



超細纖維膜應用及發展

報告人：彭兆群
紡織產業綜合研究所

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一. 製造超細纖維膜的製程

二. 超細纖維膜的特性

三. 超細纖維膜的應用



應用

過濾 -

空氣

液體

生物製藥

醫療 -

傷口護理

組織工程

性能

高表面積

微小孔隙

高孔隙率

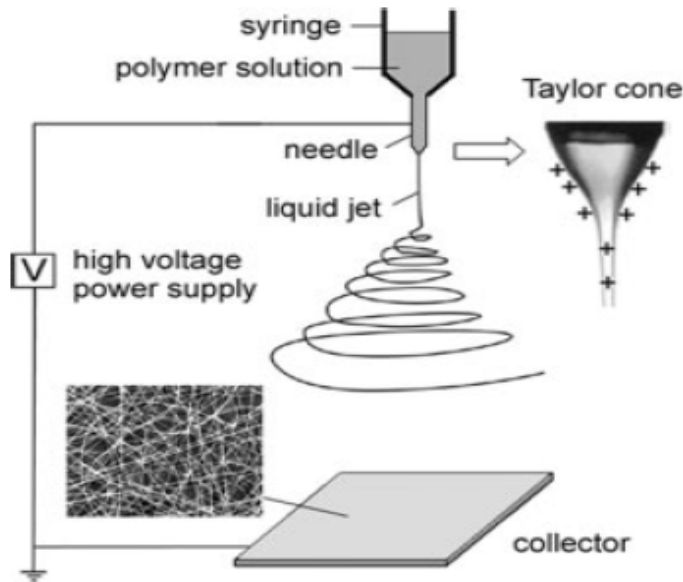
高吸附性

- 奈米： 10^{-9} m，微米： 10^{-6} m (micron or μm)
- 公尺： $1/10,000,000$ from equator to north pole
- Nanomaterial：at least 1 dimension of a material ≤ 100 nm according to US NSF
- Microfiber：fiber size $\geq$ near 1 micron
- Submicron fiber：fiber size $< 1\mu\text{m}$, $\geq 500\text{nm}$

- 電紡，Electrospinning (ES)
- 離心紡，Force spinning (FS)
- 溶噴紡，Solution blow spinning (SBS)
- 電噴紡，Electroblowing (EB)
- 複合紡，Islands in the sea, Segmented Pie, and side by side including SB and MB
- 紡黏不織布，Spunbonding (SB)
- 熔噴不織布，Meltblowing (MB)

一般而言，主要包含三個基本組成：

- 高壓電源
- 金屬噴嘴
- 收集器（接地導體）



頭髮
衣服
電紡

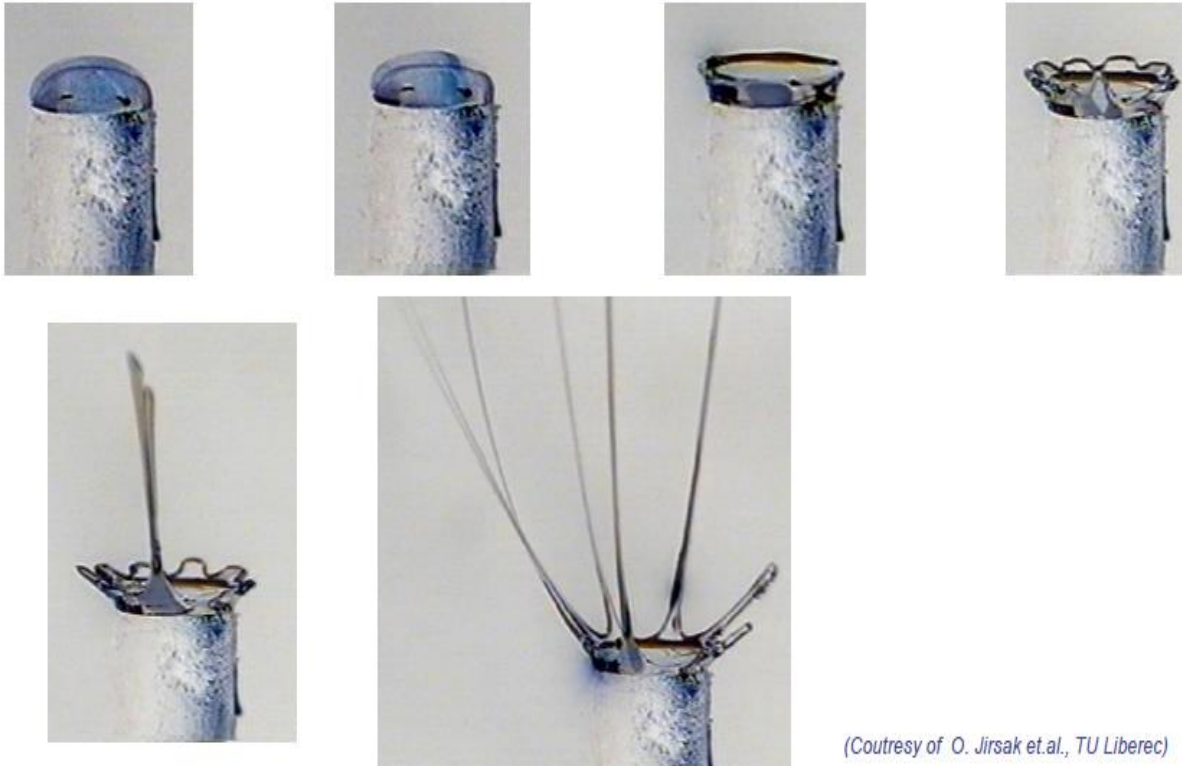
http://upload.wikimedia.org/wikipedia/commons/c/ca/Electrospinning_Diagram.jpg



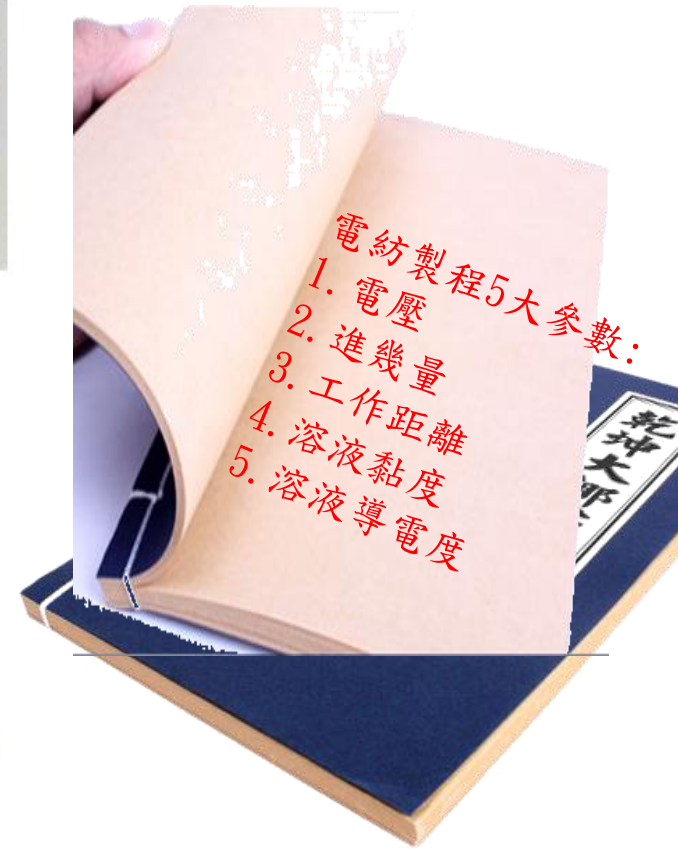
- 1902 J.F Cooley (U.S. Patent 692,631) and W.J. Morton (U.S. Patent 705,691).
- 1914 J. Zeleny, published work on the behavior of fluid droplets at the end of metal capillaries.
- 1934 to 1944 A. Formhals (U.S. Patent 1,975,504) to 1944 (U.S. Patent 2,349,950) for the fabrication of textile yarns.
- 1936 C.L. Norton (U.S. Patent 2,048,651) Melt Electrospinning.
- 1938 N.D. Rozenblum and I.V. Petryanov-Sokolov at the Karpov Institute in the USSR prepared filter materials from electrospun fibers known as "Petryanov filters". Work not well known in the West.
- 1939-1960's Petryanov filters were produced at Tver' for the manufacture of electrospun smoke filter elements for gas masks.
- 1964 to 1969 G. I. Taylor published a theoretical model describing the first stages of electrospinning.
- 1970's Some activities with commercial intent from a few companies as from patent activity, namely Bayer and Dupont .
- 1990's D. Reneker and others reinvigorated the research interest in electrospinning. Today hundreds of groups around the globe work on electrospinning.
- 2000's Several research groups published theoretical models for electrospinning (details ahead). A few companies set out to commercialize electrospun materials.
- 2005 Elmarco commercializes the first Electrospinning equipment

資料來源：NCRC

- 高分子溶液表面隨電場提高之變化

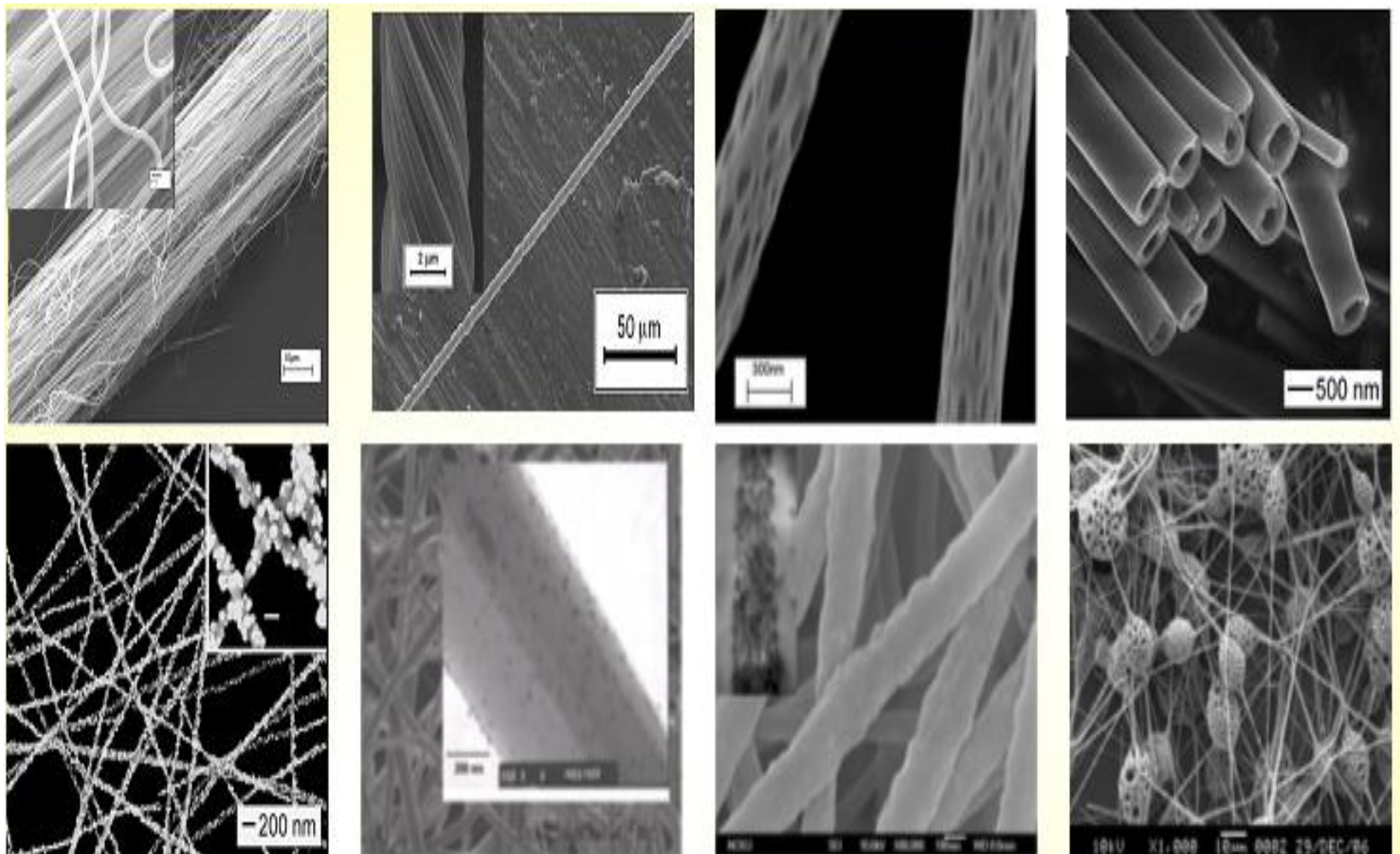


(Courtesy of O. Jirsak et al., TU Liberec)



電紡製程5大參數:
1. 電壓
2. 進幾量
3. 工作距離
4. 溶液黏度
5. 溶液導電度

- 靜電紡絲纖維型態



資料來源：MECC

- 材料多樣性

Organic

PA6

PA6/12

PAI (Polyamidimide)

PUR (Polyurethane)

PES (Polyethersulfone)

PVA (Polyvinylalcohol)

PAN (Polyacrylonitrile)

PEO (Polyethyleneoxide)

PS (Polystyrene)

PVDF (Polyvinylidenfluoride)

PVP (Polyvinylpyrrolidone)

PVP – I (Povidone-iodine)

Inorganic

TiO₂

SiO₂

SnO₂

WO₃

Al₂O₃

Li₄Ti₅O₁₂

Metallic

Pt

Cu

Mn

Biopolymers

Gelatine

Chitosan

Collagen

PAA (Polyaramide)

PVA (Polyvinylalcohol)

PLA (Polylactic acid)

PCL (Polycaprolactam)

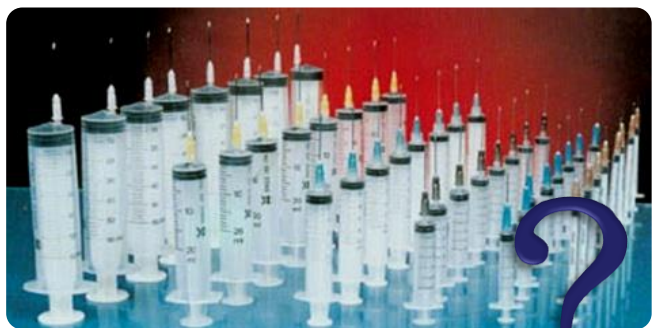


資料來源：Elmarco

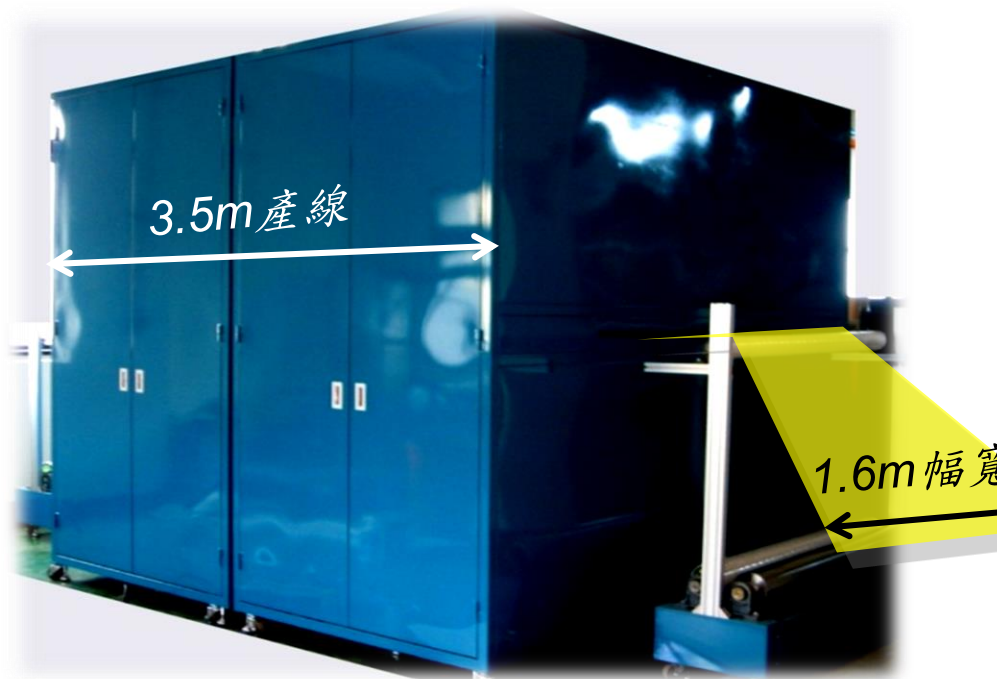
- ◎ 如何解決量化問題？
- ◎ 如何解決溶劑問題？
- ◎ 什麼應用非電紡奈米纖維不可？

◎電紡不織布（奈米纖維量產設備）

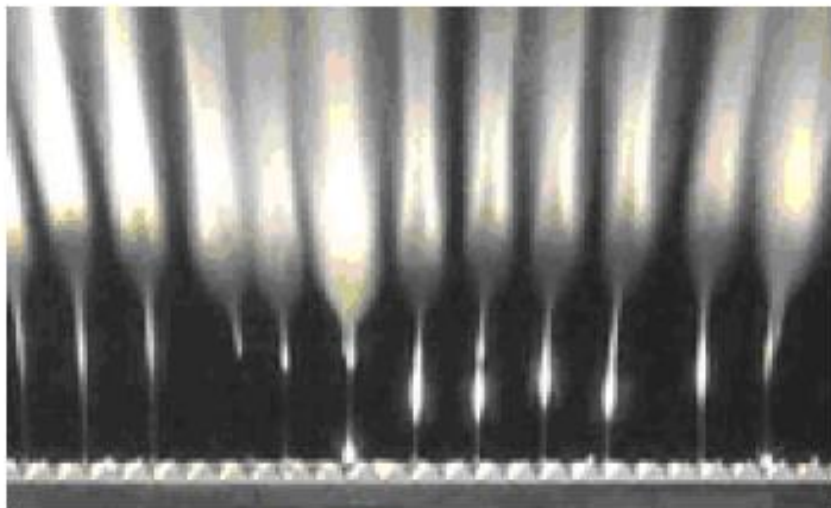
- 多針式（往覆移動）
- 無針式
- 羅拉式（螺旋式、狼牙棒、線式、印表機式）
- 離心式
- 泡泡電紡
- 溶噴電紡



如何解決量化問題



Nozzle based



Free liquid surface electrospinning of
Polyvinylalcohol
(Courtesy of David Lukas, Technical University of Liberec)

Nozzle-less



Rotating drum is dipped into a bath of liquid polymer. Thin layer of polymer is carried on the drum surface and exposed to a high voltage electric field. When the voltage exceeds the critical value E_c , a number of electrospinning jets are generated.



如何解決溶劑問題？

◎熔融電紡技術

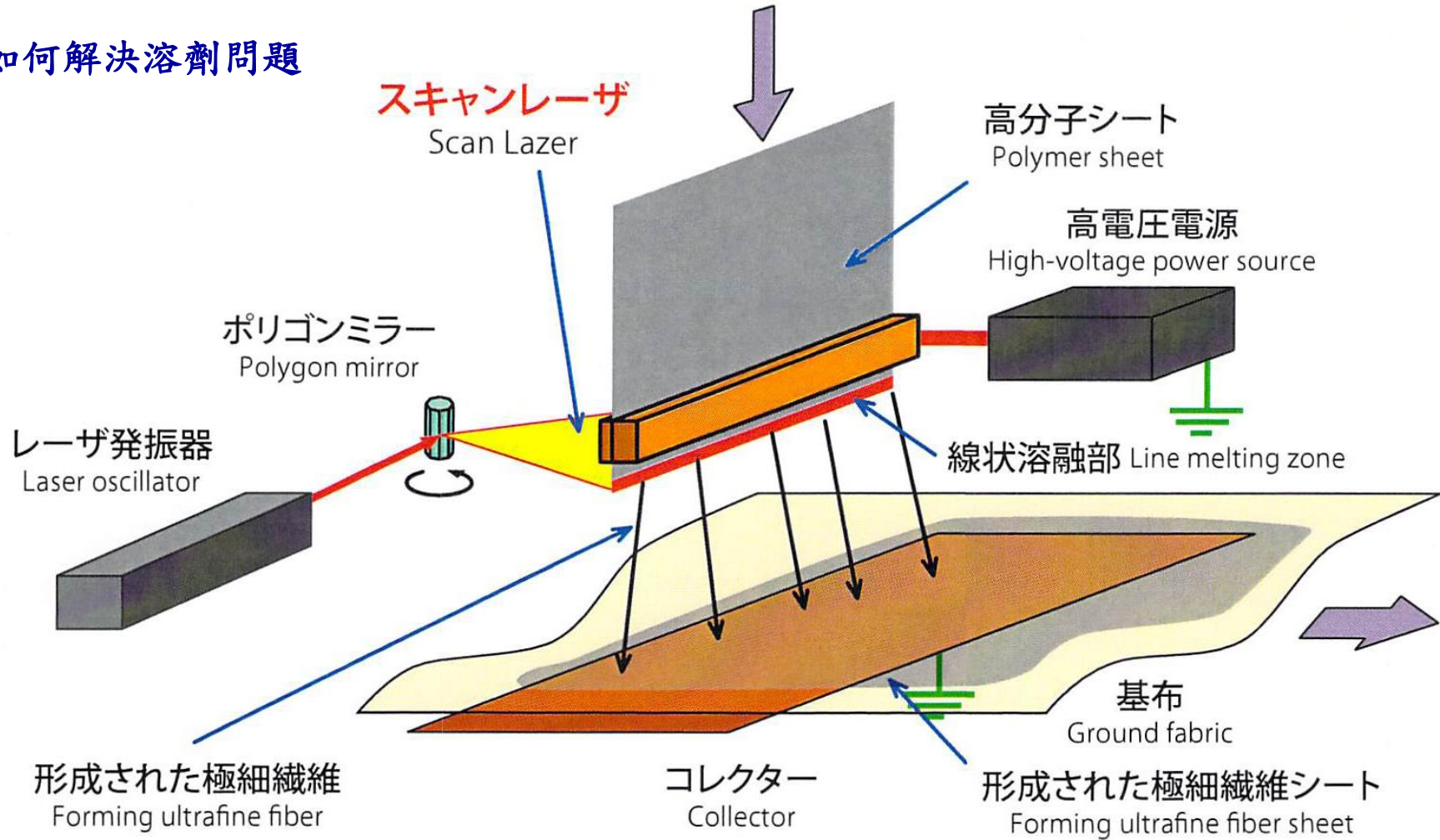
優勢

- 無溶劑使用
- 可處理難溶之高分子
 - PP、PE、PET…
- 可提高生產量

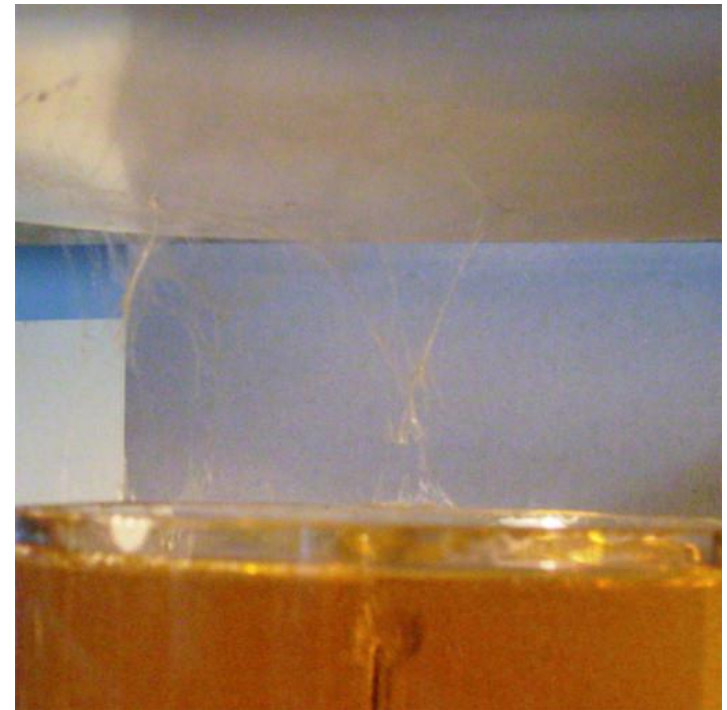
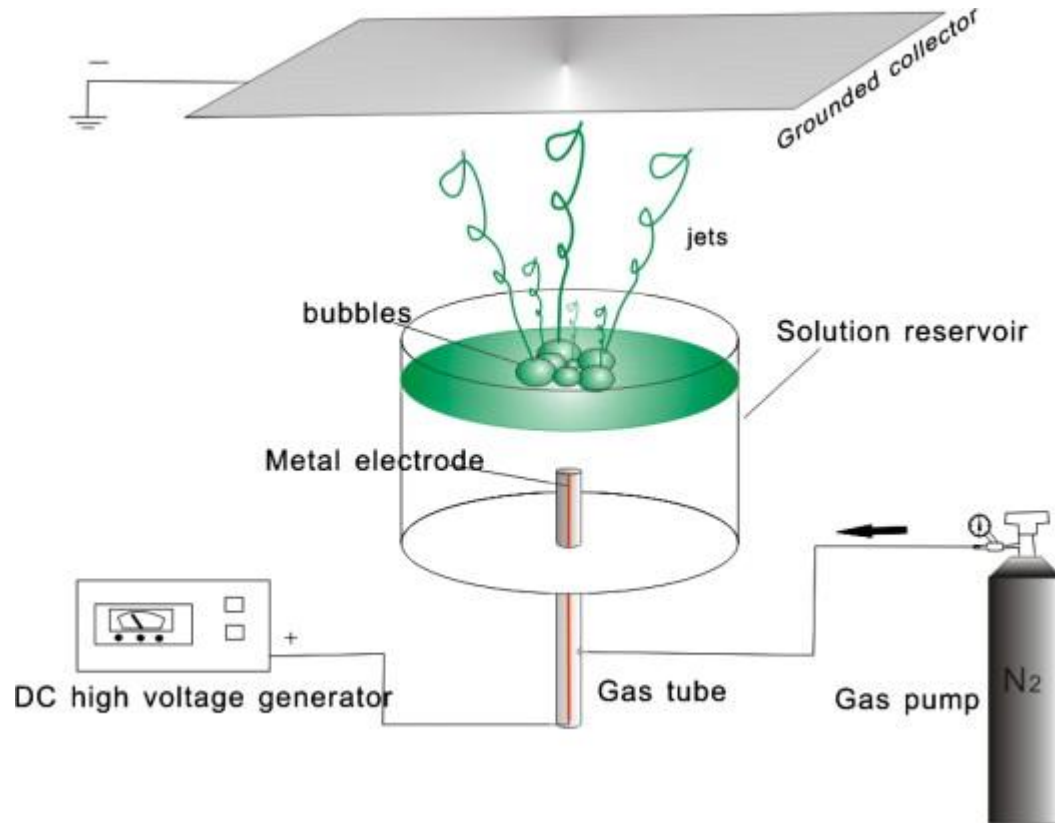
挑戰

- 對高分子原料的要求較高
 - 最適的熔融黏度
 - 最適的熔融傳導性或極性
- 絕緣及加熱

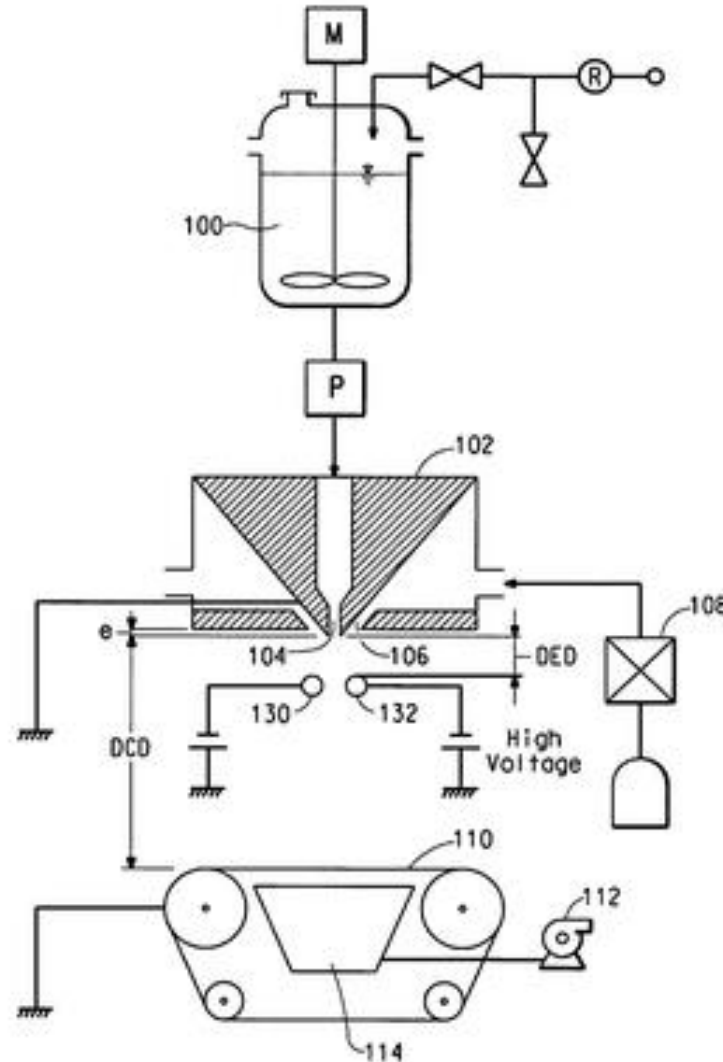
如何解決溶劑問題



Electrospinning



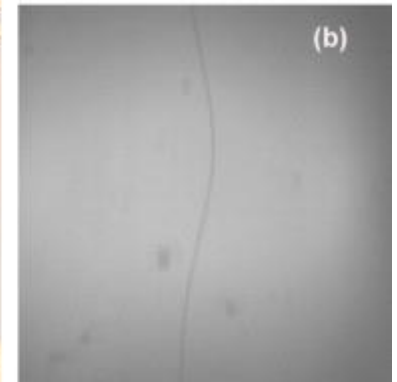
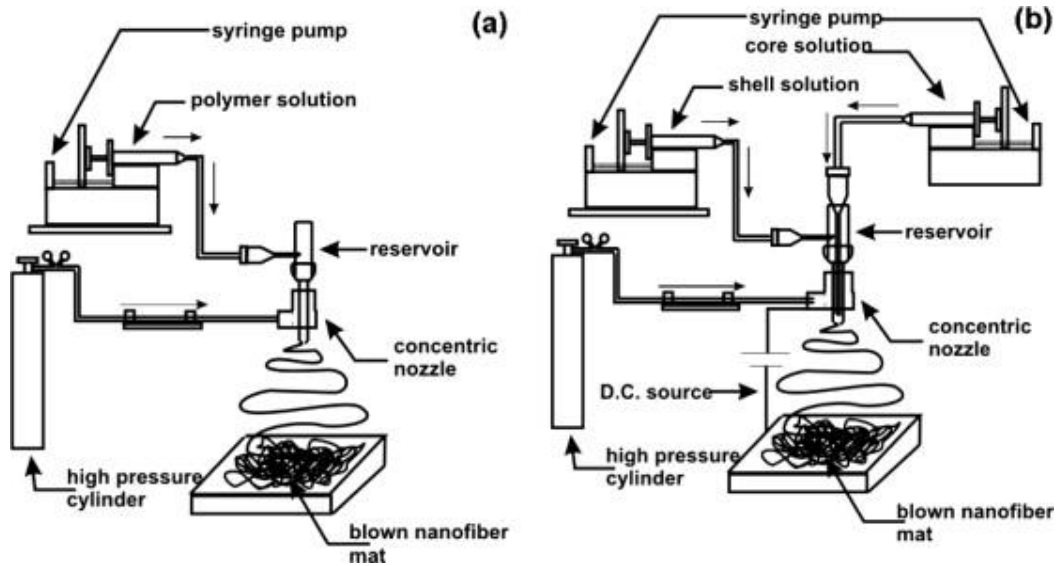
Electroblowing (EB)



US 7,931,456 B2

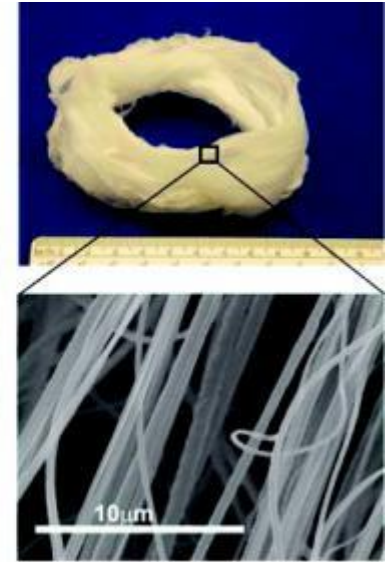
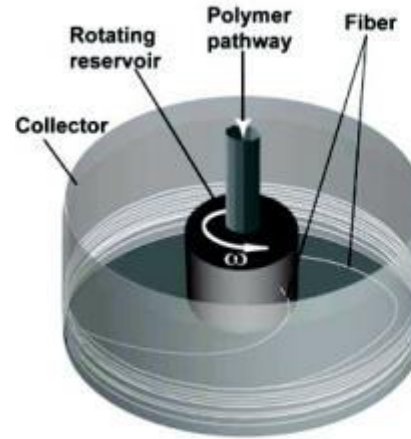
Electroblowing web formation

Solution blowing

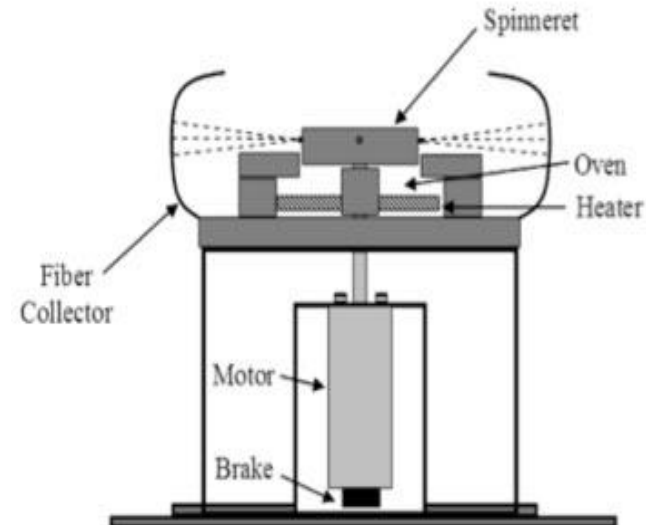


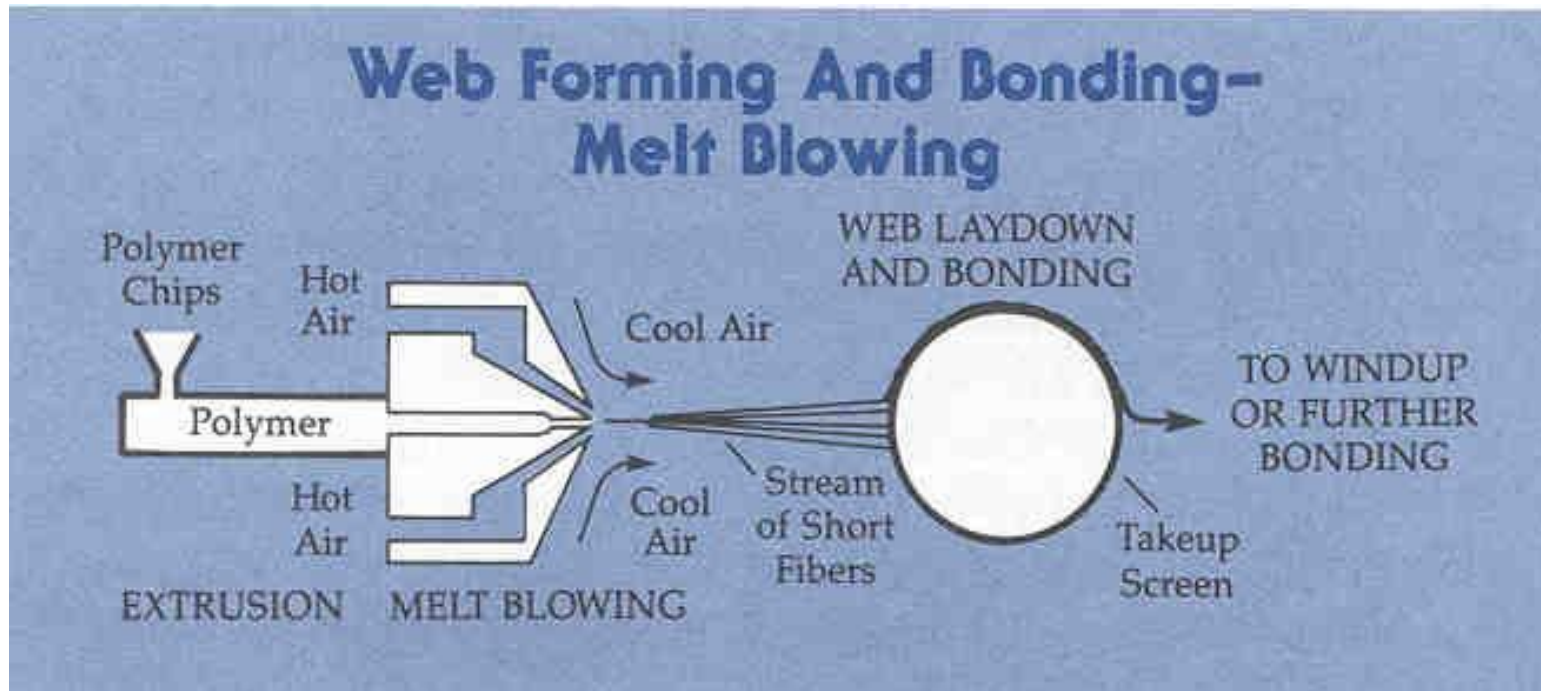
Force Spinning

- By using Centrifugal Force
- Both solutions and Melts
- No high voltage, no hot air
- **New Process – many unknowns**

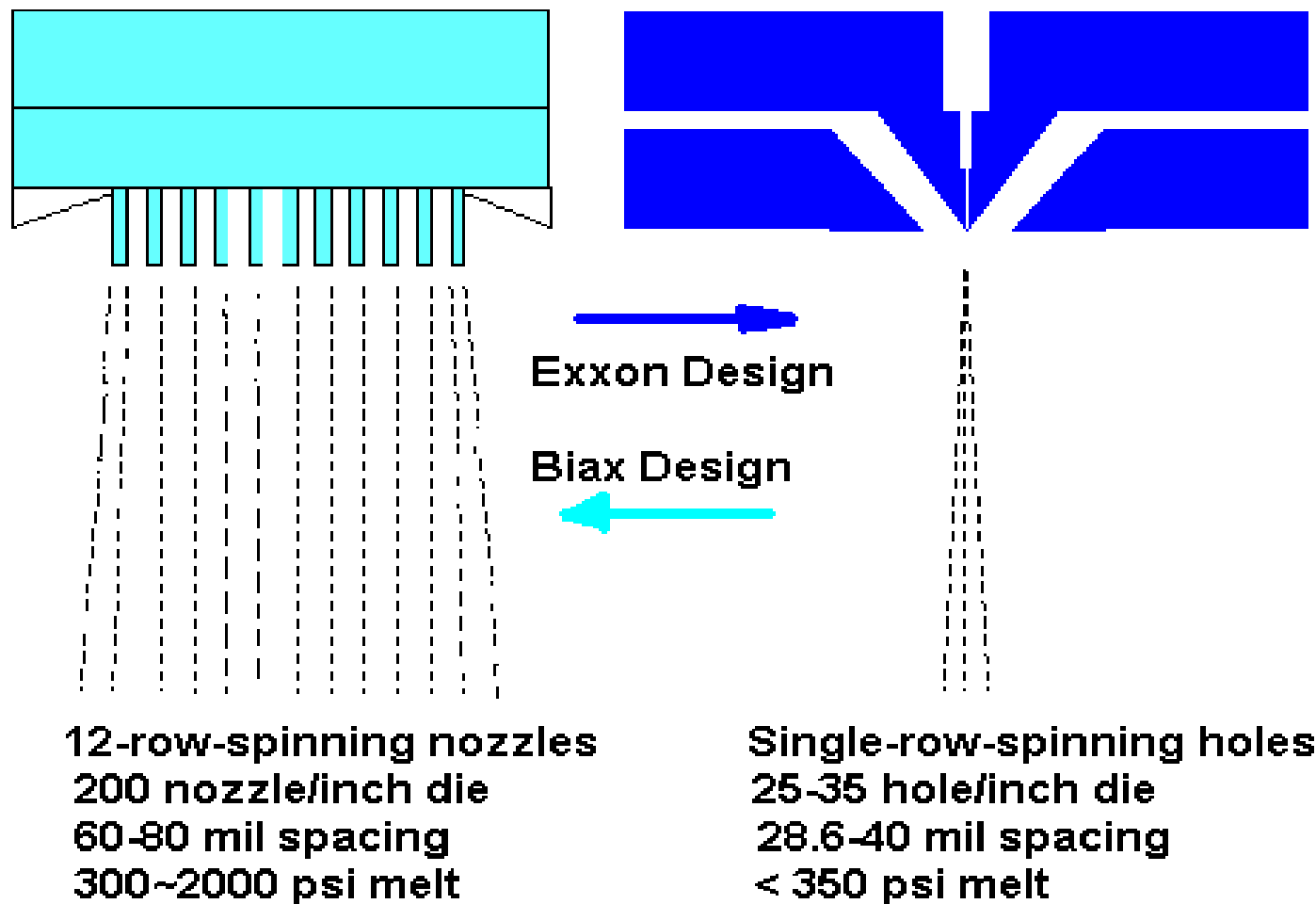


Rotary jet-spinning (RJS) process

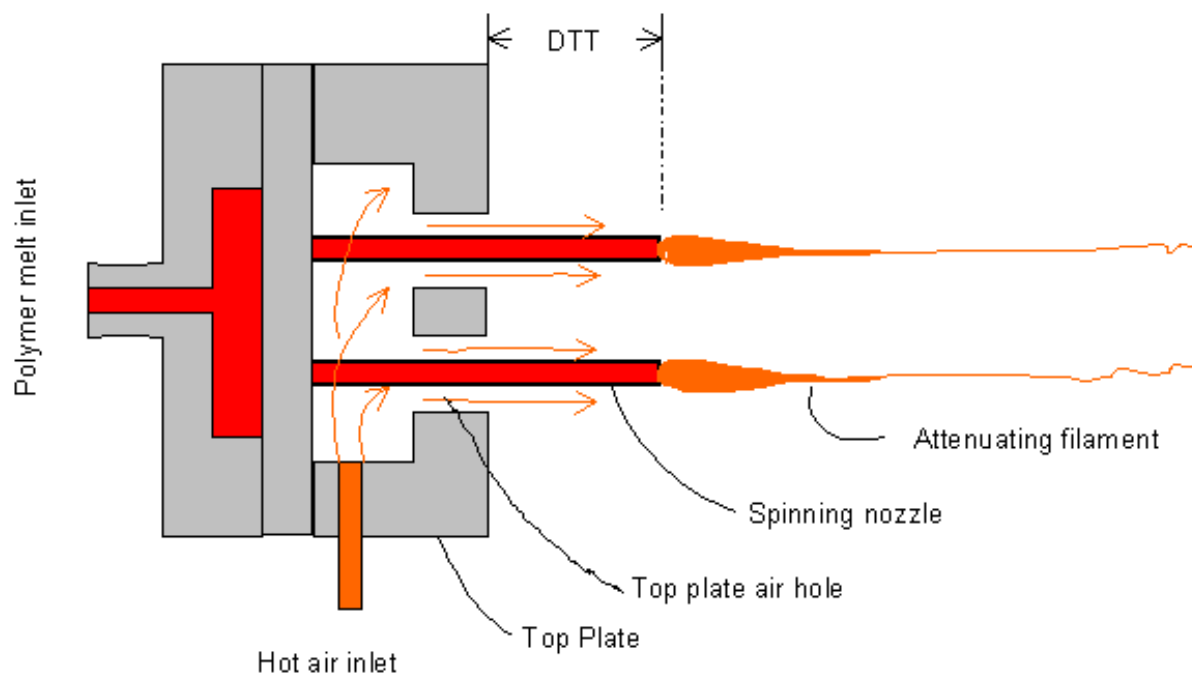




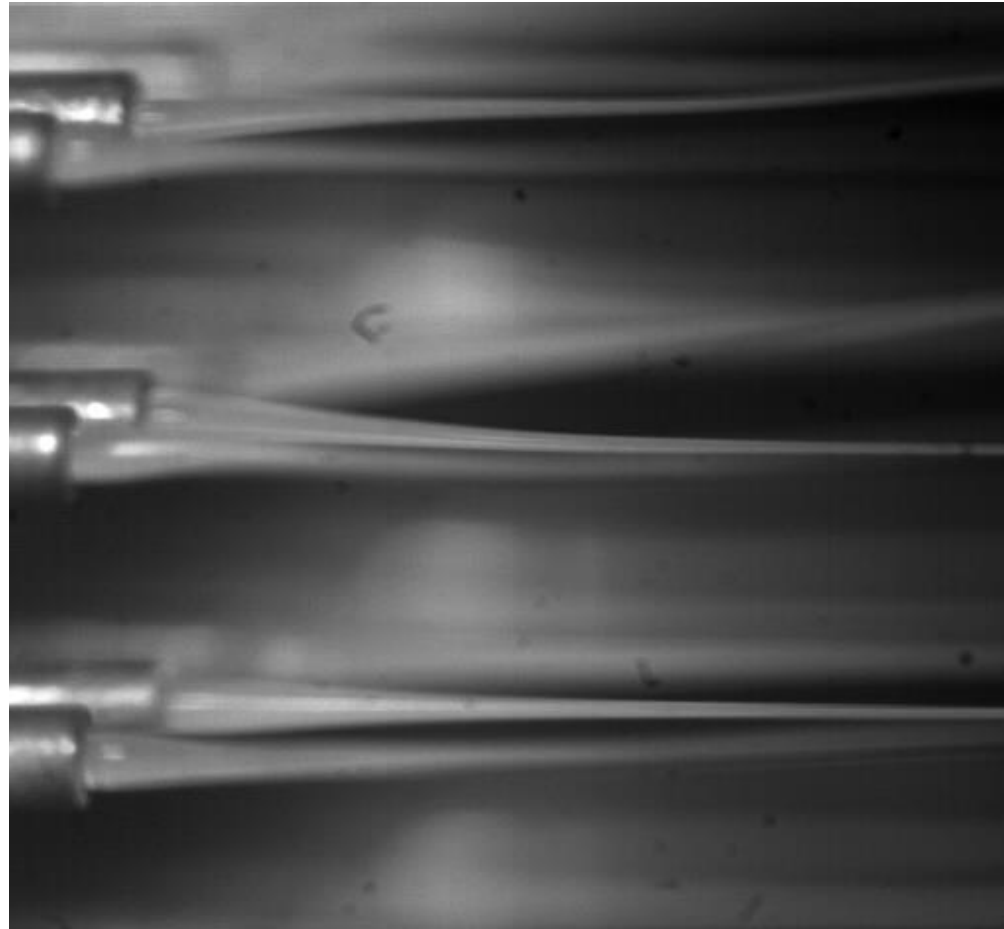
Meltblowing Dies



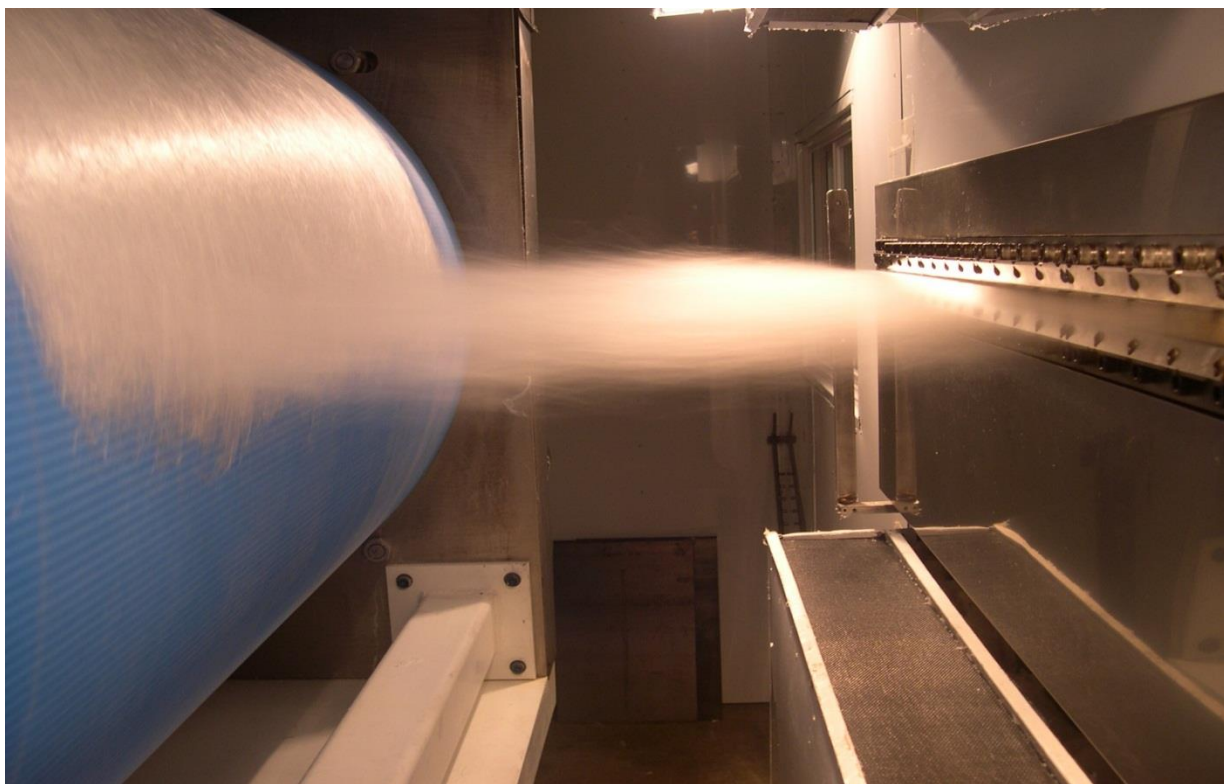
Biax Spinnerette原理



Biax Spinnerette原理

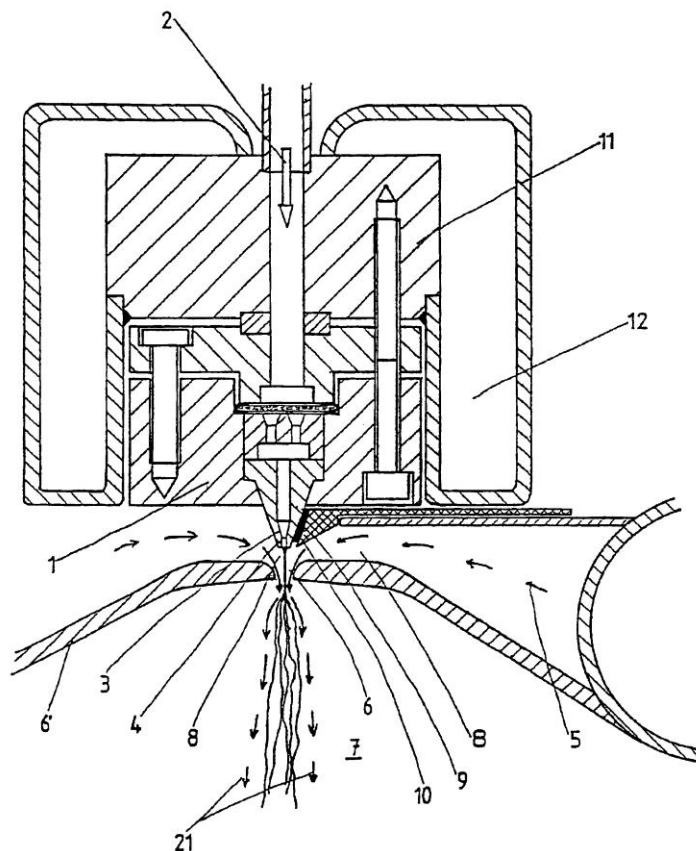


Biax 商業生產用



**100cm single drum collector with Biax
die/spinnerette system**

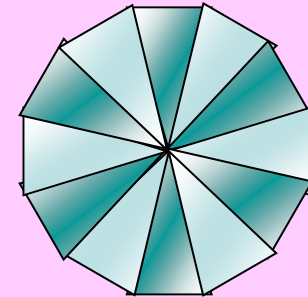
Method and device for the production of an essentially continuous fine thread United States Patent 6800226



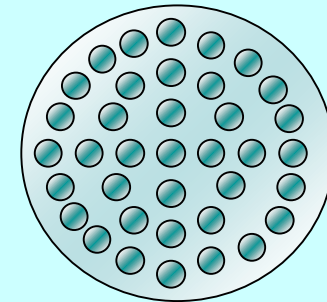
◎超細纖維（製作超細纖維之複合紡絲法）



分割型
Segment-Pie



海島型
Sea-Island



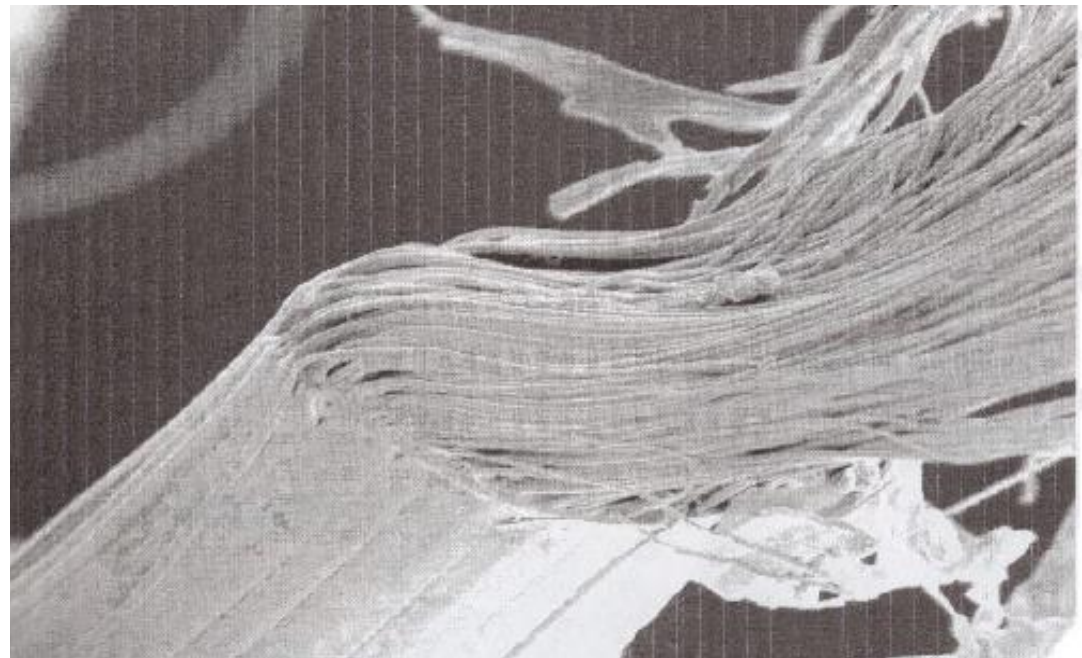
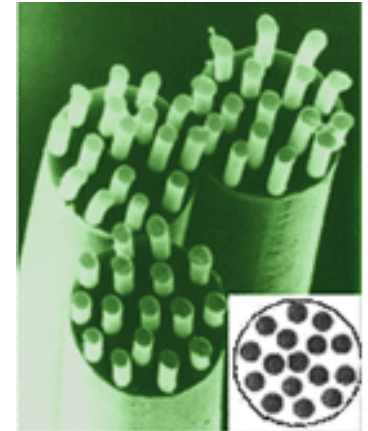
以此兩種為主要之紡口設計

◎超細纖維（複合型纖維超細化製程）

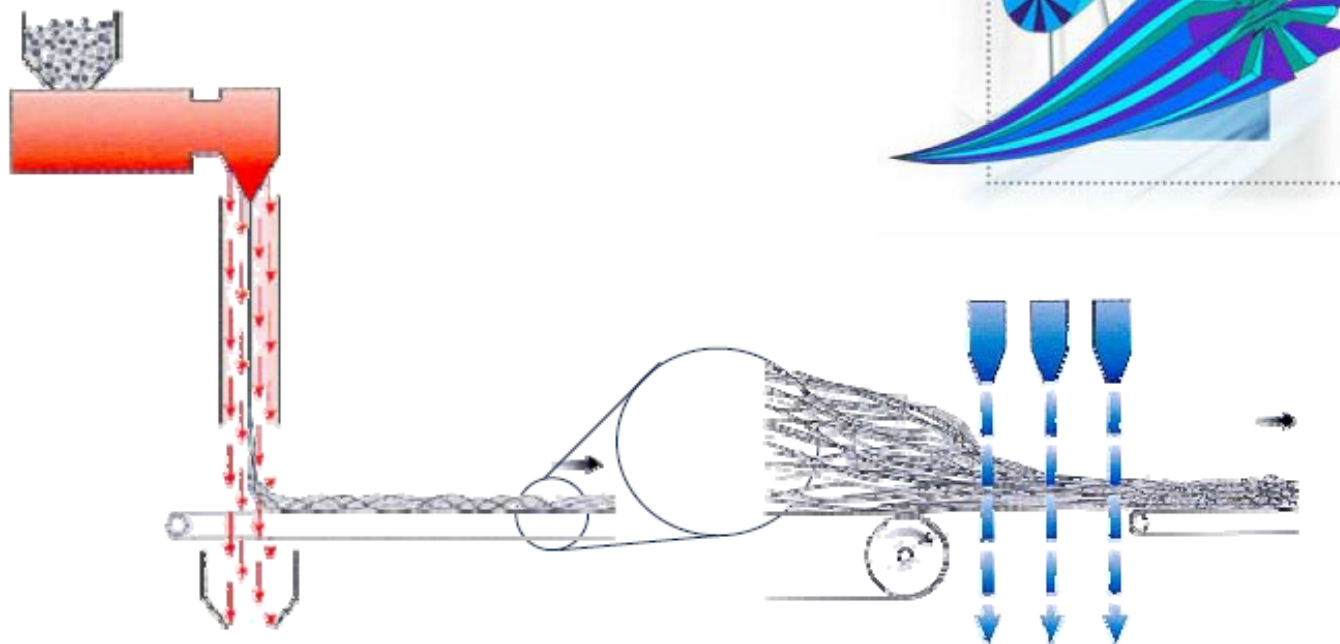
- 纖維直紡製程：0.3 de
- 透過複合紡絲：0.1 de 以下
- 利用不同材質特性，
設計加工方法使之分
裂成更細微的纖維

→ 機械法

→ 化學法



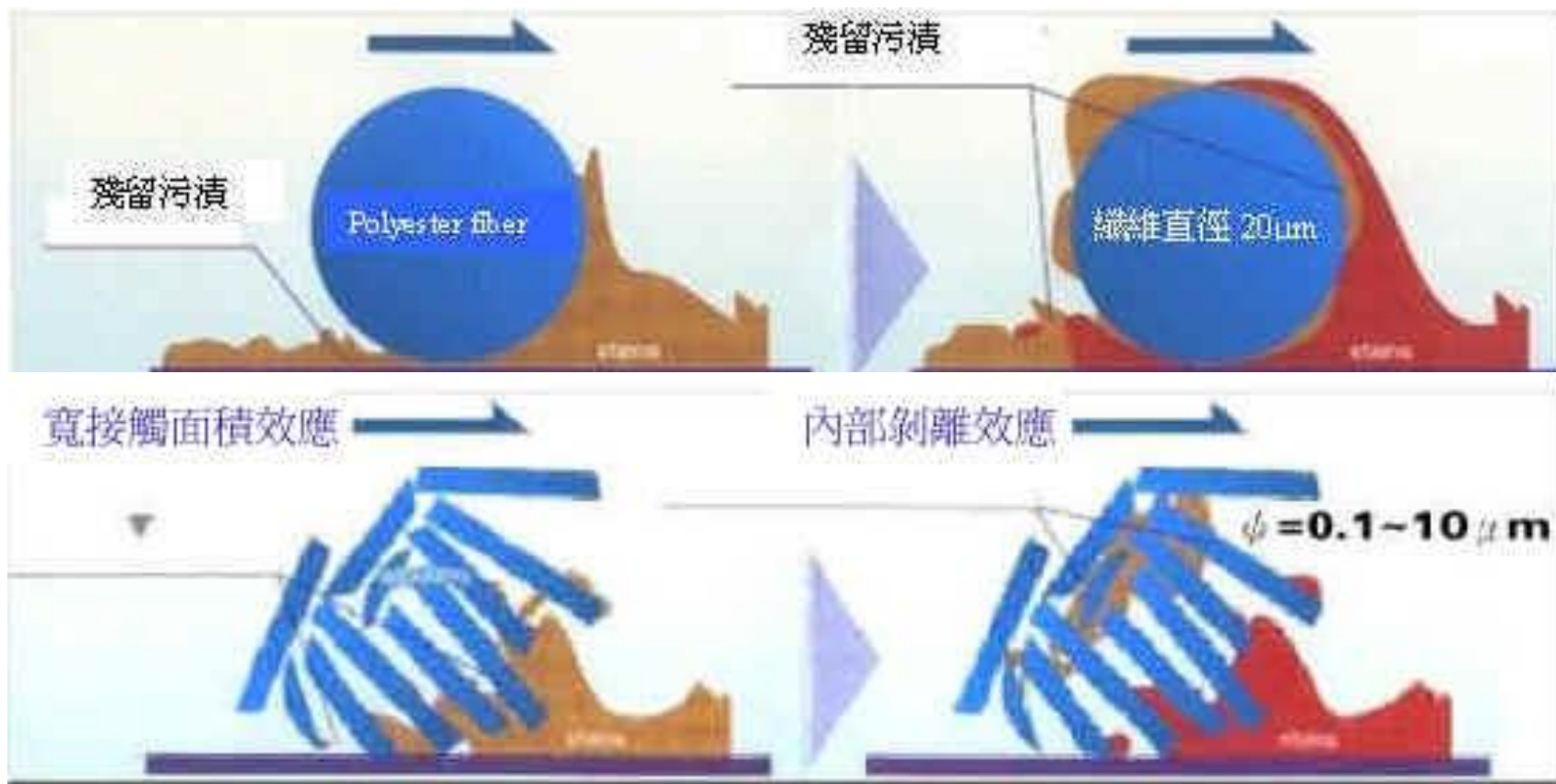
◎雙組份紡黏纖維不織布



microfilament fabrics

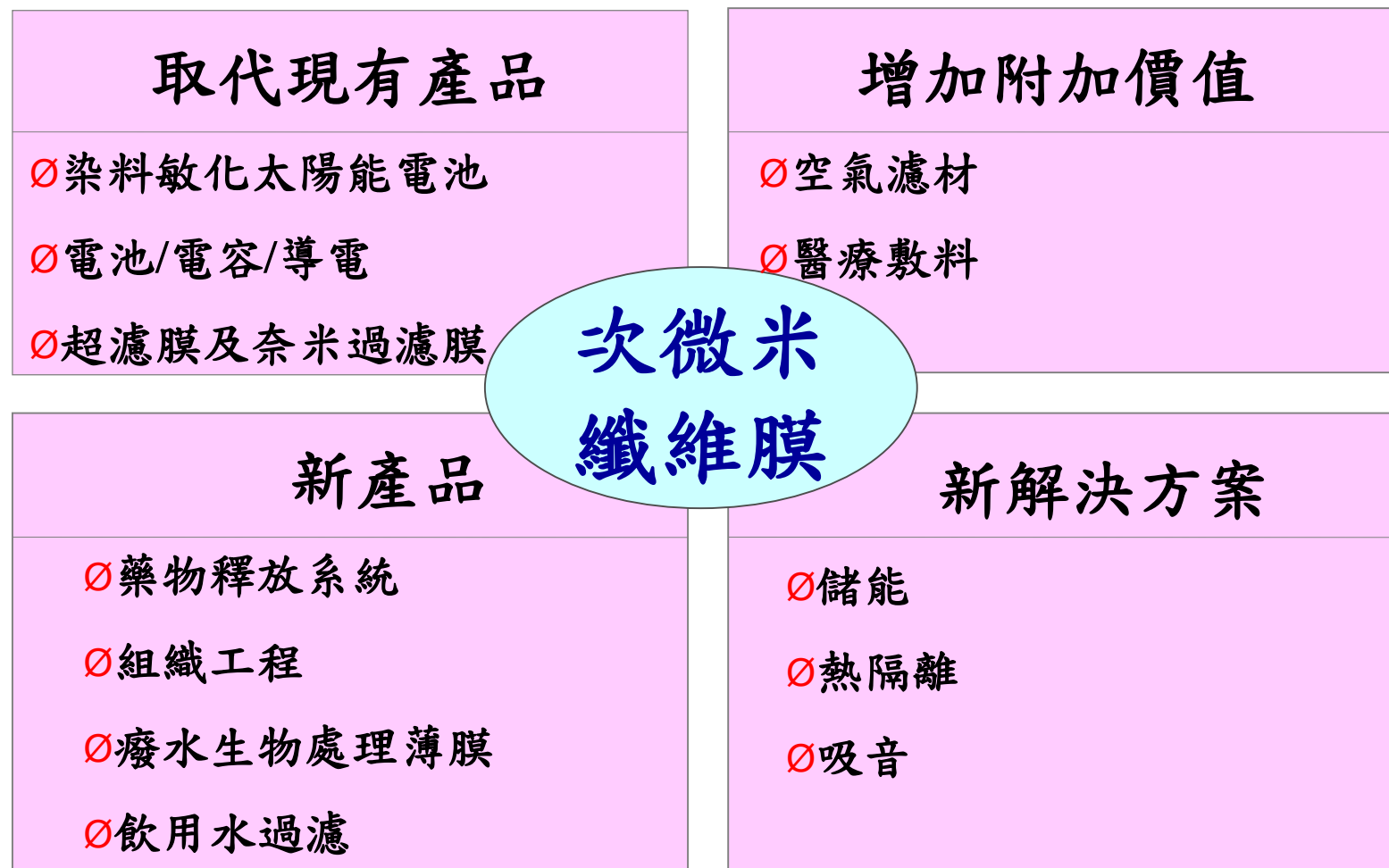
◎超細纖維特性與應用

無塵擦拭布

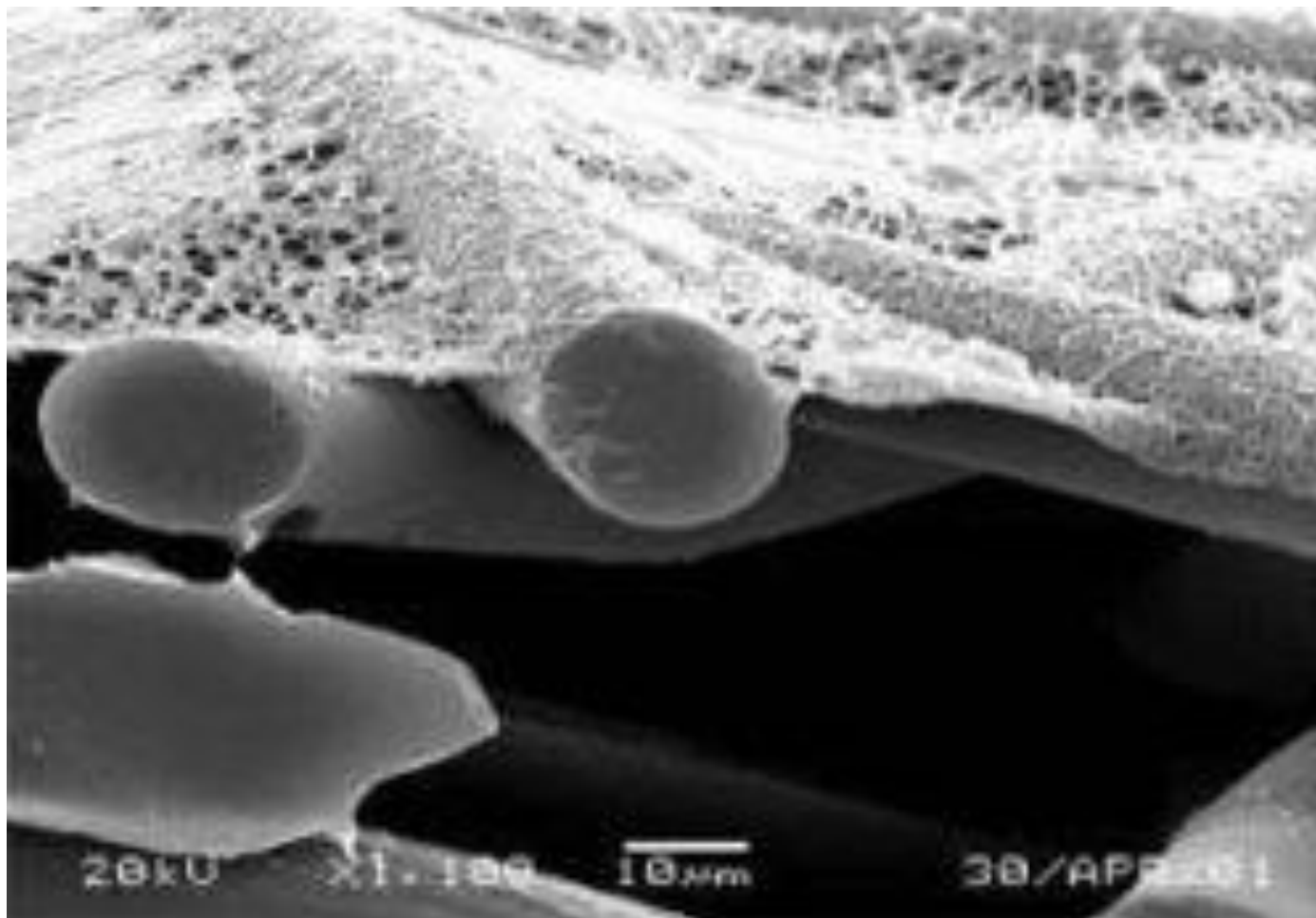


圖片來源：
Thompson網站

什麼應用非超細纖維膜不可？



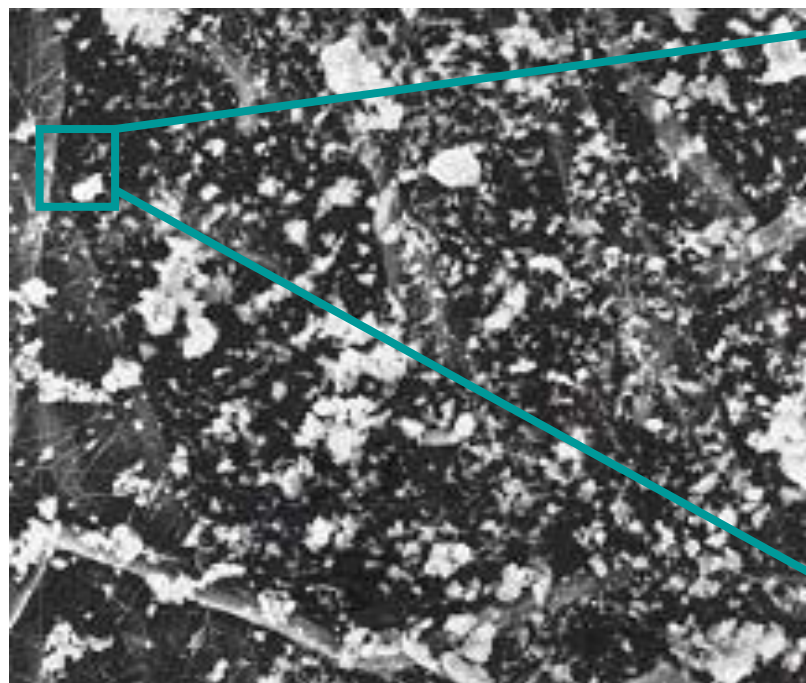
◎電紡不織布（HEPA 空氣過濾材）



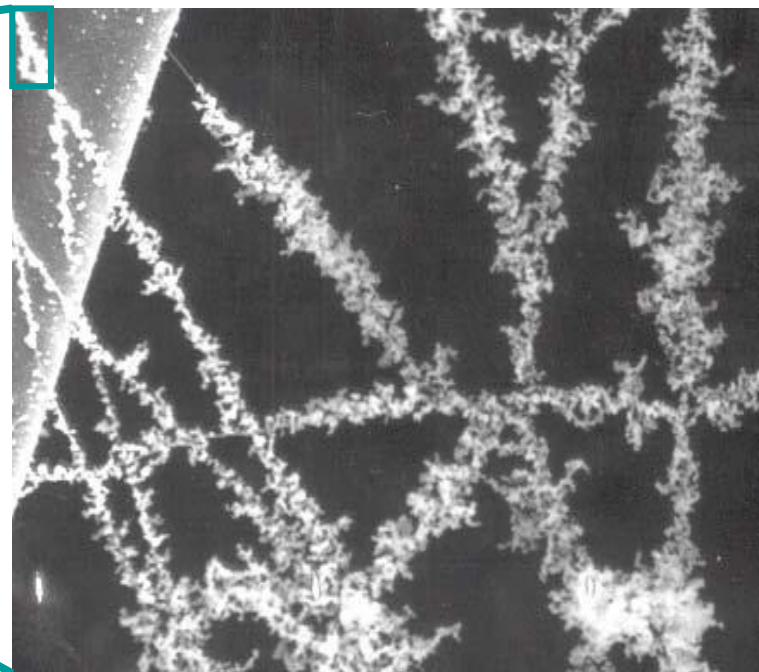
<http://www.donaldson.com/en/index.html>

◎電紡不織布（HEPA 空氣過濾材）

細微粉塵大部分受到奈米纖維過濾材的攔阻



奈米纖維複合過濾材粉塵過濾效果呈現



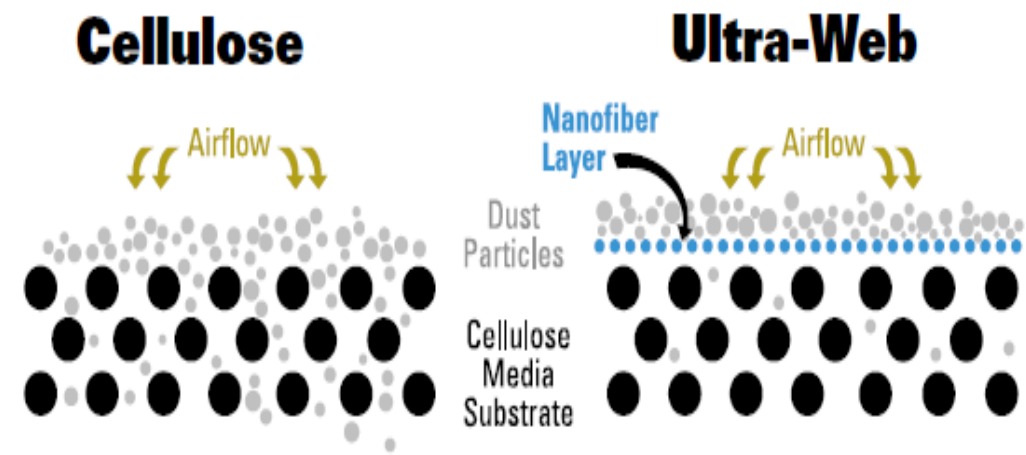
局部放大奈米纖維複合過濾材粉塵過濾效果

資料來源：Nonwovens in Filtration - Fifth International Conference, March 2003

超細纖維膜的應用

◎電紡不織布（HEPA 空氣過濾材）

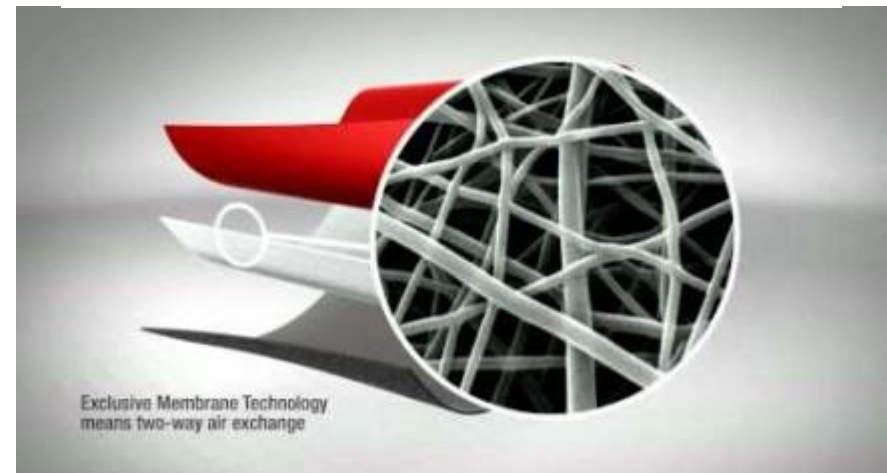
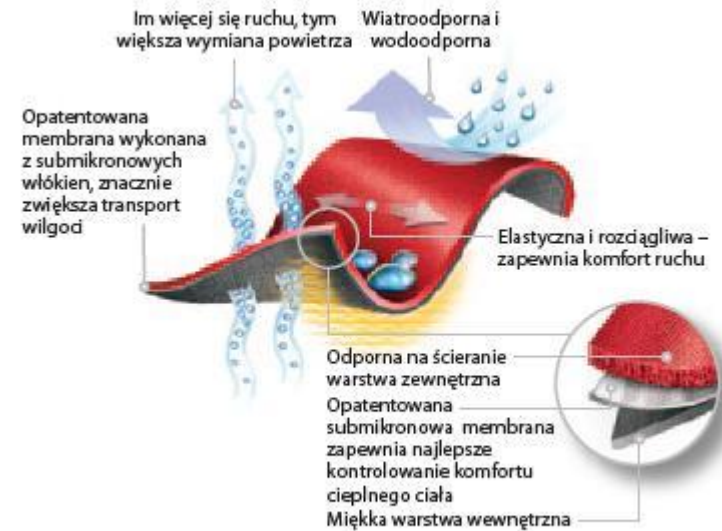
Media Comparative Cross Section



<http://www.donaldson.com/en/index.html>

超細纖維膜的應用

◎電紡不織布（透濕防水膜）

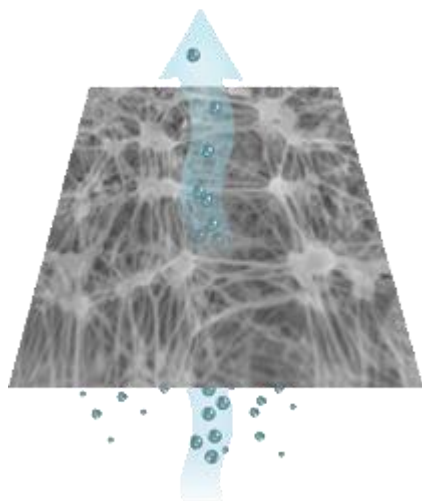


<http://www.polartec.com/shelter/polartec-neoshell/>

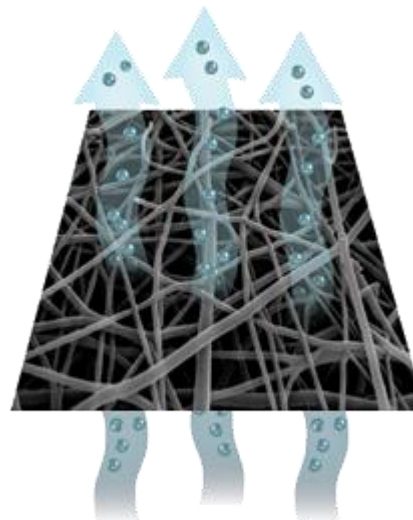
超細纖維膜的應用

◎電紡不織布（透濕防水膜）

Conventional Waterproof/Breathable



Polartec® NeoShell®



<http://www.polartec.com/shelter/polartec-neoshell/>

超細纖維膜的應用

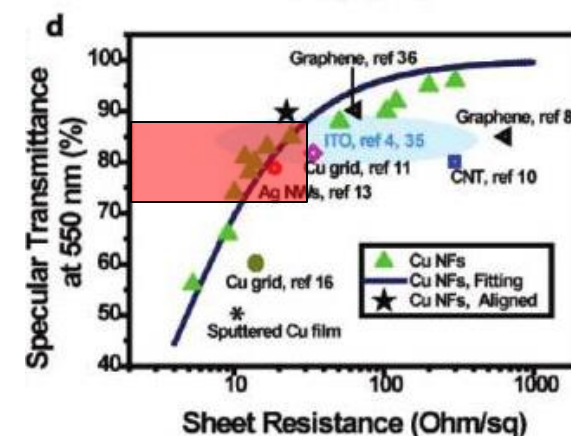
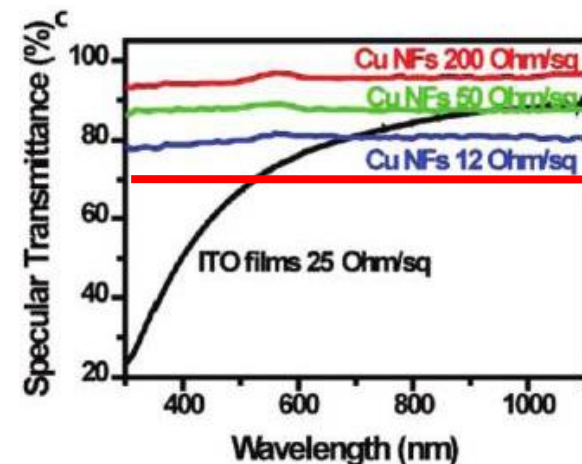
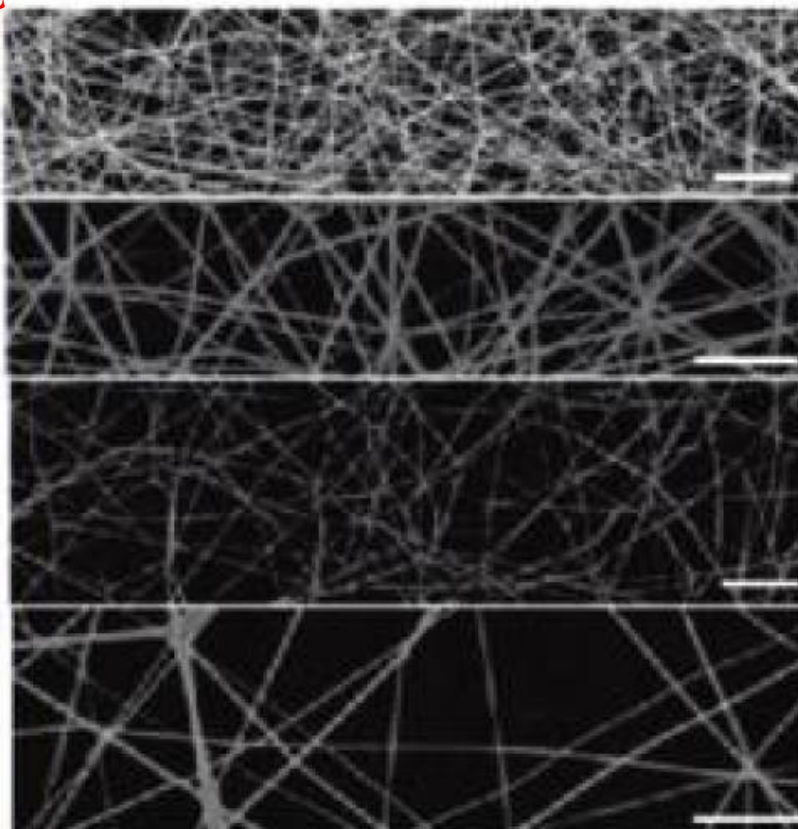
◎電紡不織布（奈米金屬導電纖維膜）

製程面：

- 無機奈米連續長纖維
- 網絡結構（networks）
- 容易製造大面積
- 低成本，易放大量化

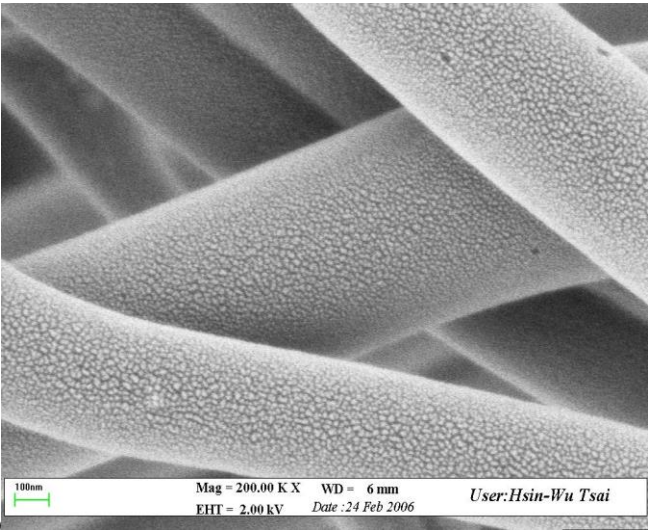
產品面：

- 可撓曲
- 電阻 $\leq 30 \Omega/\square$
- 大面積



◎超級電容電極

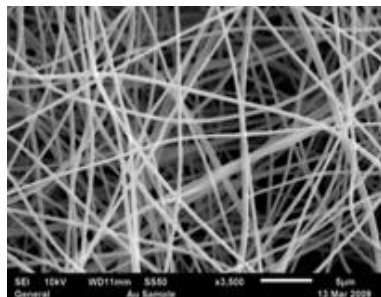
測試設備	ASAP 2020	
測試樣品	次微米活性纖維（平均纖維細度0.5μm）	
測試結果	Langmuir Surface Area	>1000 g/m ²
	大孔比表面積	110.092 g/m ²
	微孔佔比表面積比例	100.6054 g/m ² (孔隙範圍：17~3000Å)
	微孔比例（%）	91.326 %



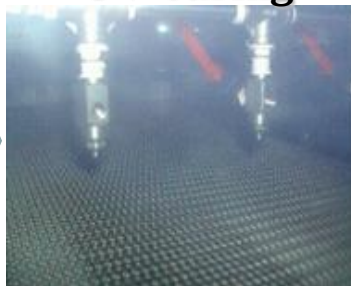
	Electrode Mass (mg)	Charge Specific Capacity (F/g)	Discharge Specific Capacity (F/g)
E1-1	9.7	161	168
E1-2	9.7	174	183
E1-3	13.1	188	209
E1 (mean)		174	187
E2-1	12.1	222	242
E2-2	5.5	256	296
E2-3	7.5	266	291
E2 (mean)		248	276
E3-1	7.5	267	288
E3-2	6.8	292	314
E3-3	5.9	264	292
E3 (mean)		274	298
Commercial active carbon fiber 1*		---	110
Commercial active carbon fiber 2*		---	130

◎電紡不織布（水過濾材/纖維膜）

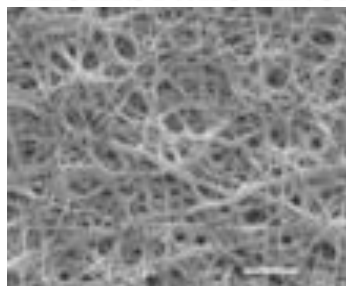
ES nanofibrous membrane



Spray coating & UV curing

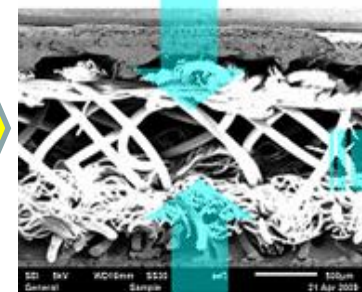


Nanofibrous membrane filter



Waste water

Sandwich non-woven filter



Pure water



Specification

- Average nanofiber diameter $\leq 200\text{nm}$
- Average pore size $\leq 0.08\mu\text{m}$
- Filtration efficiency (MWCO=300K) $>90\%$



Applications

- Filter for water purification
- Industrial wastewater treatment
- Bioseparation/Hemodialysis

Ultrafiltration module



ES membrane

Plate-type

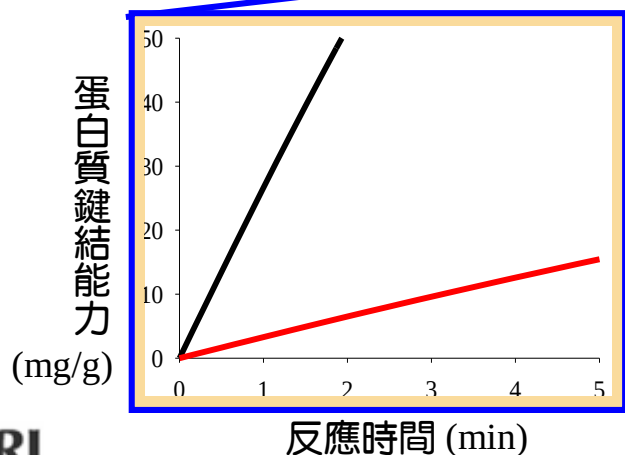
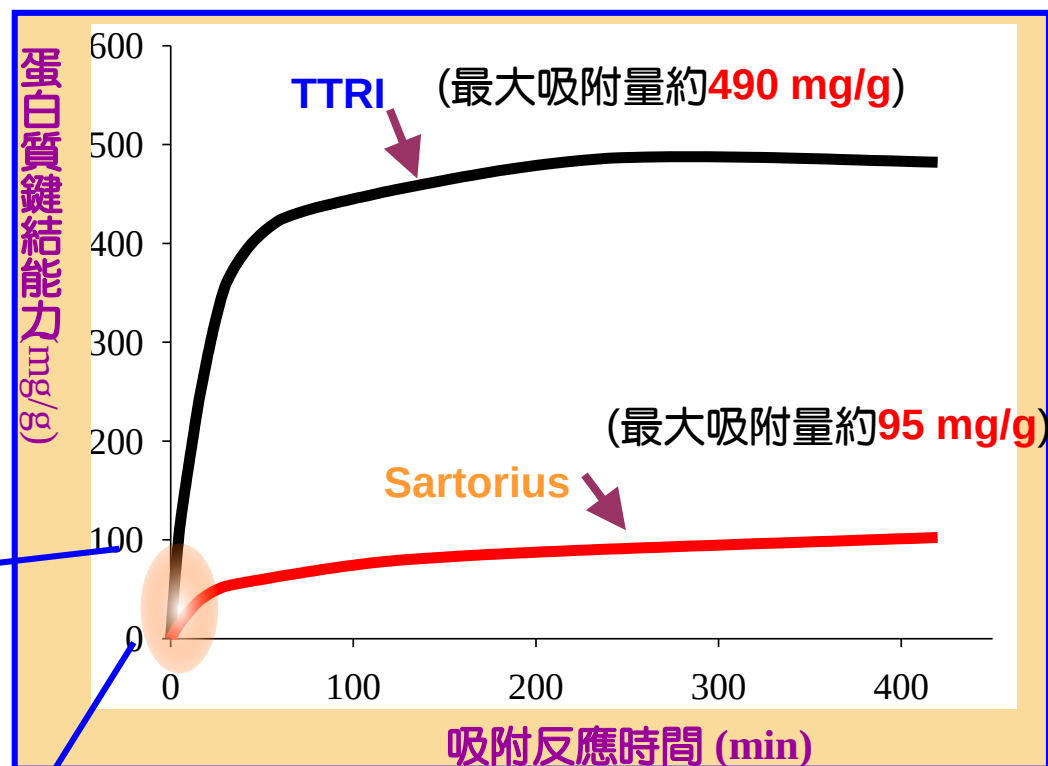


Column-type



◎電紡不織布（蛋白質分離純化）

項目 \ 產品	TTRI	SARTORIUS
基材	PAN 奈米電紡纖維膜材	一般纖維素膜材
纖維直徑	直徑<350nm	-
孔洞大小	< 0.8 μm	> 3 μm
官能基	-COOH	-COOH
離子交換量	722.09 $\mu\text{eq/g}$	135.16 $\mu\text{eq/g}$
蛋白質吸附量	490 mg/g	95 mg/g



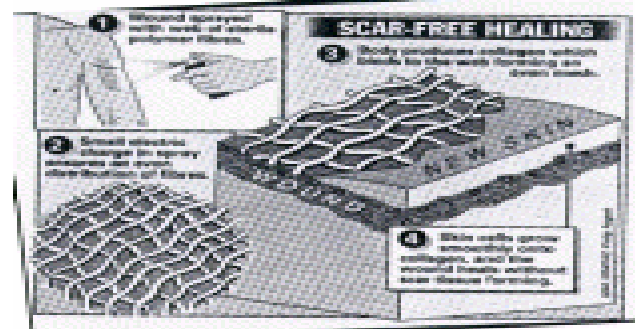
與Sartorius市售品比較

- 蛋白質最大吸附量提昇**500%**
- 吸附反應更迅速
- 節省約**7倍**的純化時間

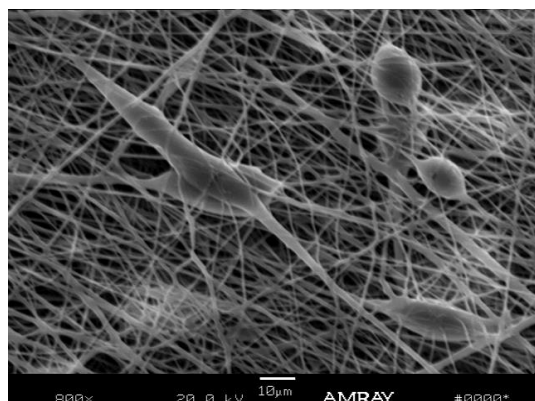
◎電紡不織布（組織工程）

2歲的英國小男孩梅瑞克，被滾燙的茶水潑到身體，整個胸口二度灼傷後，但是經過一種全新的植皮技術4個月的時間，梅瑞克的傷疤卻不見了。

<http://tw.myblog.yahoo.com/chiropractic-house/article?mid=6822>



◎電紡不織布（組織工程-細胞培養）

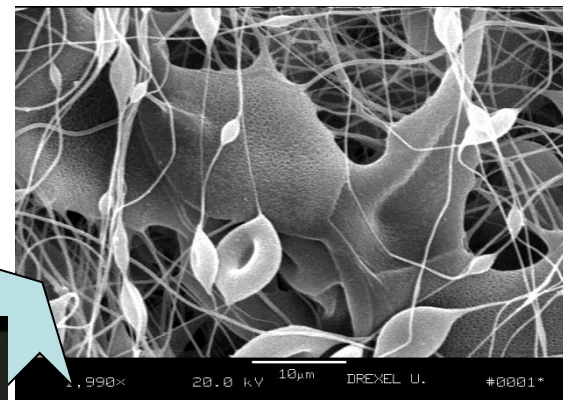


膠原蛋白電紡奈米纖維

應用於

- 1.細胞生長培養基材
- 2.組織修復材
- 3.膠原蛋白面膜

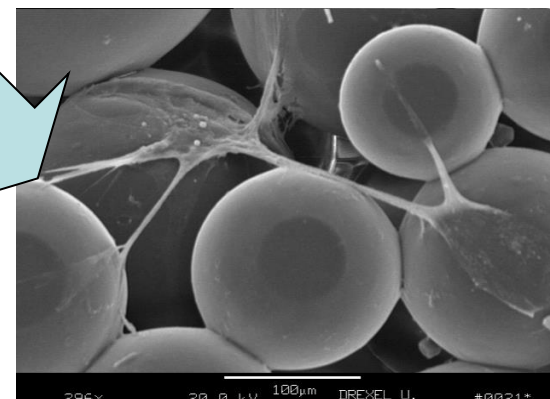
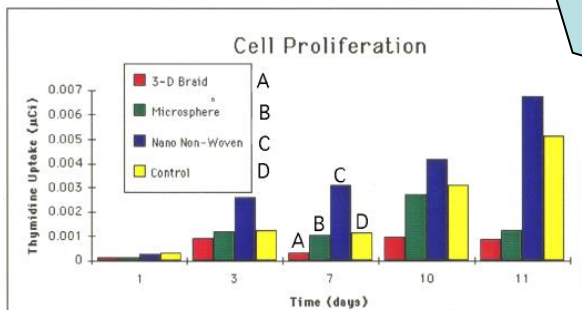
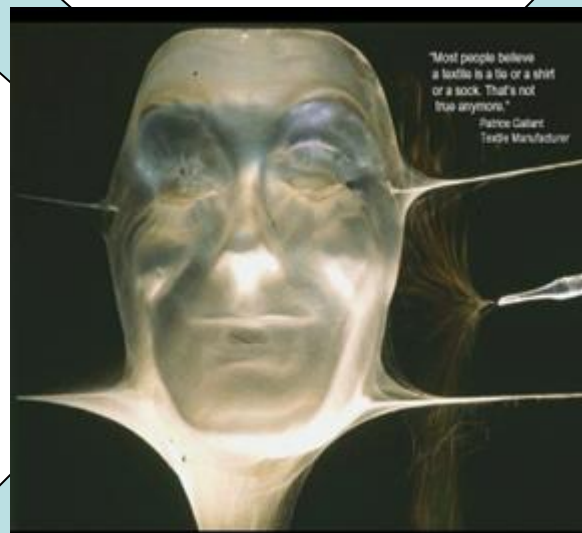
優點：細胞生長效果佳、細胞生長較佳細度為60~300 nm



蠶絲蛋白電紡奈米纖維

應用於

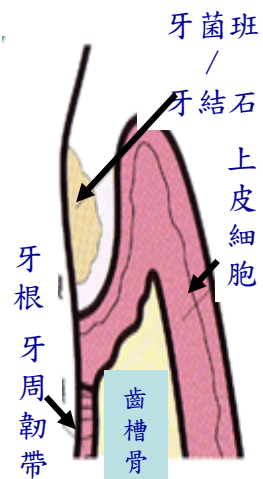
- 1.細胞生長培養基材
- 2.蠶絲蛋白面膜



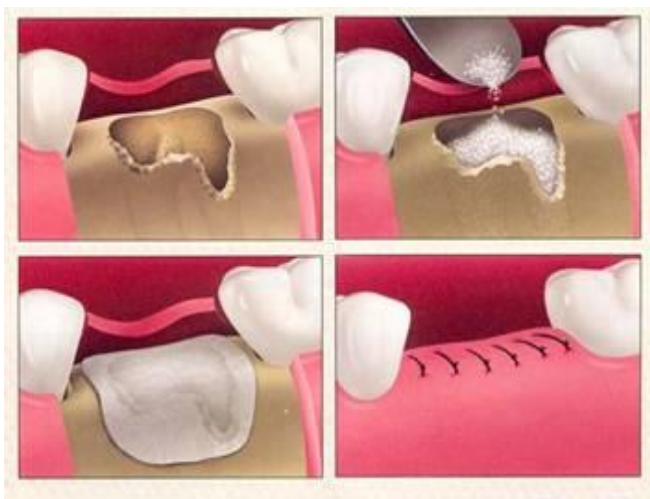
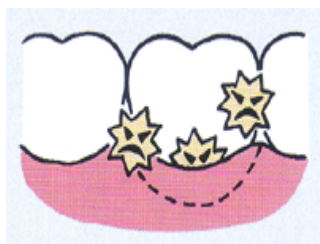
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◎生醫敷材



牙周病



GTR/GBR 膜片發展趨勢

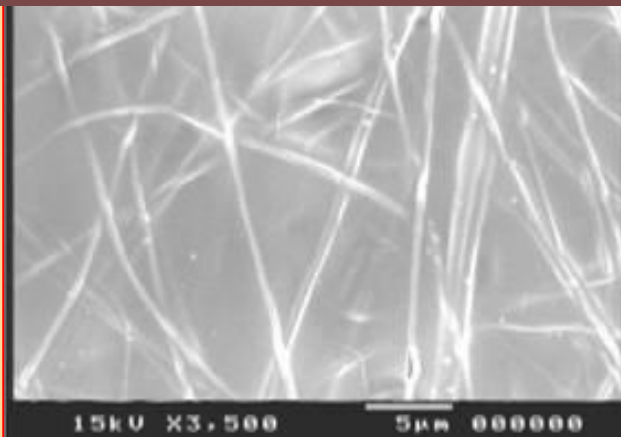


◎產品特性

產品/製程設計	產品功能性
醫療級聚乳酸 (PLA)	具生物可吸收性，不需二次手術移除。
生醫陶瓷—磷酸三鈣與硫酸鈣 (TCP & CaSO_4)	具骨整合性，加速骨整合效果，縮短治療時間
靜電紡絲量化製程 (Electrospinning)	單一加工方式、可快速製備、可控制孔洞大小與厚度，材料具有高強力表現。

◎電紡不織布（直接甲醇燃料電池）

TTRI 奈米纖維質子交換膜

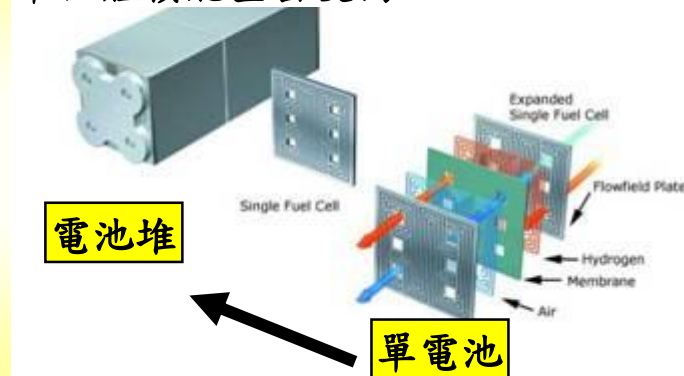


質子交換膜	Nafion-117	TTRI
膜厚 (mm)	175	<51
氣體滲透(25°C, 1 atm)	> 60 hr	> 60 hr
抗拉強度 (MPa) @23°C with water soaked	34	40
延伸率 %	200	180
導電度(S/cm) @ 70°C/ 95% RH	4.38×10^{-2}	1.21×10^{-2}
單位面積阻抗(Ω) @ 70°C/95% RH	0.128	0.134
3.0 M 甲醇穿透率@70°C (cm^2/s)	5.17×10^{-6}	8.03×10^{-7}
DMFC單電池電位 @ 70°C, $i = 200 \text{ mA}/\text{cm}^2$, 2 M methanol aqueous solution	0.643 V	0.598 V

與Nafion117市售品比較TTRI奈米纖維質子交換膜之優勢

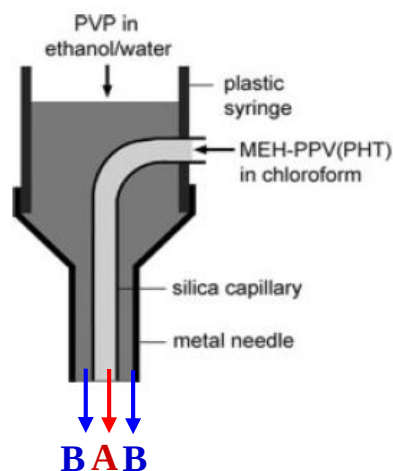
- ① 甲醇滲透率減少 **84.47%**
(有效降低燃料的滲透)
- ② 單電池電位僅僅減少 **7%**
(突顯出甲醇滲透降低之特點)
- ③ 膜材厚度減少 **70.86%**
(成本降低)
- ④ 高能量密度 (組裝燃料電池堆,
TTRI膜厚度薄, 單位空間中能放置質子交換膜數量多!!)

單位體積能量密度高!!

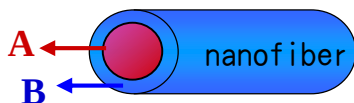


◎電紡不織布（螢光放射纖維膜）

Sheath-core spinneret

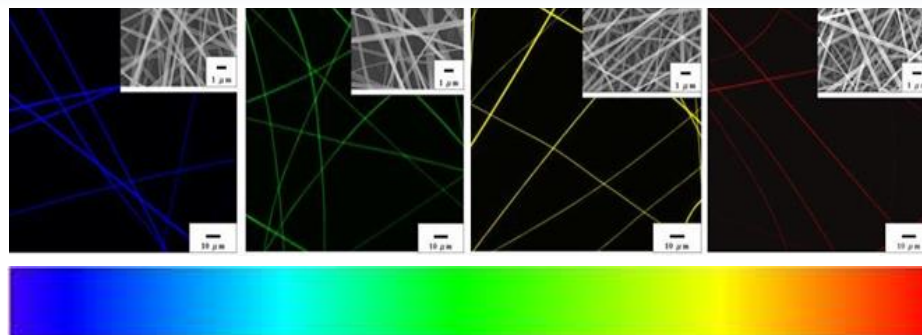


Bicomponent ES fiber



A: fluorescent material
B: polymer (helping to form fibers)

Fluorescent nanofibrous mat with different colors



[TTRI's sample]



超細纖維膜的進展

以往的狀況：

- 成本及強力造成發展限制

最近的進展：

- 應用熔紡製程
- 改裝熔紡製程
- 纖維細度及分佈
- 生產效率



- 北卡大學不織布教材
- 田納西大學不織布教材
- INDA