<tr>
<td>9</td>
<td>PEO</td>
<td>5000</td>
<td>Chloroform</td>
<td>1,2</td>
</tr>
</tbody>
</table>
BRUSH-ON PROCESS AS OBSERVED UNDER AN OPTICAL MICROSCOPE
Graphene and GaAsP AIR BRIDGES


THERMO GRAVIMETRIC ANALYSIS

- CB
- PMMA/Kentera
- MWNT
- Fe$_2$O$_3$

Sample mass (wt %)

Temperature (ºC)

PMMA-CB
- MWNT-CB
- PMMA-MWNT-CB

Mostly PMMA
- Kentera

$rac{dm}{dT}$ (arbitrary units)

Temperature (ºC)
RAMAN SPECTROSCOPY

[Graphs showing Raman spectra for different samples with labels and peaks at various Raman shifts.]
HYPOTHETICAL PROCESSES IN THE FORMATION OF FIBRIN NANOSTRUCTURES

Left Top: 1D fibers
Middle Left: 2D fibers
Bottom: Nanotrampolines

DECREASING BRUSHING SPEED

[Diagram showing the processes with decreasing brushing speed: 1D fibers, 2D fibers, and nanotrampolines]
# VARIATIONS WITH PROCESSING CONDITIONS

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<th>Brush pillar arrays with</th>
<th>Resulting structures are</th>
<th>Mechanical properties</th>
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<tr>
<td>Thrombin</td>
<td>No bridges form</td>
<td>N/A</td>
</tr>
<tr>
<td>Fibrinogen or Fibrinogen + Factor XIIIa</td>
<td>Sparse array of fiber bridges</td>
<td>Fibers dissolve instantly in buffer</td>
</tr>
<tr>
<td>Thrombin followed by Fibrinogen</td>
<td>Arrays of</td>
<td></td>
</tr>
<tr>
<td>Thrombin followed by Fibrinogen + Factor XIIIa</td>
<td>Arrays of</td>
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MEASURING YOUNG’S MODULUS OF NANOFIBERS WITH NEEDLE BUCKLING

Young’s modulus measured to be $E = 2.96$ GPa

\[ E = \frac{\text{stress}}{\text{strain}} = \frac{T}{(\pi r_f^2)} \frac{\Delta L_f}{L_f} \]
SELF ASSEMBLY IN LIQUIDS

- Governed by surface tension which is a result of intermolecular forces
- Surface tension works to minimize the free energy of the liquid by minimizing the surface area.
- For this reason liquid droplets tend to form into spheres
SINGLE END SUPPORTED FIBERS

DIRECT-WRITE OF 20 WT % PMMA IN DICHLOROMETHANE
Very small and sensitive gas sensors could be constructed. Can also be used for 3D interconnects.
PHASE SEPARATION OF BLOCK COPOLYMERS
AFFECT OF VISCOSITY

Capillary thinning of liquid bridges for PMMA as measured by a CaBER.

Concentration

Molecular weight
SELF ASSEMBLY IN-TERMS OF THERMODYNAMICS AND KINETICS

FREE ENERGY DIAGRAM

FREE ENERGY DIAGRAM
PMMA FIBER WITH RANDOM ORGANIZATION OF PORES.
DIFFERENT LIQUID GEOMETRIES DRIVEN BY THE FORCE OF SURFACE TENSION

(A) In a continuous liquid jet, (B) in liquid dripping from a faucet, (C) liquid wetting a surface at an angle $\theta$, (D) capillary wicking onto a rod, (E) stable liquid meniscus in between two parallel plates, (F) unstable liquid bridge after separating the parallel plates from equilibrium configuration shown in (F).
Spreading of solvated polymer at air-water interface.

Figure. Schematic for fabrication of free standing polymer films at air-water interface based on spreading coefficient. (A) transferring solvated polymer into a bath of water (B) puddle formation which instantaneously spreads across the air-water interface due to difference in surface tension between the solvated polymer solution and water (C) evaporation of the solvent from the polymer film resulting in the formation of solid free standing polymer film

polymer solution example: 5% Poly (L-lactic acid) in chloroform
Spun-on fabrication of polymer film followed by lift off

(A) Transferring the solvated polymer onto the silicon wafer. (B) Spinning the water distributes the polymer uniformly. (C) Allowing the film to settle for complete removal of solvent. (D) Transferring the substrate into water for peeling the film. (E) Suspended film at the air-water interface.

Solutions tried: Polystyrene in toluene, Poly (L-lactic acid) in chloroform
Flow coating

- Films drawn from 0.5 - 4 wt % solutions of PS ($M_n = 400$ kDa) in toluene
  - Thickness varies between ~ 4 – 150 nm
- Acceleration can be used for a gradient thickness film
  - 1.5, 3, and 6 mm/s² used
- Film thickness measured via interferometry
- Film floated onto pillar array via water
- Annealed above $T_g$ at ~155 °C ($T_g$ ~ 110 °C)