

Electrospinning: Historical Overview

Dr. Mohamed El-Newehy

Associate Professor

Department of Chemistry - College of
Science

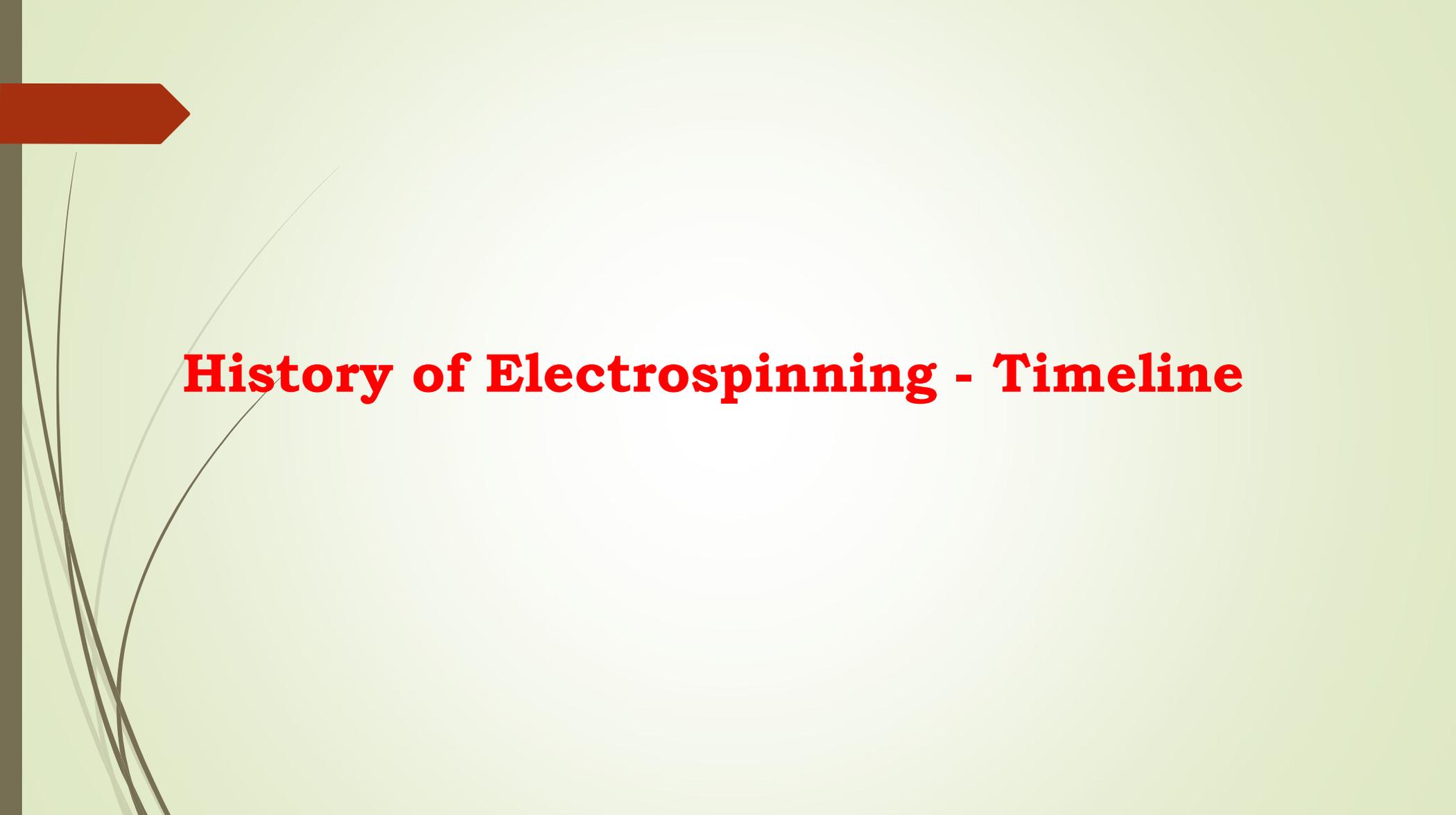
King Saud University

Riyadh 11451 – Saudi Arabia

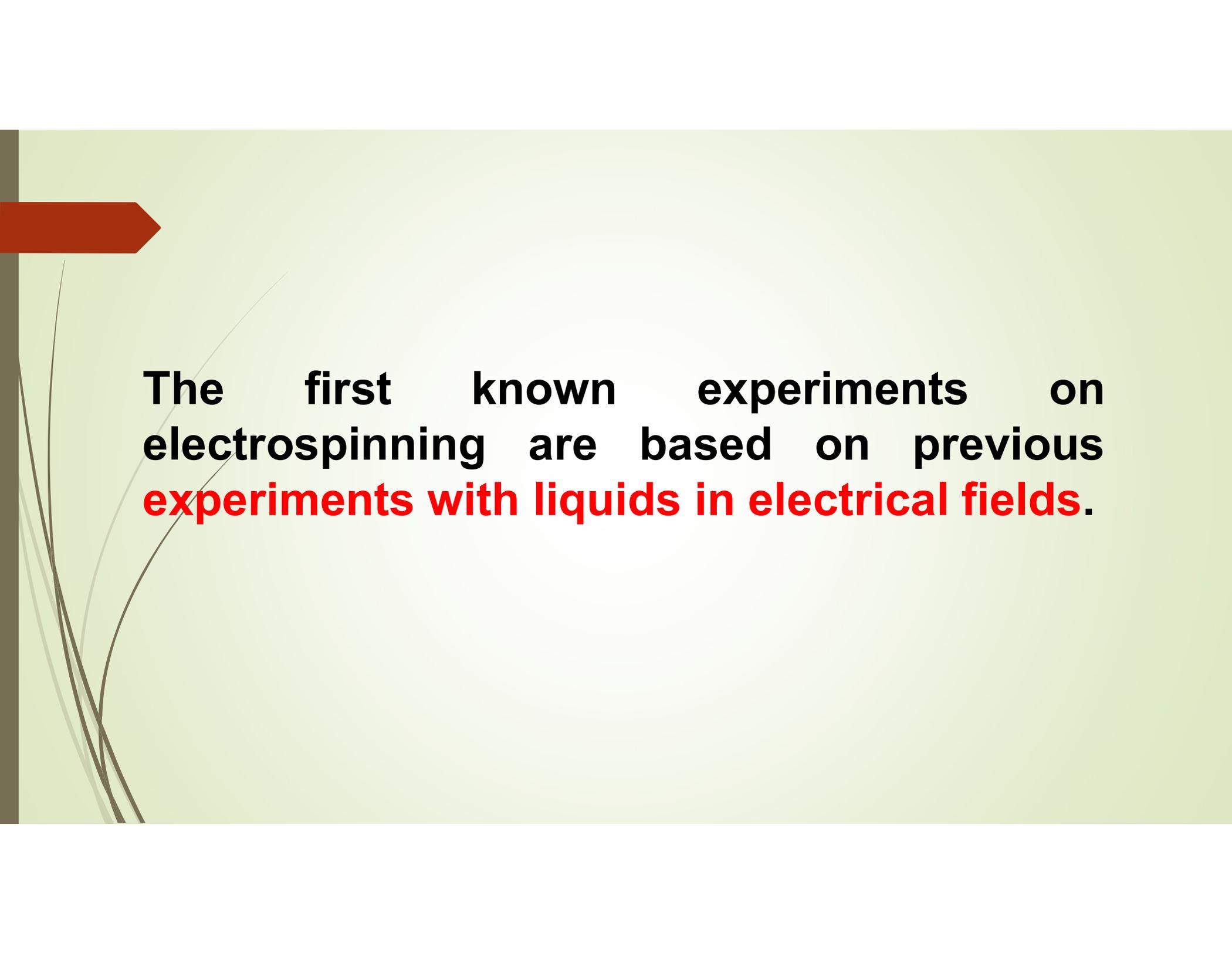
E-mail: melnewehy@ksu.edu.sa

Presentation Outlines

- ❖ **Timeline History**
- ❖ **Milestone Electrospinning**
- ❖ **Types of Electrospinning; Examples**



History of Electrospinning - Timeline



The first known experiments on electrospinning are based on previous experiments with liquids in electrical fields.

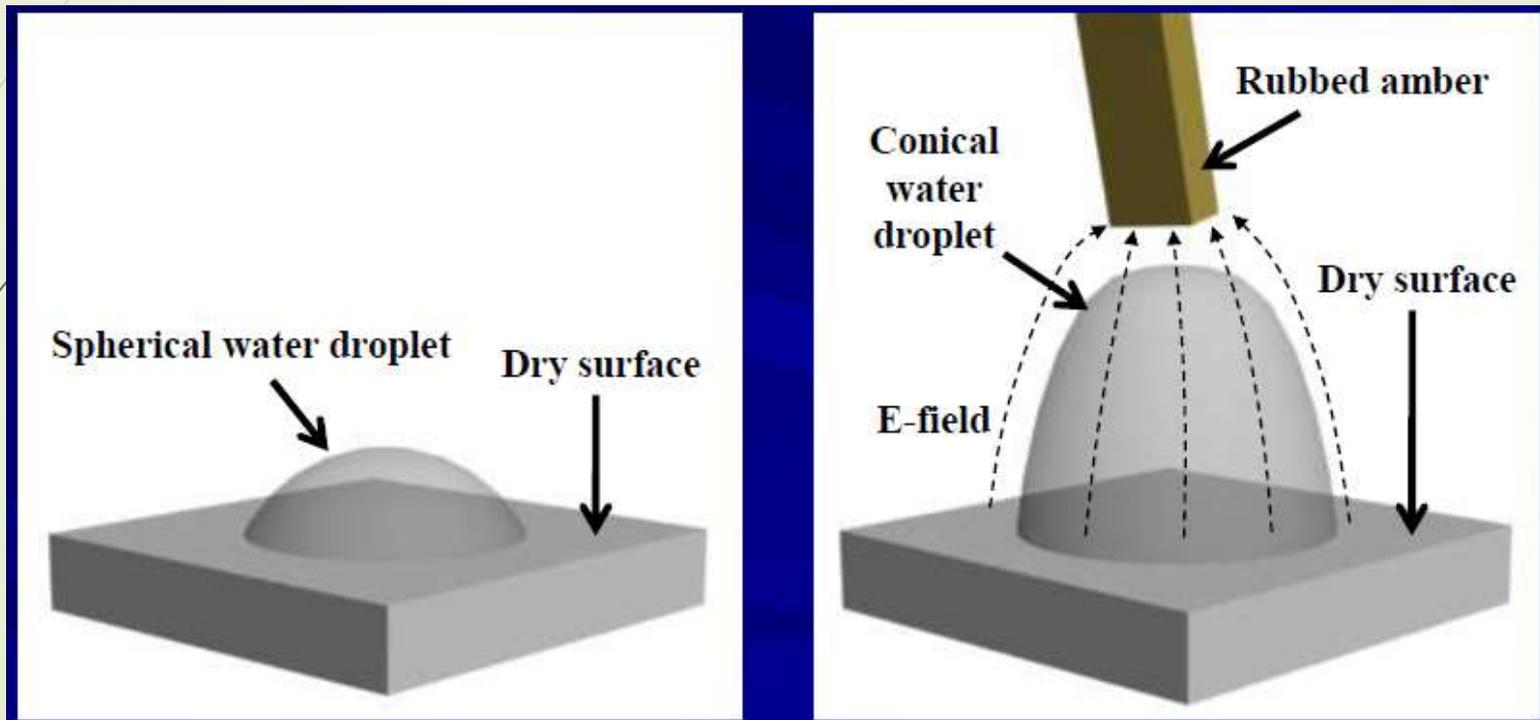
□ William Gilbert (1500s)

(24 May 1544 – 30 November 1603), was an English physician, physicist and natural philosopher.



□ In the late 1500s Sir. William Gilbert set out to describe the behavior of magnetic and electrostatic phenomena.

- ❖ He observed that when a suitably electrically charged piece of amber was brought near a droplet of water **it would form a cone shape and small droplets would be ejected from the tip of the cone: this is the first recorded observation of electrospaying.**

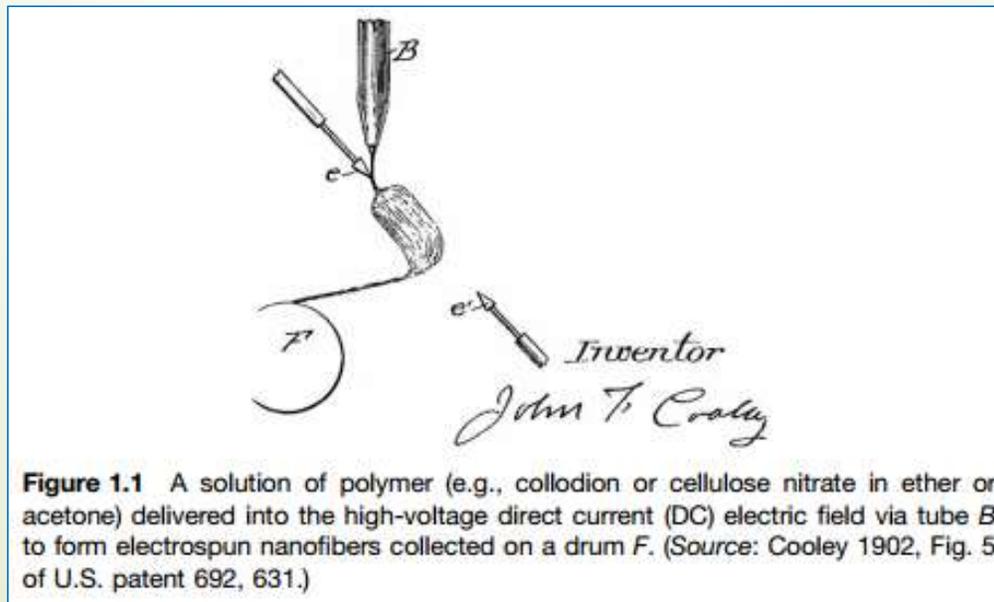


□ Raleigh (1885)

- ❖ The amount of **charge required for the deformation** of droplets was described by Lord Raleigh.

□ J.F. Cooley (1902) and W.J. Morton (1903)

- ❖ In 1902 and 1903, Cooley and Moore described in patents, **apparatus for spraying of liquids by use of electrical charges**.



□ John Zeleny (1914)

(1872–1951) was a Czech-American physicist at the University of Minnesota, who in 1911 invented the Zeleny electroscope.

- ❖ **Zeleny** published work on the behavior of fluid droplets at the end of metal capillaries.
- ❖ His effort began the attempt to **mathematically model** the behavior of fluids under electrostatic forces.
- ❖ **Zeleny** reported that *the fine fiber-like liquid jets could be emitted from a charged liquid droplet in the presence of an electrical potential*, which is **considered to be the origin of principle for the modern needle Electrospinning**.

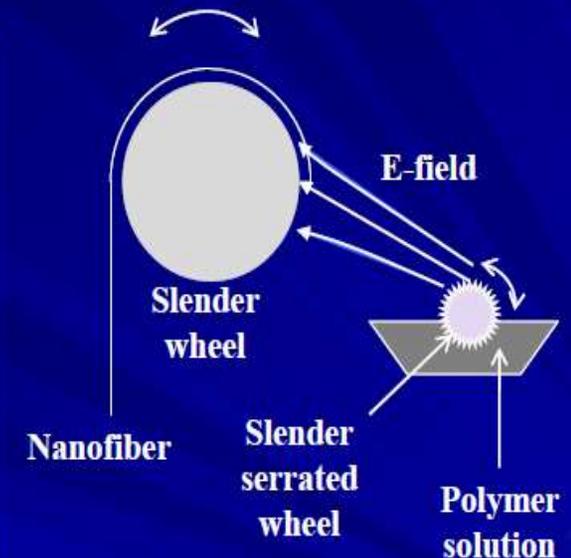
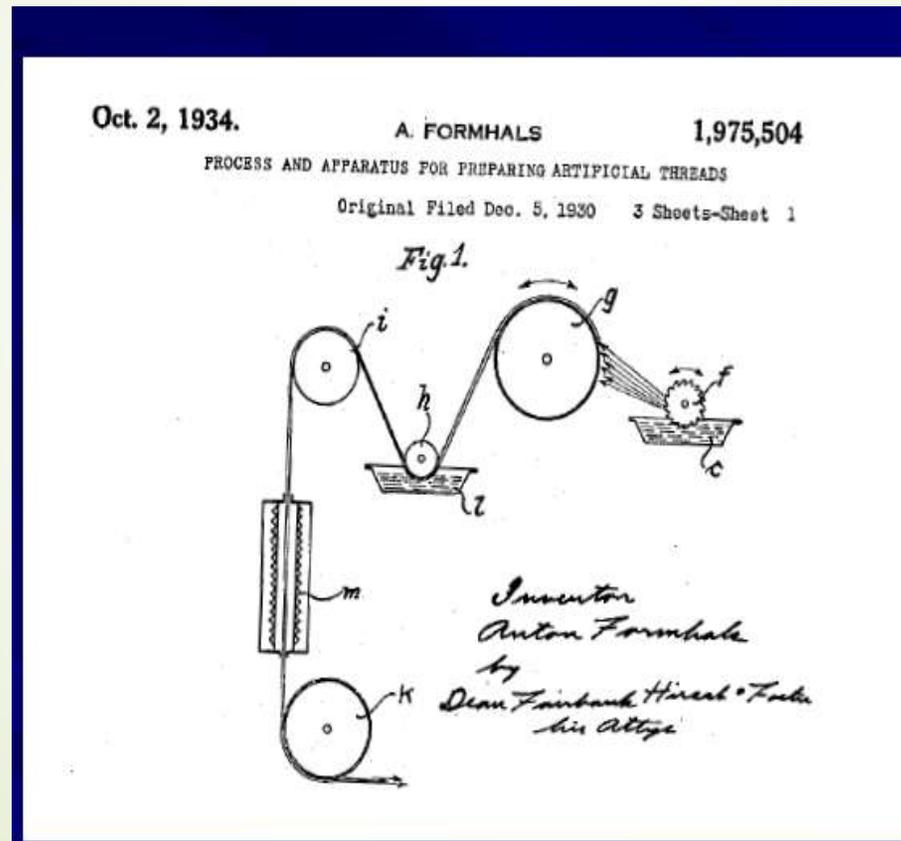
□ Hagiwaba (1929)

- ❖ Preparation of **artificial silk** by electrical charges.

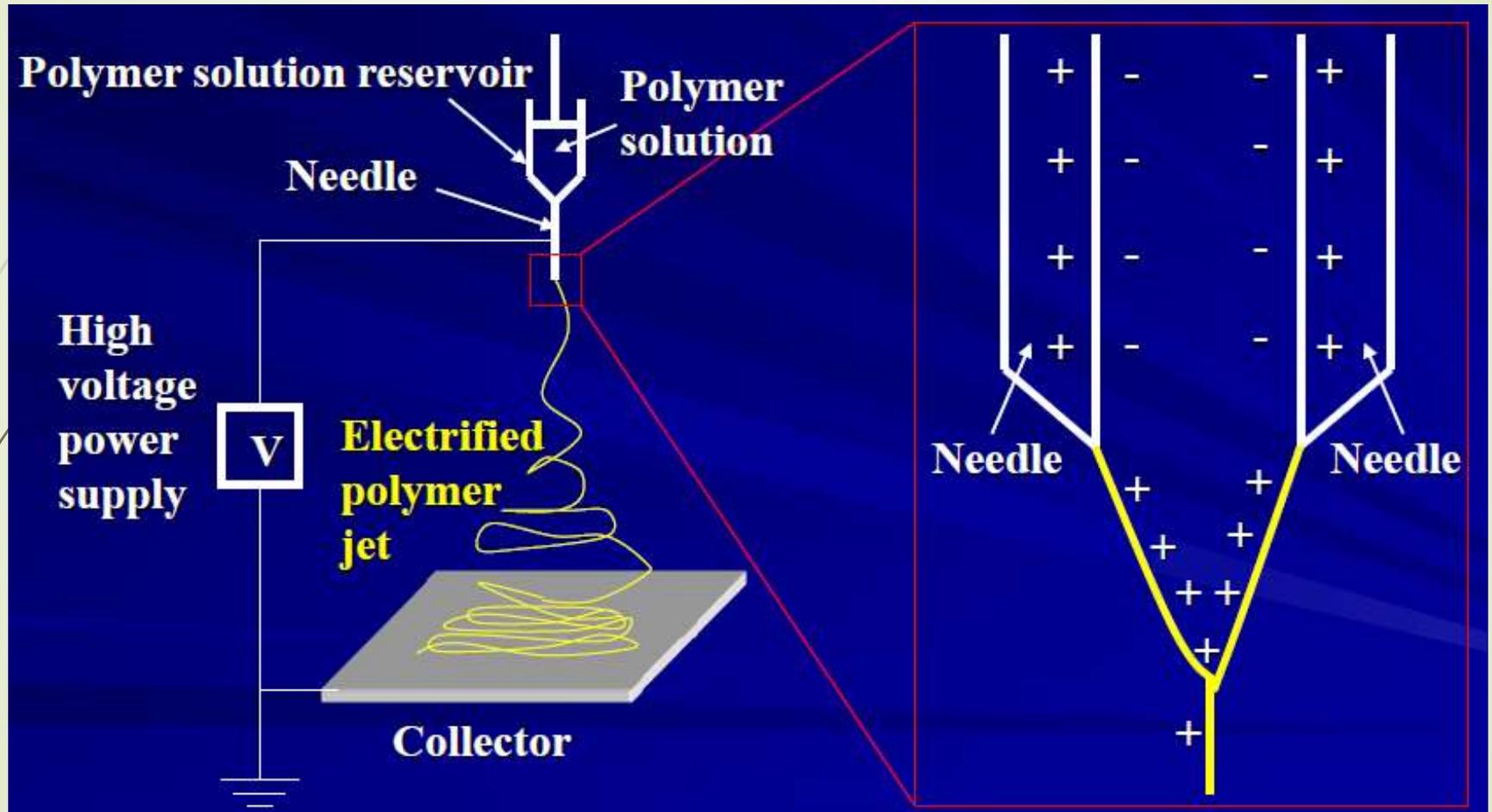
□ Anton Formhals (1934-1944)

- ❖ In 1934, a **crucial patent**, revealing the **experimental apparatus** for the practical production of artificial filaments using electrical field was issued for the first time by Formhals

Fabrication of textile yarns and a voltage of 57 kilovolt (kV) was used for electrospinning cellulose acetate using acetone and monomethyl ether of ethylene glycol as solvent.



- ❖ Later on, a series of patents were issued, which focused on **improvements and modifications on the electrospinning apparatus.**



□ C.L Norton (1936)

- ❖ **Electrospinning from a melt** rather than a solution using an air-blast to assist fibre formation.

□ N.D. Rozenblum and I.V. Petryanov-Sokolov (1938)

- ❖ They working in Prof. N.A. Fuks's group at the Aerosol Laboratory of the L. Ya Karpov Institute in the **USSR**, generated electrospun fibres
- ❖ They developed into filter materials known as "**Petryanov filters**".
- ❖ **By 1939**, this work had led to the **establishment of a factory** in "Tver" **for the manufacture of electrospun smoke filter elements for gas masks.**
- ❖ The material, dubbed BF (Battlefield Filter) was spun from cellulose acetate in a solvent mixture of dichloroethane and ethanol.
- ❖ **By the 1960s** output of spun filtration material was claimed as 20 million m² per annum.

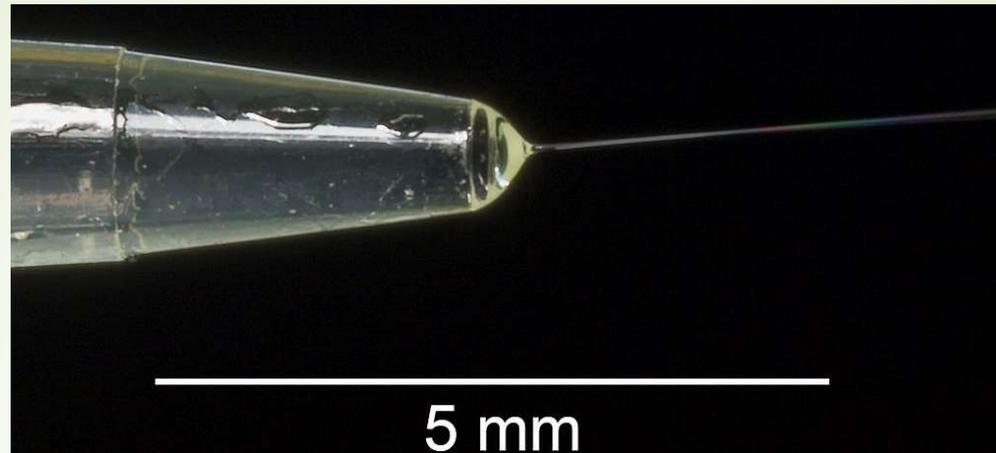
□ Geoffrey Ingram Taylor (1960s)

Geoffrey Ingram Taylor (7 March 1886 – 27 June 1975) was a British physicist and mathematician



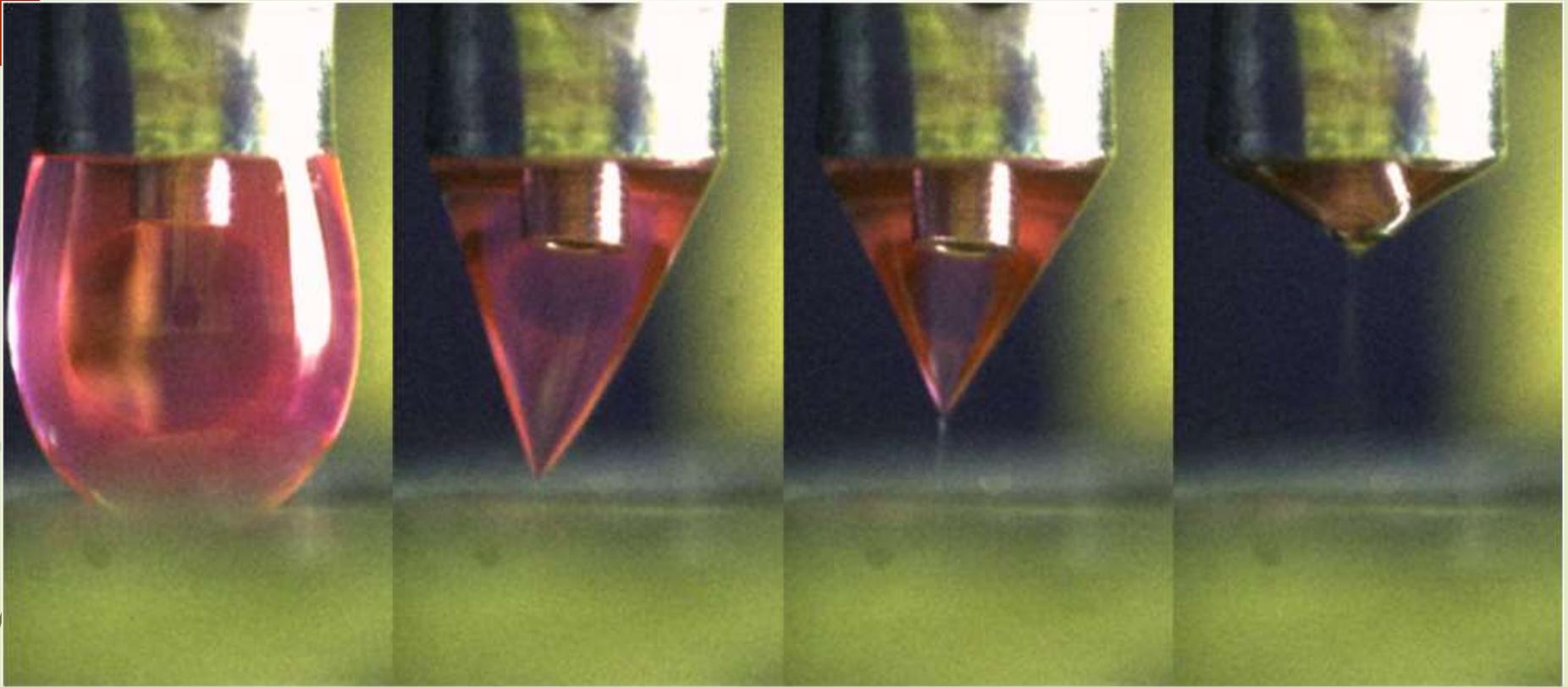
- ❖ **Taylor** produced the theoretical underpinning of electrospinning.
- ❖ **Taylor's** work contributed to electrospinning by *mathematically modelling the shape of the cone formed by the fluid droplet under the effect of an electric field.*
- ❖ This characteristic droplet shape is now known as the **Taylor cone**.

□ Geoffrey Ingram Taylor (1960s)



Taylor Cone

- ❖ A Taylor cone refers to the cone observed in electrospinning, electrospaying and hydrodynamic spray processes from which a jet of charged particles emanates above a threshold voltage
- ❖ This cone was described by Taylor in 1964 before electrospay was "discovered"
- ❖ When a small volume of electrically conductive liquid is exposed to an electric field, the shape of liquid starts to deform from the shape caused by surface tension alone.



Dripping

Coning

Stable cone-jet

Multi-jet

Increased voltage



□ 1971

- ❖ **Baumgarten** reported on electrospinning of **acrylic microfibers**.
- ❖ **Larrondo and Manley** reported in a series of papers on electrospinning of polymer melts.

□ 1970s

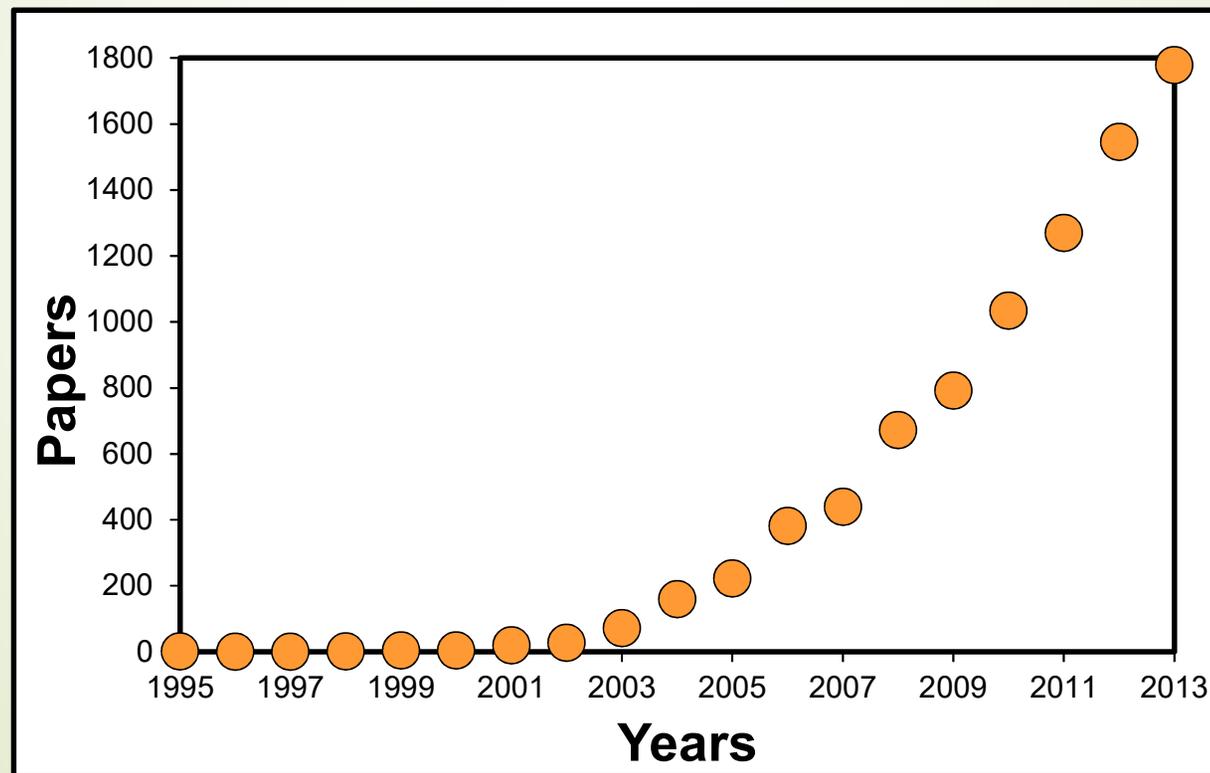
- ❖ Some attempts at commercialization were undertaken.
- ❖ For example:
 - Simm, from the Bayer company, submitted a series of patents on electrospinning of plastics.**
- ❖ A variety of electrospinning setups were suggested in early electrospinning setups that have some similarities to recent efforts.

□ Industry vs. Academia

- ❖ The first technical application for electrospinning was suggested for the nonwoven industry.
- ❖ Academia picked-up electrospinning slowly in the 1990s.
- Some companies such as **espin Technologies**, **Nano Technics**, and **KATO Tech** are constantly benefited by the utmost features derived from electrospinning.
- While companies such as **Donaldson Company** and **Freudenberg** have already applied the outcome of electrospinning process in their **air filtration** products since past two decades.

□ 1990s

- ❖ Academia picked-up electrospinning slowly in the 1990s.
- ❖ Several research groups, especially the **Reneker's group (The University of Akron)**, revived electrospinning by demonstrating the fabrication of ultra-thin fibers from various polymers.



Growing Popularity of Electrospinning (1994-2013)

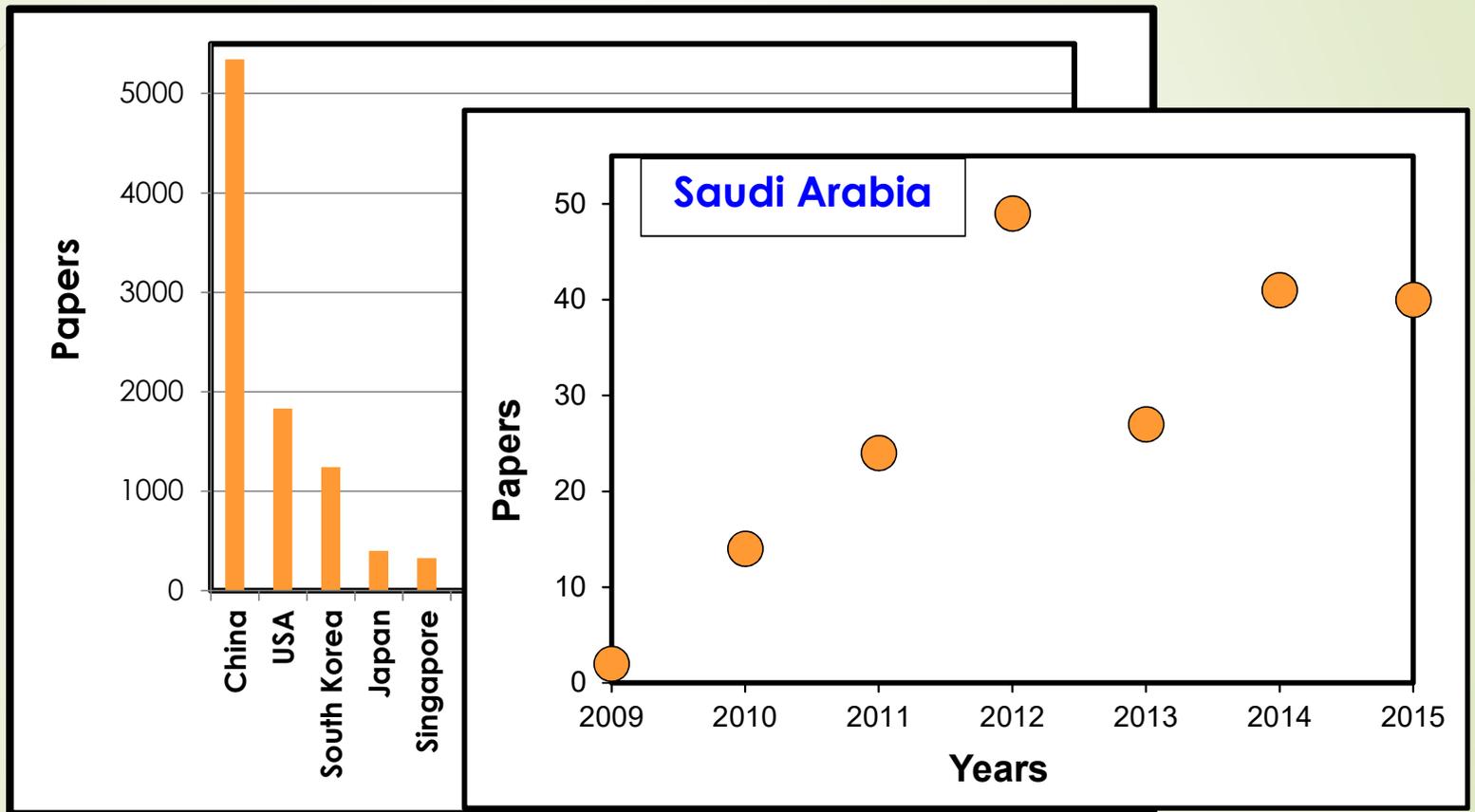
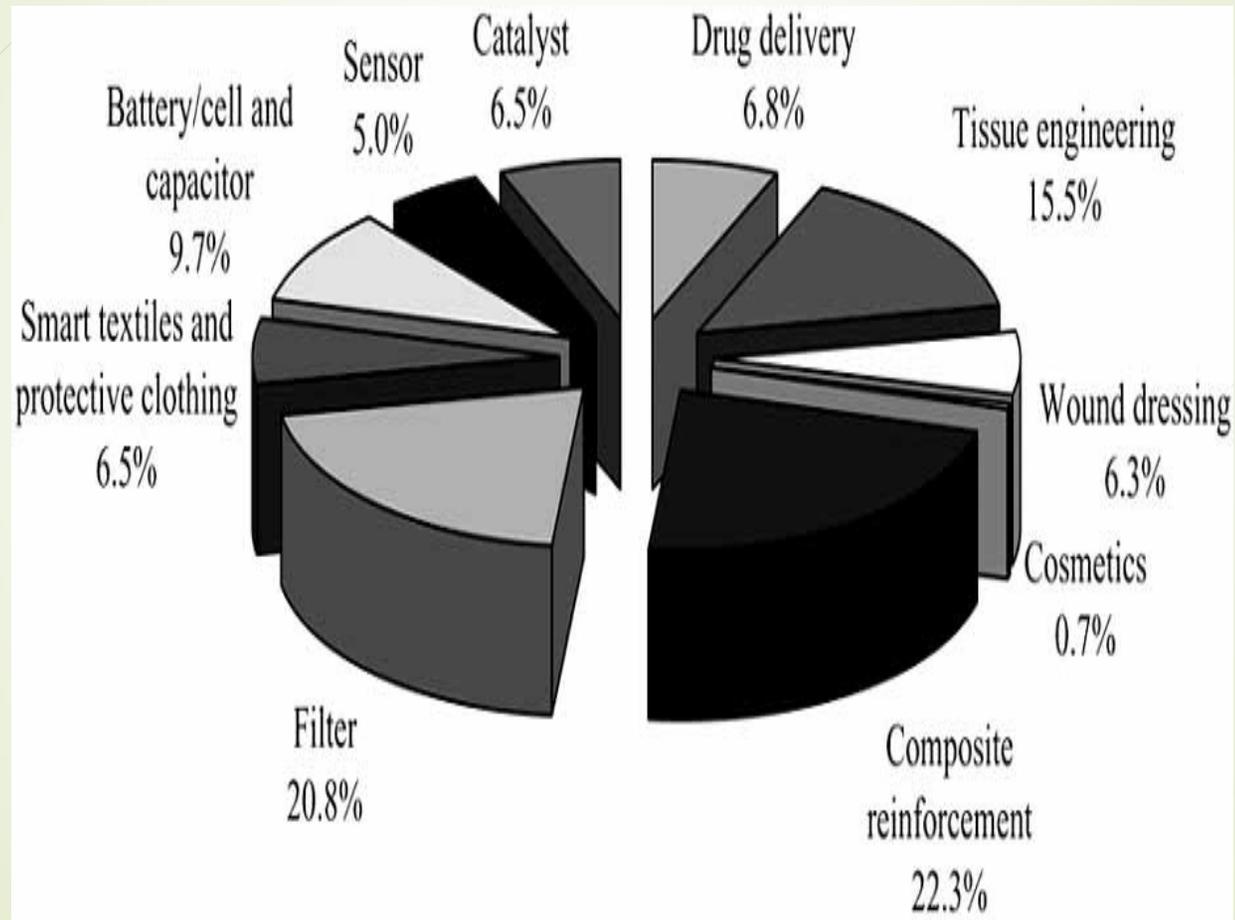


TABLE 1.2 Chronological development of electrospinning patents

| Year | Persons | Description |
|-----------|---------------------------------------|---|
| 1902 | Cooley, J. F. | U.S. pat. # 692,631 |
| 1902 | Morton, W. J. | U.S. pat. # 705,691 |
| 1903 | Cooley, J. F. | U.S. pat. # 745,276 |
| 1934–1944 | Formhals, A. | U.S. pat. #s 1,975,504; 2,077,373; 2,109,333; 2,116,942; 2,123,992; 2,158,415; 2,158,416; 2,160,962; 2,187,306; 2,323,025; 2,349,950 |
| 1929 | Hagiwara, K. | U.S. pat. # 1,699,615 |
| 1936 | Norton, C. L. | U.S. pat. # 2,048,651 |
| 1939 | Gladding, E. K. | U.S. pat. # 2,168,027 |
| 1943 | Manning, F. W. | U.S. pat. # 2,336,745 |
| 1966 | Simons, H. L. | U.S. pat. # 3,280,229 |
| 1976 | Simm, W., et al. | U.S. pat. # 3,944,258 |
| 1977/1978 | Martin, G. E., et al. | U.S. pat. # 4,043,331; 4,044,404; 4,127,706 |
| 1978 | Simm, W., et al. | U.S. pat. # 4,069,026 |
| 1980 | Fine, J., et al. | U.S. pat. # 4,223,101 |
| 1980/1981 | Guignard, C. | U.S. pat. # 4,230,650; 4,287,139 |
| 1982 | Bornat, A. | U.S. pat. # 4,323,525 |
| 1985 | How, T. V. | U.S. pat. # 4,552,707 |
| 1987 | Bornat, A. | U.S. pat. # 4,689,186 |
| 1989 | Martin, G. E., et al. | U.S. pat. # 4,878,908 |
| 1991 | Berry, J. P. | U.S. pat. # 5,024,789 |
| 2000 | Scardino, F. L. and Balonis, R. J. | U.S. pat. # 6,106,913 |
| 2004 | Chu, B., et al. | U.S. pat. # 6,713,011 |

□ Application of Nanofibers



□ 1995

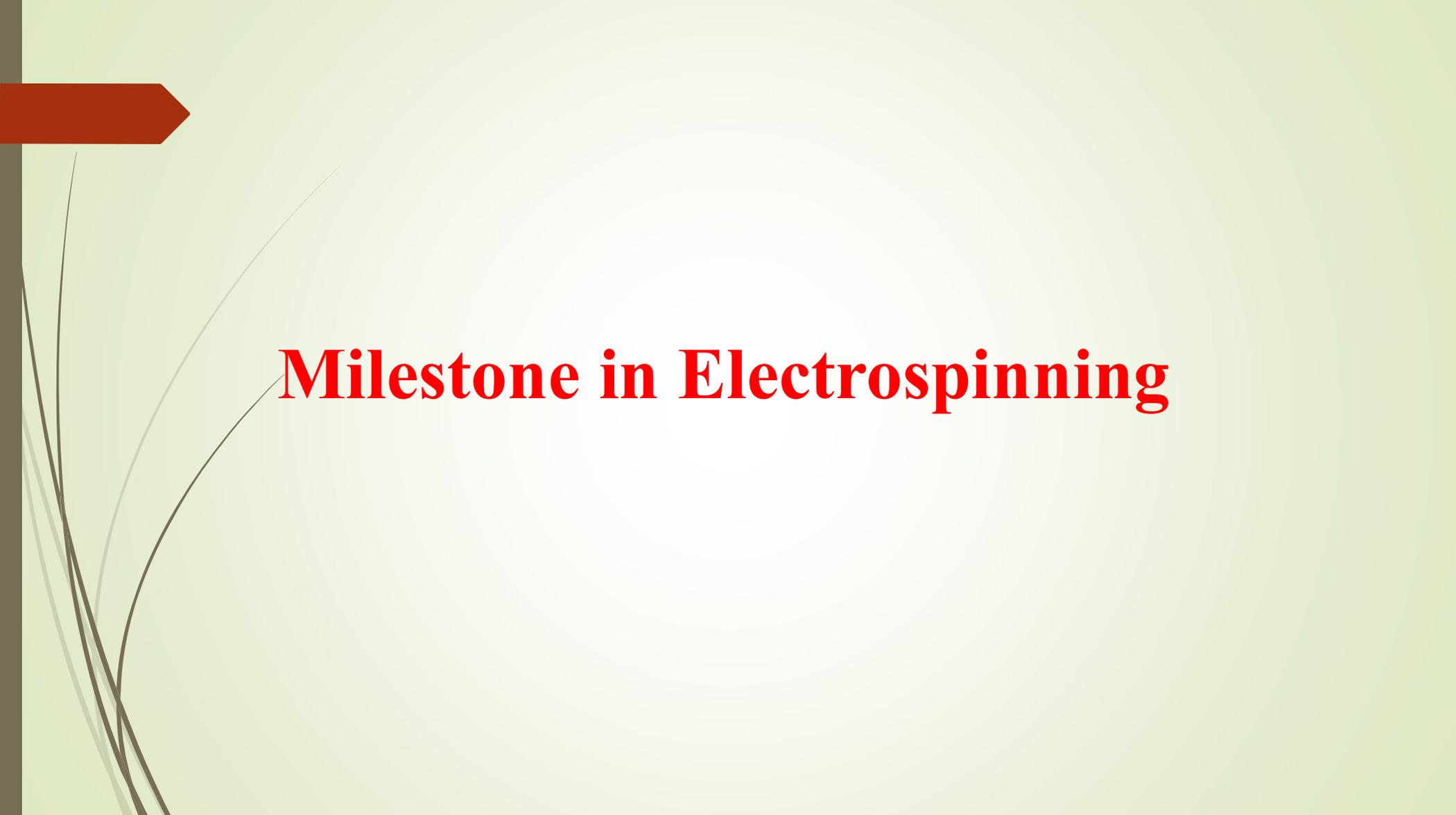
- ❖ Since 1995 there have been further **theoretical developments of the driving mechanisms** of the electrospinning process.

□ 2001

- ❖ **Hohman *et al.*** investigates the relative growth rates of the numerous **proposed instabilities in an electrically forced jet once in flight.**
- ❖ **Yarin *et al.*** endeavoring to **describe the most important instability to the electrospinning process**, the bending (whipping) instability.

□ Reznik (2004)

- ❖ **Reznik *et al.*** describes extensive work on the **shape of the Taylor cone and the subsequent ejection of a fluid jet.**



Milestone in Electrospinning

Milestone in Electrospinning

2008

- Biomimetic extracellular matrix nanofibrous scaffolds

2007

- **Emulsion electrospinning**

- Growth factor released nanofibrous scaffolds

2006

- Guiding effect of aligned electrospun nanofibers on human cells

2005

- Drug eluting nanofibers

2004

2003

- **Core-shell electrospinning**

- Drug delivery and Ceramic nanofibers

2002

- Scaffolds for tissue engineering

2001

- Aligned nanofibers

2000

- Theoretical model for electrospinning Jet formation

1999

- Electrospinning nanocomposites

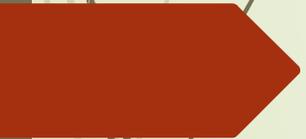
1981

- **Melt electrospinning**

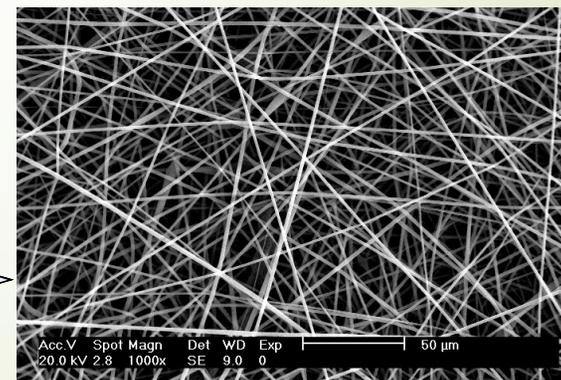
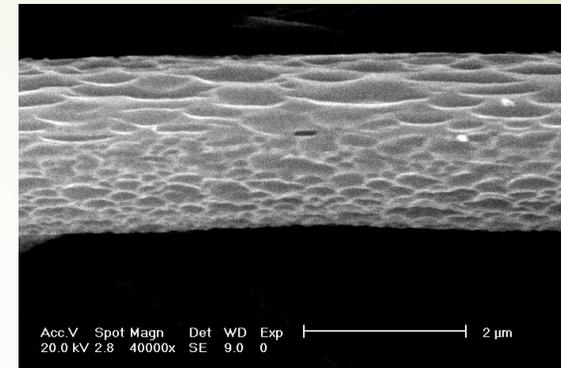
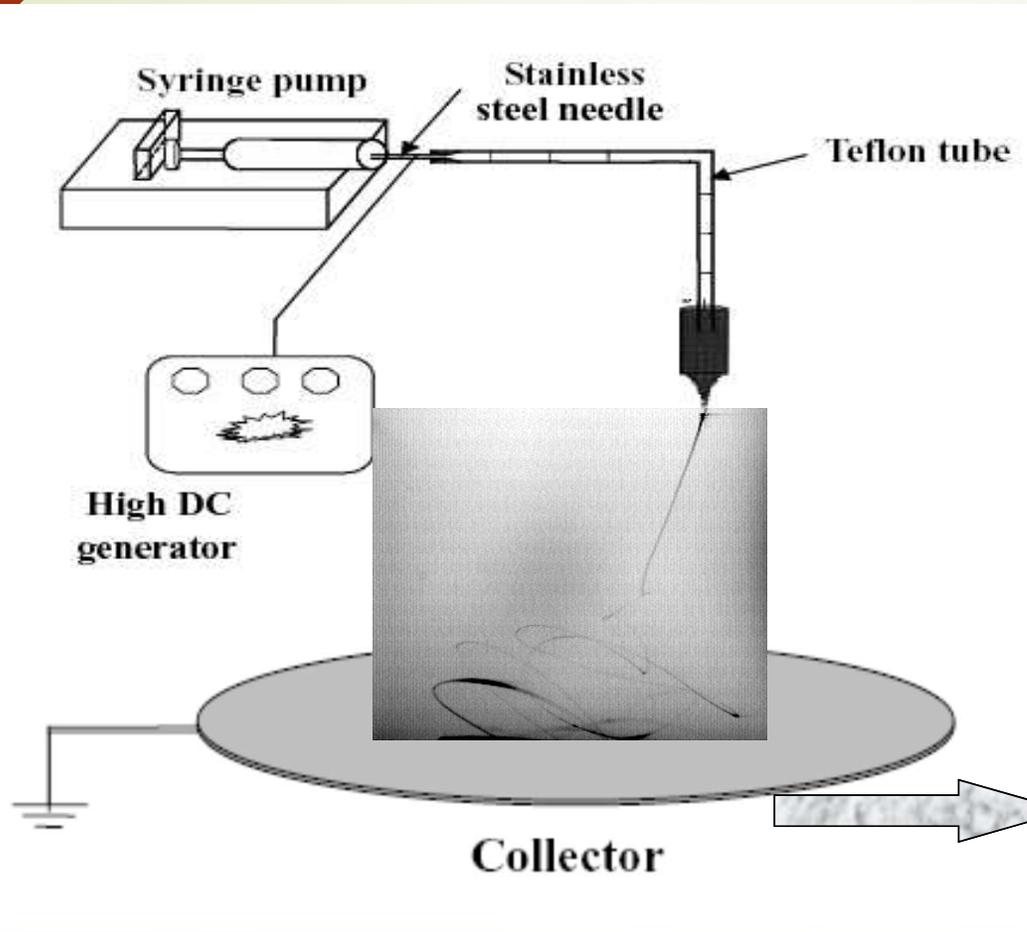
1902

- **Solution electrospinning**

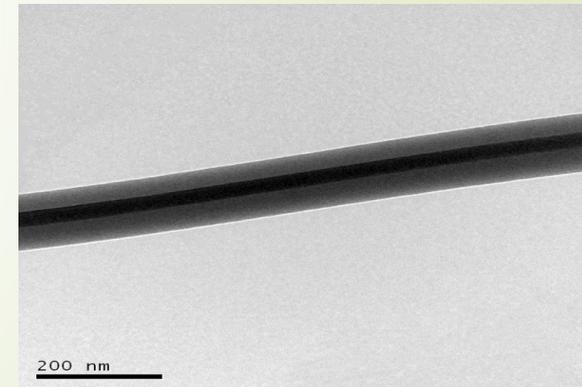
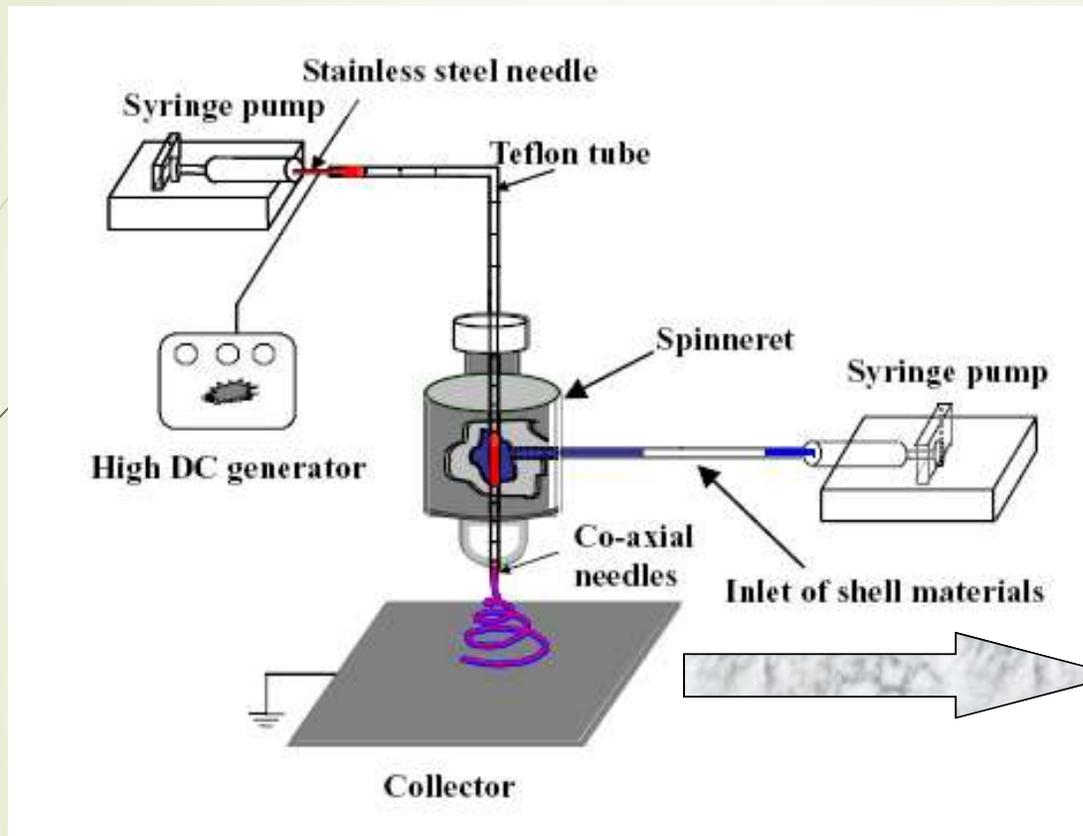
Types of Electrospinning; Examples



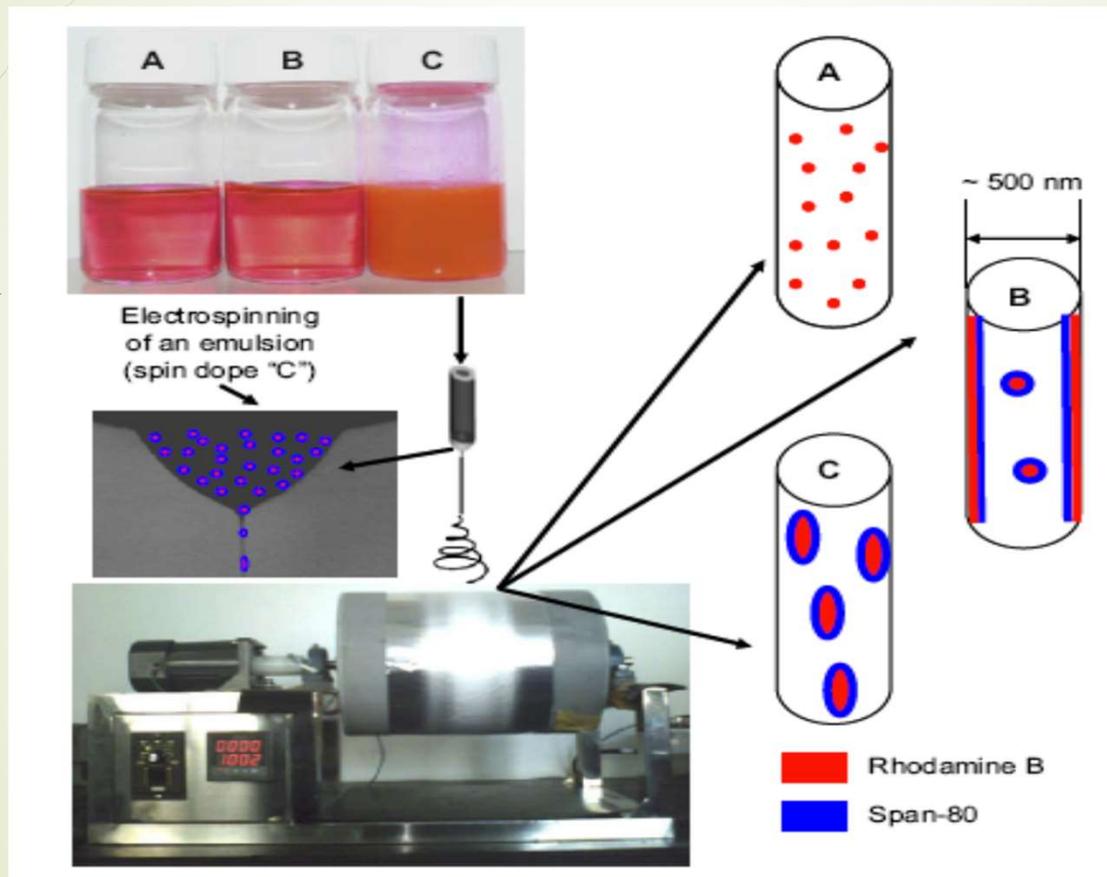
□ Electrospinning Process



□ Coaxial Electrospinning



□ Emulsion Electrospinning



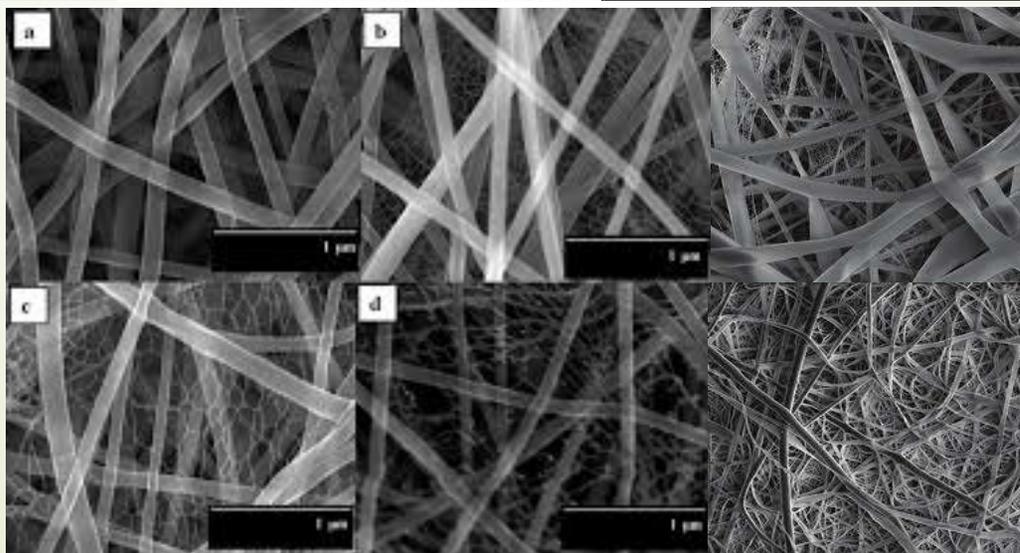
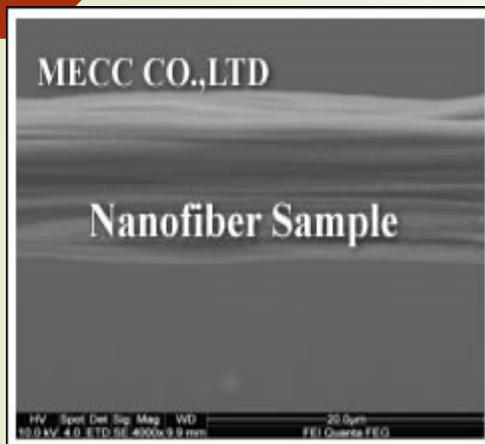
Nozzle-Less Electrospinning Unit

The nozzle-less principle using rotating electrodes has been developed into a commercially available industrial scale



Nozzle-less production electrospinning line (NanospiderTM)

□ Electrospun Architectures



At KSU: Nanofibers Facilities (Electrospinning Setup)



Electrospinning is an Old

But

Yet Fascinating Technique

Thank You

Mohamed El-Newehy