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Food Waste-derived Medical Textiles via Electrospinning for Healthcare Apparel and Personal Protective Equipment

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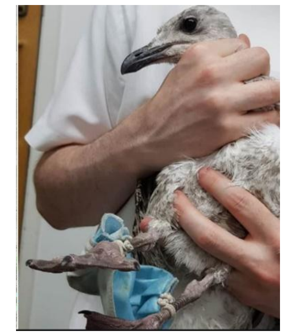
CORFU 2022 9th International Conference on Sustainable Solid Waste Management
17th June 2022

Market Needs for Biodegradable & Sustainable PPE

Vast amount of wastes of consumed PPE during pandemic of COVID19!

Limited raw materials supply cause uncontrollable quality and high cost



Large consumption of surgical mask cause severe plastic pollution problem

- Many regulations in countries, including China, to ban the use of non-biodegradable plastic for single use/disposable items

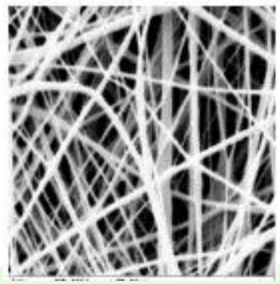
- **Biodegradable and sustainable raw materials for PPE will be the trend in the future!!!**

BIODEGRADABLE

Proposed Research Project

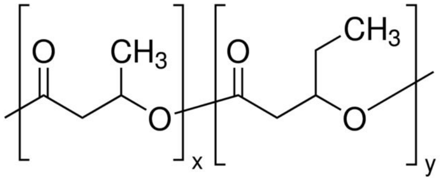
Reducing the transmission of novel coronavirus and other infectious diseases using **food waste-derived medical textiles via electrospinning and electrospraying** for healthcare apparel and personal protective equipment

<u>Task 1:</u>
Fermentative PLA and PHBV production using food waste hydrolysate

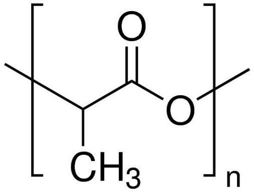


<u>Task 2:</u>
Synthesis of PLA and PHBV blend for production of non-woven textile materials via electrospinning and electrospraying

<u>Task 3:</u>
Testing properties of fabricated non-woven textile material



Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV)



Polylactic acid (PLA)

Aims & Objectives

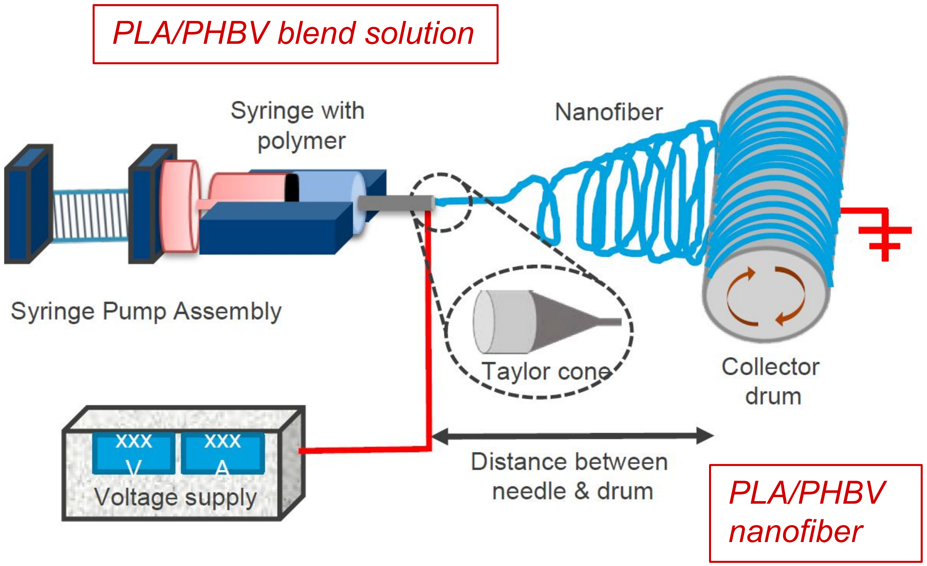
- Produce **non-woven textile materials via electrospinning and electrospraying** which can be used as personal protective equipment which are **bio-based and biodegradable fibres** derived from food waste

- Achieve **superhydrophobicity and high conductivity non-woven materials** that can offer protection even higher than the FFP3 standard, that is >99% protection not only for submicroscopic particles or virus (UNI EN 149:2009 standard) but also nanoscopic (up to 5-10nm).

- UNI-EN reference standards validation tests:
  - **Filtration efficiency** of nano and microparticles, BFE test
  - **Maximum breathing resistance** inspiration and expiration
  - **Bacteria/ virus deposition rate, >50% reduction deposition rate using surrogate coronaviruses.**

Potential Application

Methodology:
Fabrication of Non-Woven Material by Electrospinning



Optimized parameters

- *Polymer blend ratio/conc.*
- *Voltage*
- *Feed rate of polymer solution*
- *Needle to drum distance*

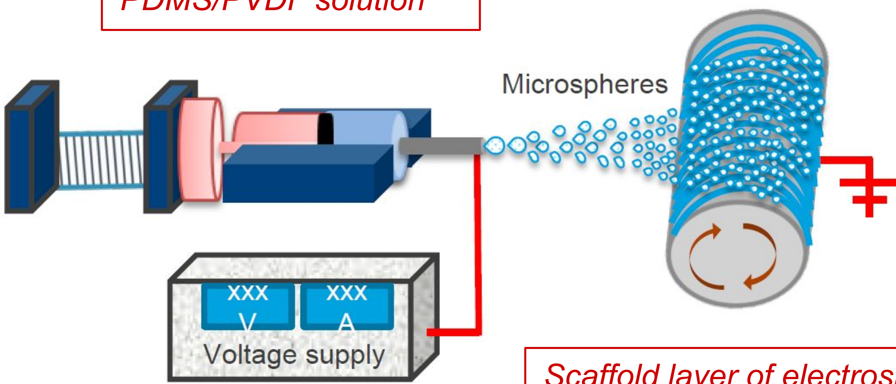
Desired properties

- *Porosity, pore size*
- *Fibre diameter, size range*
- *Thickness*

Target: Fabricate **non-woven scaffold material** by **electrospinning** with desired properties for further electrospraying

Methodology: Fabrication of Superhydrophobic Membrane using Electrospraying

Aerogel incorporated PDMS/PVDF solution



Scaffold layer of electrospun PLA/PHBV fabric coated with PDMS/PVDF aerogel

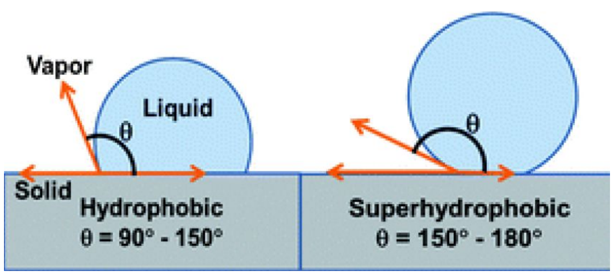
Optimized parameters

- *PDMS/PVDF/aerogel ratios*
- *Voltage*
- *Flow rate*
- *Nozzle to drum distance*

Desired properties

- *Hydrophobicity*
- *Surface roughness*
- *Membrane performance*

Target: Fabricate **non-woven superhydrophobic membrane** by **electrospraying** with desired antiwetting function

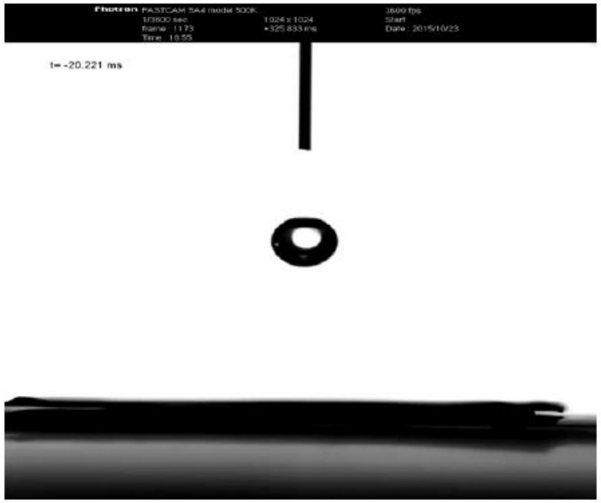


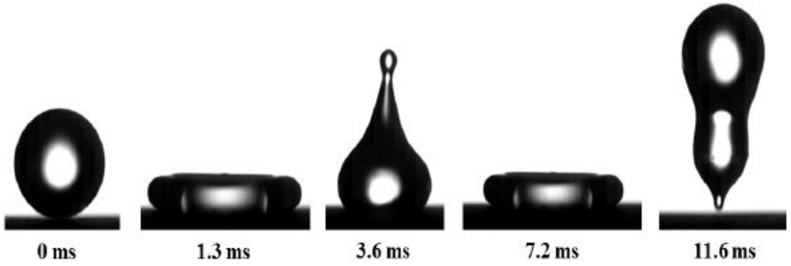
Methodology: Membrane Characterization

Characters	Testing methods
Morphology	Scanning Electron Microscope (SEM), Field Emission Scanning Electron Microscope (FESEM)
Functional groups	Fourier transform infrared spectroscopy (FT−IR) analysis X-ray diffraction (XRD)
Elemental analysis	Energy-dispersive X-ray spectroscopy
Hydrophobicity	Contact angle measuring system for wettability High-speed camera to record dynamics of droplets
Surface roughness	Atomic force microscope (AFM)
Density, porosity, pore size	Imaging software and liquid displacement method

Target: Validation of non-woven membrane physical and chemical properties, **especially reduction of bacteria/ virus deposition rate**

Methodology: Membrane Characterization





Water droplet dynamics on the superhydrophobic surface of E-M3-A30 membrane, selected snapshots representing the whole rebounding phenomenon.

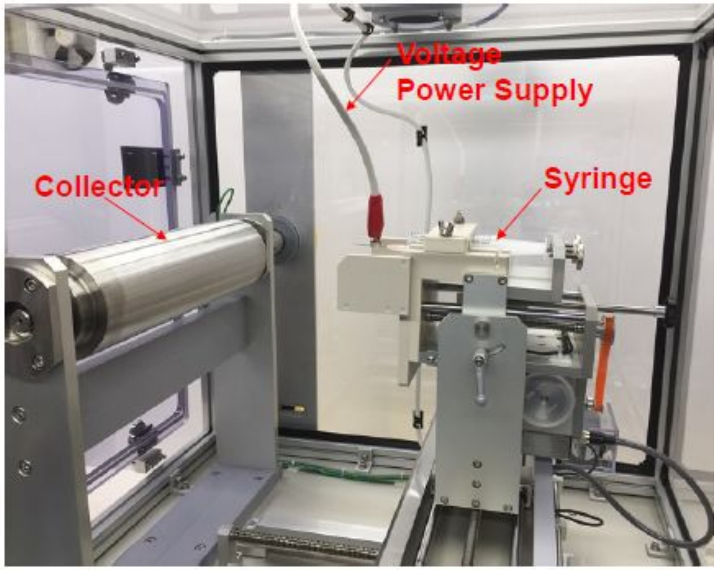
Deka, B.J., Lee, E.-J., Guo, J., Kharraz, J., An, A.K. 2019. Electrospun Nanofiber Membranes Incorporating PDMS-Aerogel Superhydrophobic Coating with Enhanced Flux and Improved Antiwettability in Membrane Distillation. *Envir Sci Tech*, **53**(9), 4948-4958.

Target: Validation of non-woven membrane physical and chemical properties, **especially reduction of bacteria/ virus deposition rate**

Optimization of Parameters for PLA/PHBV Electrospinning

Optimization of parameters for polymer solution and electrospinning conditions:

- **Polymer solvent selection**
- **Solvent Ratio**
- **Polymer concentration**
- **Electrospinning flow rate**
- **Electrospinning voltage**
- **Electrospinning needle to collector distance**



Polymer Solvent Selection

- ***To identify a good solvent system for PLA/PHBV for electrospinning based on similarity on solubility parameter index***

Solubility Parameters (δ)

Polymer	δ ($MPa^{1/2}$)
PLA	**20.2**
PP	16.2
Nylon 6,6	28

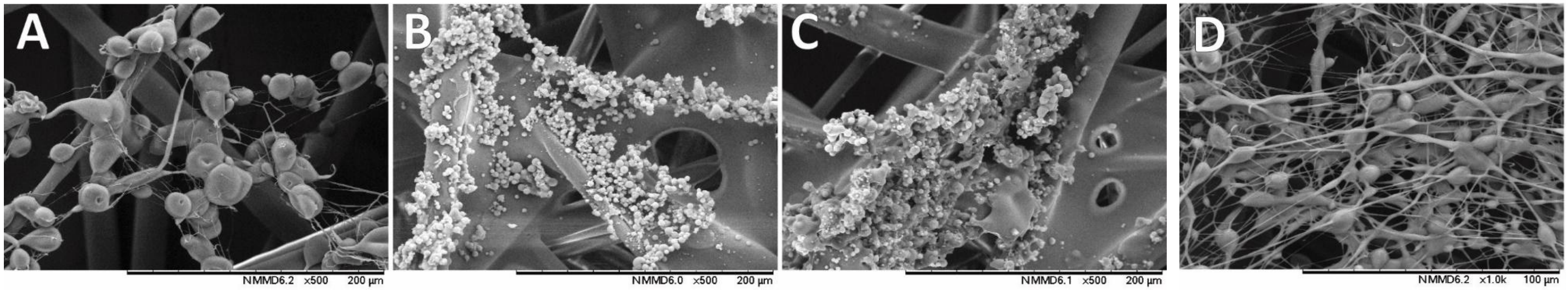
Solvent	Solubility Parameters (δ) ($MPa^{1/2}$)	Vapor Pressure (Pa) 25°C	Conductivity ($\mu S\ cm^{-1}$)	Boiling Point (°C)
Chloroform	18.7	26,264	1.0E-4	52
Acetone	19.9	32,450	0.2	56
Dimethylformamide (DMF)	24.2	516	6.0E-2	153
Dimethylacetamide (DMAc)	22	300	/	165

- The more similar the solubility parameters (δ) of polymer/ solvents, **better miscibility**
- $\Delta\delta < 2\ MPa^{1/2}$: **good miscibility**
- $\Delta\delta > 10\ MPa^{1/2}$ being **immiscible**

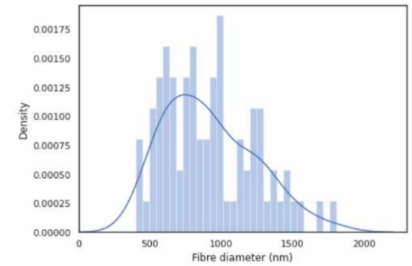
- PLA solubility parameters are less than 2 $MPa^{1/2}$, making them miscible

Solvent Selection

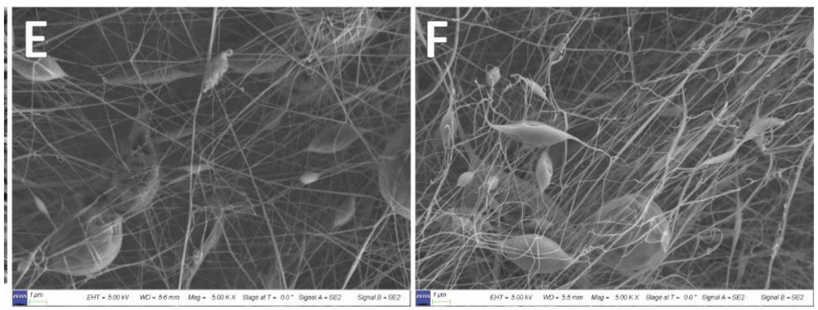
Single Solvent



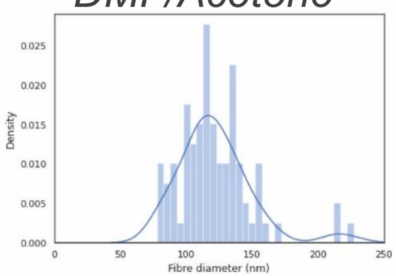
Chloroform *DMF* *DMAc* *Acetone*

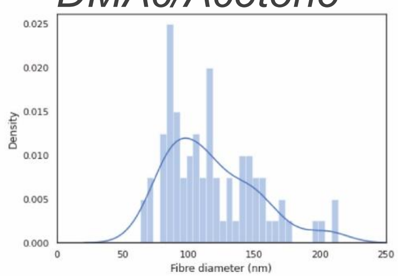


Binary Solvent



DMF/Acetone *DMAc/Acetone*



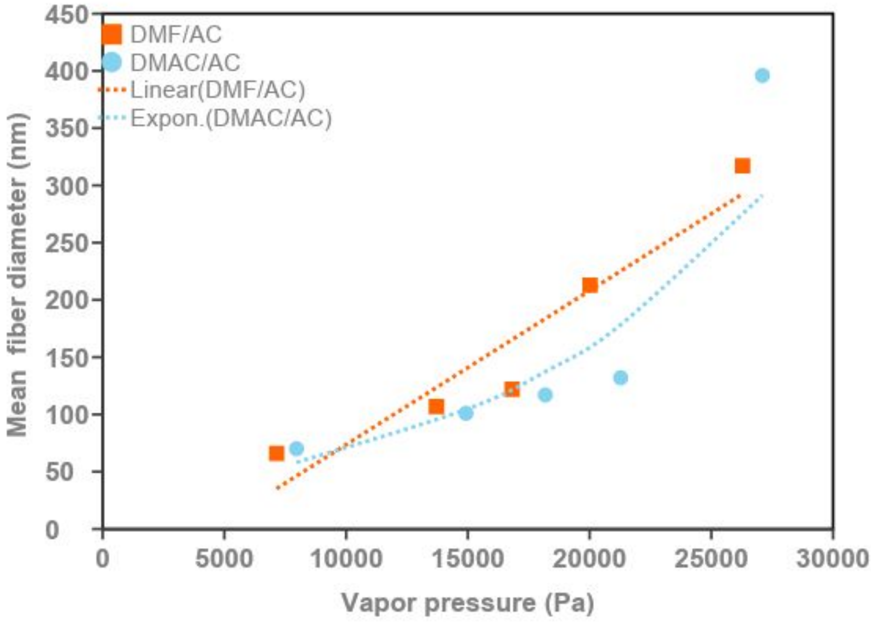


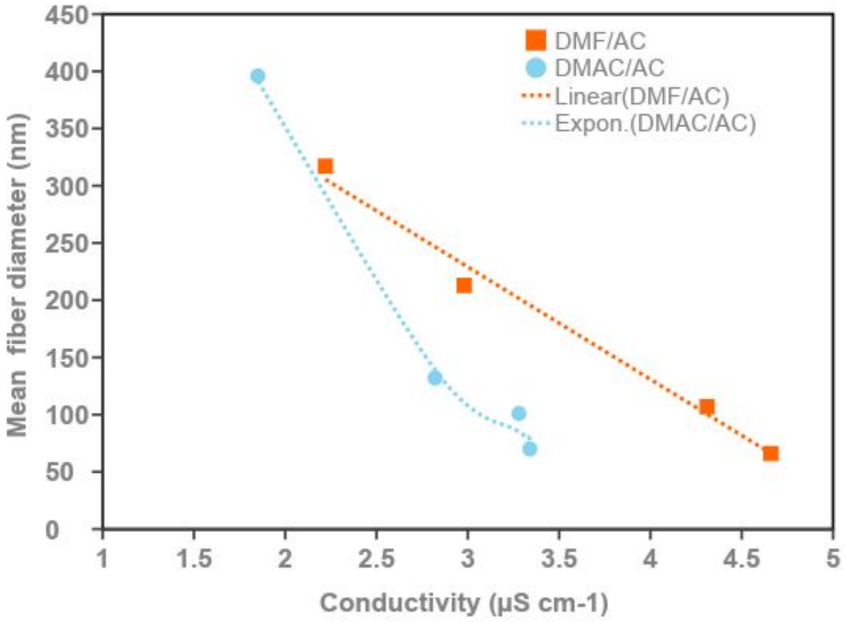
Solvents	Electrospinnability	Morphology	Mean fiber diameter (nm)
Acetone	-	Beaded nanofiber	929±670
Chloroform (CHL)	-	Beads only	N/A
Dimethylformamide (DMF)	+	Beads only	N/A
Dimethylacetamide (DMAc)	+	Beads only	N/A
DMF/Acetone 5:5	+	Beaded nanofiber	122±28
DMAc/ Acetone 5:5	+	Beaded nanofiber	117±34

Solvent Ratio

Solvents	Ratio	Electro-spinnability	Morphology	Conductivity (μS cm^{-1})	Vapour Pressure (Pa)	Mean fiber diameter (nm)
DMF/ AC	8:2	+	Beads only	4.66	7141	66±20
	6:4	+	Beaded nanofiber	4.31	13712	107±60
	5:5	+	Beaded nanofiber		16814	122±28
	4:6	+	Beaded nanofiber	2.98	20013	213±60
	2:8	-	Nanofiber	2.22	26286	317±184
DMAc/ AC	8:2	+	Beads only	3.34	7963	70±25
	6:4	+	Beaded nanofiber	3.28	14925	101±44
	5:5	+	Beaded nanofiber		18179	117±34
	4:6	+	Beaded nanofiber	2.82	21277	132±72
	2:8	+	Nanofiber	1.85	27098	396±240

Solvent Ratio





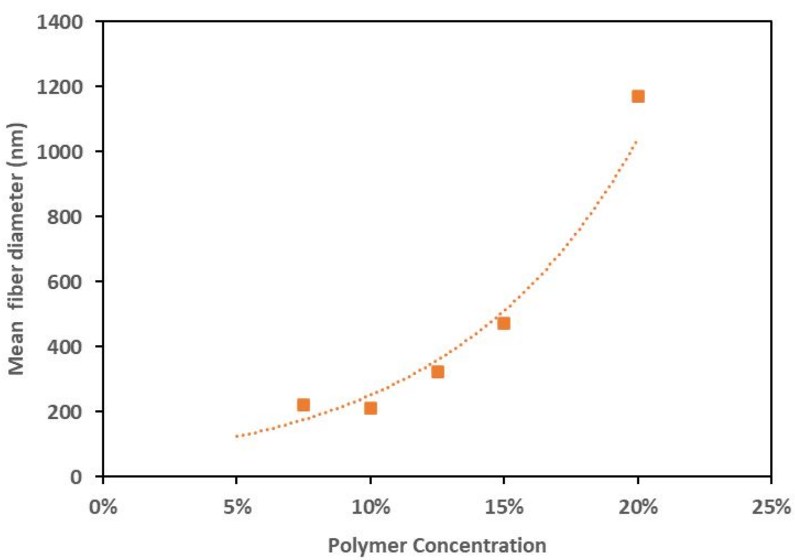
- **Mean fiber diameter increases with vapor pressure and decreases with conductivity**

Polymer Concentration

Polymer Concentration (w/v)	Electro-spinnability	Morphology	Conductivity (μS cm^{-1})	Viscosity (mPa.s)	Mean fiber diameter (nm)
5%	+	Beads only	2.42	/	N/A
7.5%	+	Beaded nanofiber	3.25	91	221±120
10%	+	Beaded nanofiber	/	98	213±60
12.5%	+	Nanofiber	3.34	213	325±106
15%	-	Nanofiber	3.59	383	473±310
20%	-	Defect-free nanofiber	3.70	1488	1172±752

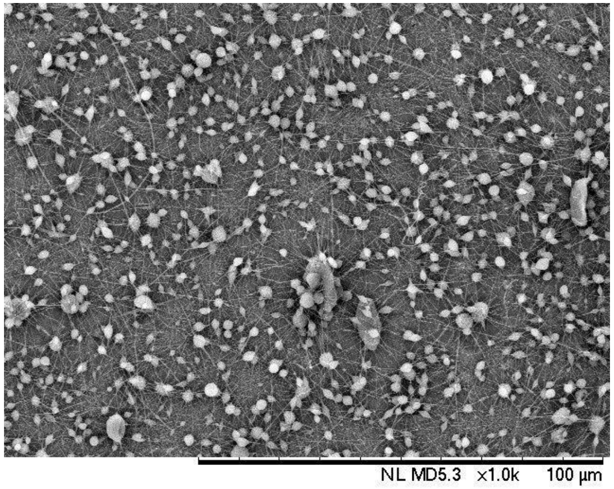
As polymer concentration increases, the viscosity of the solution increases

- *Mean fiber diameter increases*
- *Increased stuttering of the jet and drying at needle tip, stable electrospinning obtained up to 12.5% (w/v)*



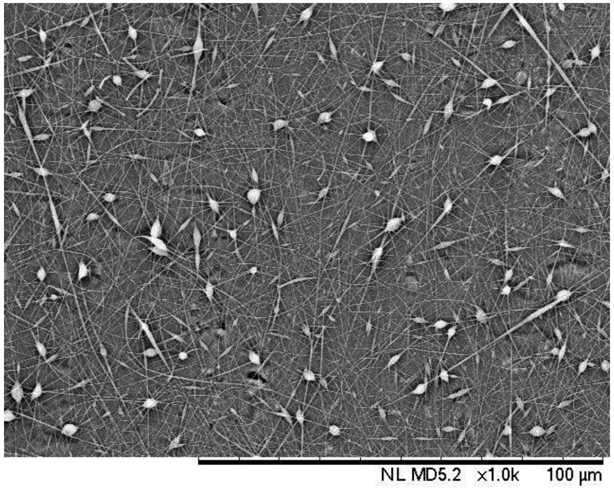
SEM Morphology (Polymer Concentration)

5%



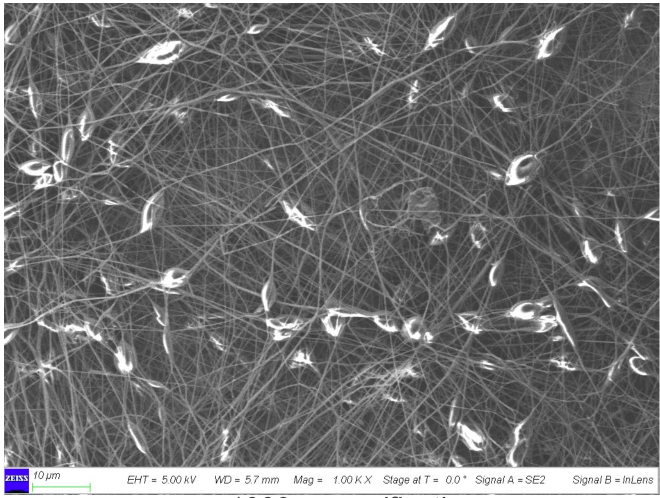
1000x magnification

7.5%



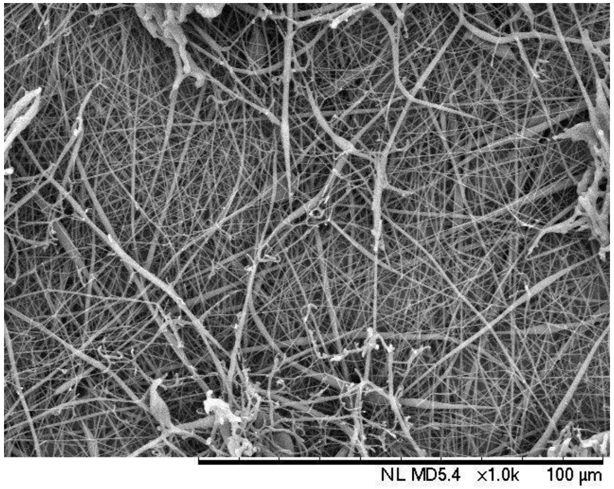
1000x magnification

10%



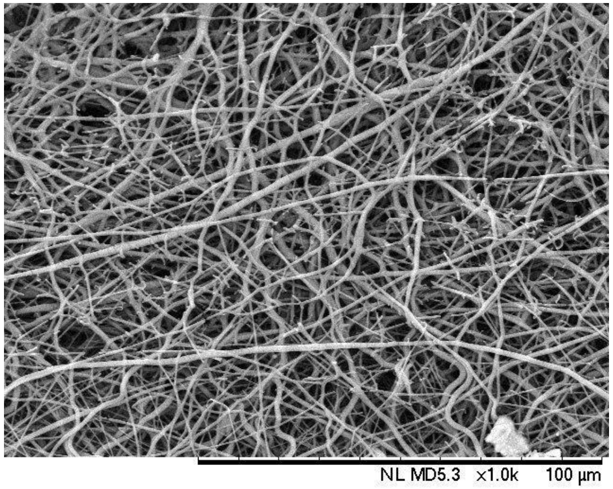
1000x magnification

12.5%



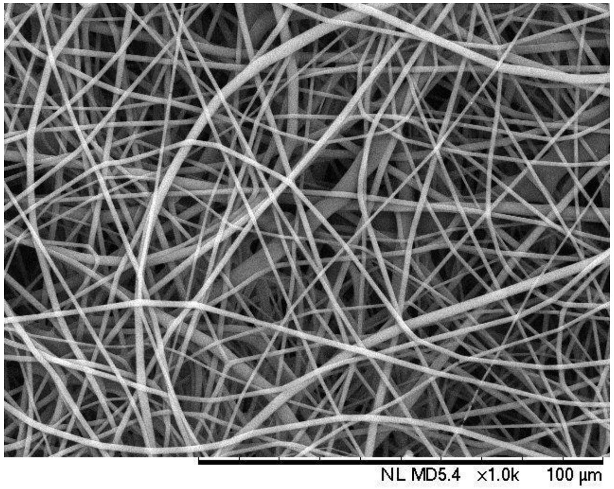
1000x magnification

15%



1000x magnification

20%

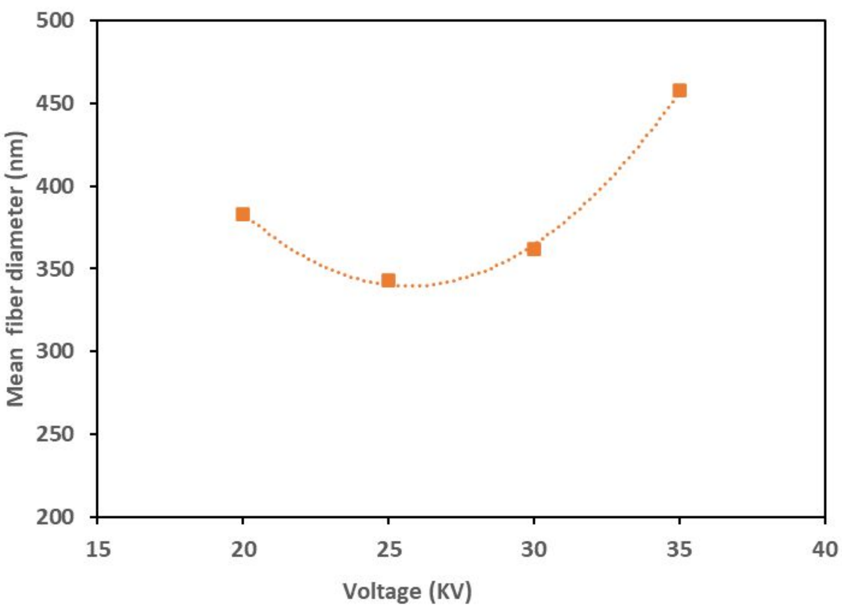


1000x magnification

Electrospinning Voltage

Electrospinning voltage (KV)	Electrospinnability	Morphology	Mean fiber diameter (nm)
15	-	No fiber	N/A
20	+	Nanofiber	383 ± 144
25	+	Defect-free nanofiber	343 ± 145
30	+	Defect-free nanofiber	362 ± 178
35	+	Fragmented nanofiber	458 ± 239

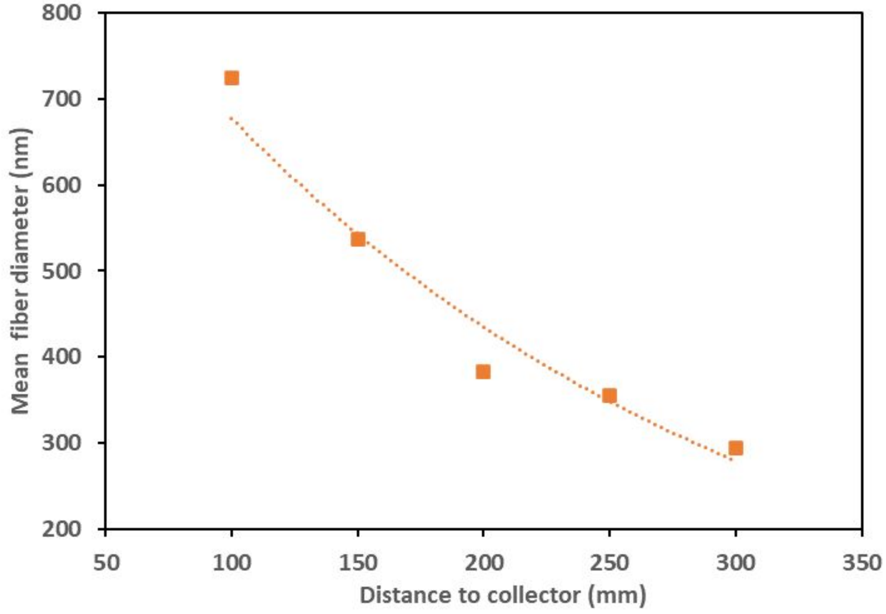
- *At lower voltage (i.e. <20KV): Stretching forces of jet is insufficient to form NF, leading to direct dripping of polymer solution*
- *As voltage increases(15 KV to 30KV), viscoelastic force increases, leading to defect-free nanofiber with lower diameter*
- *Further increase in voltage (>30KV), causes NF fragmentation, increased diameter and variation*



Distance to Collector

Distance to collector (mm)	Electrospinnability	Morphology	Mean fiber diameter (nm)
100	+	Beaded, fragmented nanofiber	724 ± 310
150	+	Beaded, fragmented nanofiber	537 ± 284
200	+	Nanofiber	383 ± 144
250	+	Beaded nanofiber	355 ± 158
300	+	Beaded nanofiber	294 ± 160

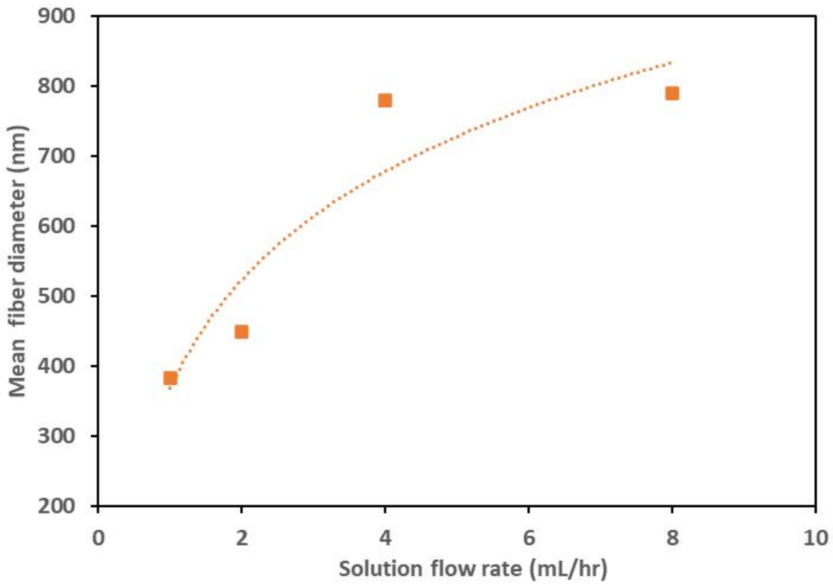
- *Stable and uniform jet observed for distance to collector (100-300mm)*
- *At shorter distances (i.e. 100-150mm), jet has insufficient stretching time, leading to fragmented nanofibers with increased diameter and variation*
- *At longer distances (i.e. 250-300mm), long stretching time lead to lower diameter but increased bead formation*



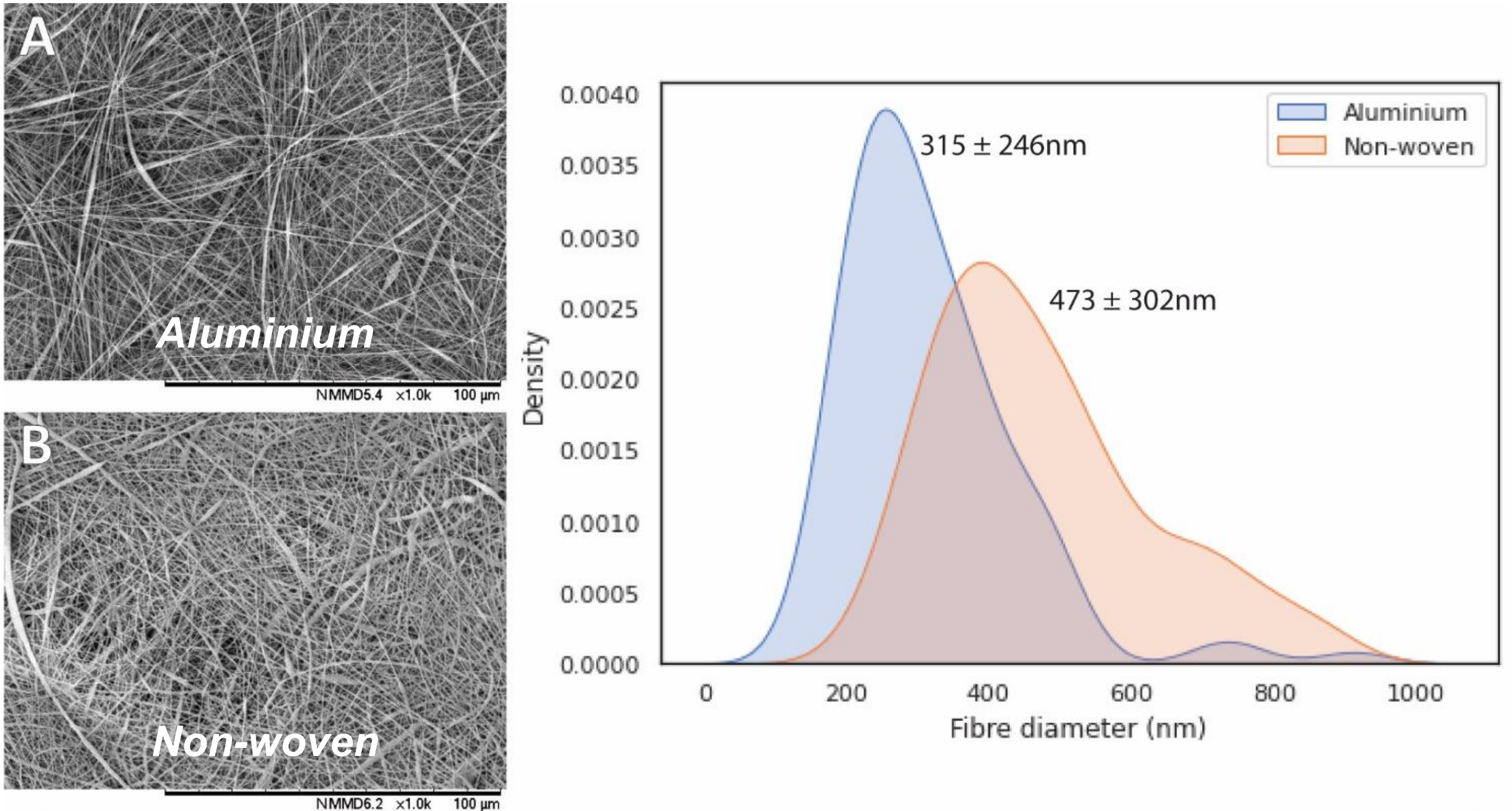
Electrospinning Flow Rate

Solution flow rate (mL/hr)	Electrospinnability	Morphology	Mean fiber diameter (nm)
1	+	Nanofiber	383 ± 144
2	+	Beaded nanofiber	448 ± 238
4	+	Beaded, fragmented nanofiber	780 ± 522
8	+	Beaded, fragmented nanofiber	790 ± 660

- *Stable and uniform jet (no dripping) observed for flow rates (1-8mL/hr)*
- *Flow rate: 1mL/hr best observed morphology and fibre diameter*
    - *Increasing flow rate leads to increased fragmentation, beads and high variation in fibre diameter*

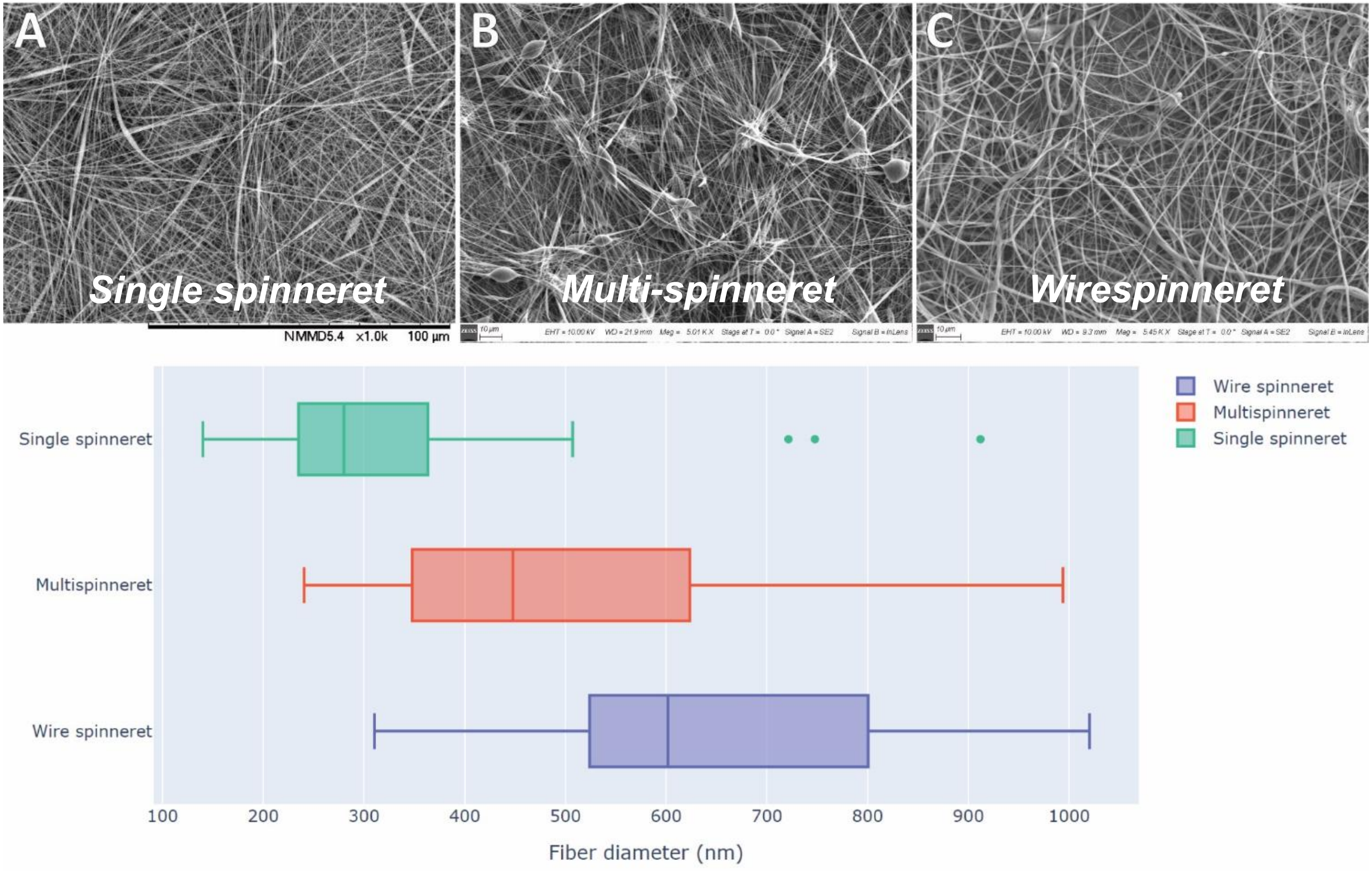


Electrospun substrate for Fiber Deposition



Nanofiber deposited on non-woven substrate had significantly increased mean fiber diameter and distribution when compared to nanofiber deposited on aluminum foil, usually by a range of 30-50%

Electrospinning Techniques



Summary

- **Parameters identified to favour continuous and uniform electrospinning and nanofiber formation:**
  - Polymer solvent: DMF/acetone (4:6 v/v)
  - Polymer concentration: 12.5%
  - Electrospinning flow rate: 1mL/hr
  - Electrospinning voltage: 25-30kV
  - Electrospinning needle to collector distance: 250-300mm

Acknowledgements

- Project Coordinator:
  - Dr. Carol Sze Ki Lin (City University of HK)
- Team Members:
  - Dr. Bhaskar Jyoti Deka (IIT)
  - Dr. Shauhrat Chopra (City University of HK)
  - Dr. Chi Yan Tso (City University of HK)
  - Dr. Walid Daoud (City University of HK)
  - Dr. Tin Lau (NAMI)

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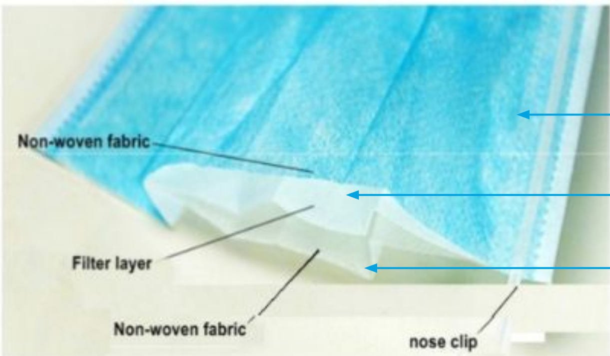
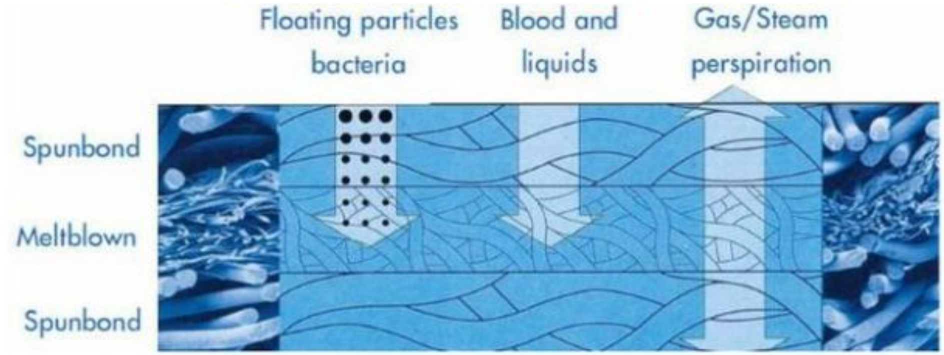
Difficulty of Food Waste-Derived PPE

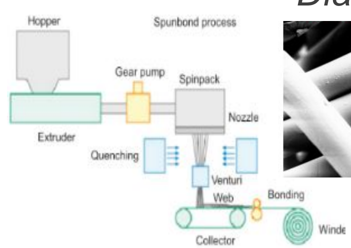


Outer
Middle
Inner



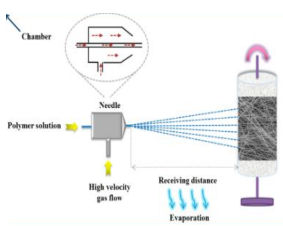
SMS layer for typical face mask composition

Spunbond

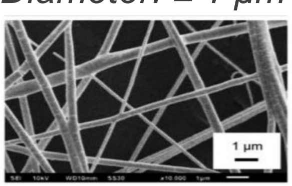


Diameter: 15 μm

Electrospinning



Diameter: ≤ 1 μm



Material	Melt Flow Rate (g/10 min)
PP	~1,500 (high accuracy & quality)
PLA/ PHBV	15 - 20

- *Extremely* ***LOW*** *MFR limits the quality and process accuracy of PLA / PHBV non-woven textile*
- *Electrospinning can effectively replace meltblown process for middle filtration layer*

Appendix: Biodegradable Certificates & Standards

Certificates	Standard methods
EN 13432/ASTM D6400 Standard Specification for Labeling of Plastics Designed to be Aerobically Composted in Municipal or Industrial Facilities **≥ 90% biodegraded within 180 days**	**ASTM D5511** Standard Test Method for Determining Anaerobic Biodegradation of Plastic Materials Under High-Solids Anaerobic-Digestion Conditions
ASTM D 6866 Standard Test Methods for Determining the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis **≥ 20% of biobased material**	**ASTM D 5526** Standard Test Method for Determining Anaerobic Biodegradation of Plastic Materials Under Accelerated Landfill Conditions

Appendix: Surgical Mask Standard (ASTM F2100)

Properties	Test Method	Meaning	Level 1 Barrier (*Target for general use*)	Level 2 Barrier	Level 3 Barrier
BFE (%)	ASTM F2101	Bacterial Filtration Efficiency - % of particles filtered out at particle size of 3 μm	≥95	≥98	≥98
PFE (%)	ASTM F2299	Sub-micron particulate filtration efficiency - % of particle filtered out at a particle size of 0.1 μm	≥95	≥98	≥98
Fluid resistance (mmHg)	ASTM F1862	Resistance to penetration by synthetic blood at different blood pressure (Pass/fail)	80	120	160
Differential pressure (mm H_2O/cm^2)	Military Standard MIL-M-3695 4C	Pressure drop across mask, or resistance to air flow in Greater resistance = better protection but less breathability	<4.0	<5.0	<5.0
Flame Spread	Federal standard 16 CFR 1610	Measures the flame spread of the mask materials	Class 1	Class 1	Class 1

Appendix:Surgical Mask Standard (EN 14683)

Target for general use

Properties	Type 1	Type II	Type IIR
Bacterial Filtration Efficiency (BFE %)	≥95	≥98	≥98
Differential pressure (Pa/cm^2)	< 40	< 40	< 60
Splash resistance (kPa)	Not required	Not required	> 16
Microbial cleanliness	≤ 30	≤ 30	≤ 30