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NANOFIBRES
by electro-spinning of polymer solution
Nanofibres background

1. Nanofibres properties

   Increase of the surface to volume ratio -> solar and light sails and mirrors in space

   Reduction of characteristic dimension -> nano-biotechnology, tissue engineering, chemical catalysts, electronic devices

   Bio-active fibres: catalysis of tissue cells growth

   Mechanical properties improvement -> new materials and composite materials by alignment in arrays and ropes

2. Nanofibres production:

   Air-blast atomisation

   Pulling from melts

   Electrospinning of polymer solutions
Classical liquid jet

Orifice – 0.1mm
Primary jet diameter ~ 0.2mm
Micro-jet diameter ~ 0.005mm

• Gravitational, mechanical or electrostatic pulling limited to l/d ~ 1000 by capillary instability
• To reach nano-range:
  jet thinning ~10^{-3}
  draw ratio ~10^6!
Electro-spinning

Moving charges (ions) interacting with electrostatic field amplify bending instability, surface tension and viscoelasticity counteract these forces.
Electro-spinning

Bending instability enormously increases path of the jet, allowing to solve problem: how to decrease jet diameter 1000 times or more without increasing distance to tenths of kilometres.
Electro-spinning
Simple model for elongating viscoelastic thread

Stress balance: $\mu$ - viscosity, $G$ – elastic modulus stress, $\sigma$ stress tensor, $dl/dt$ – thread elongation

Momentum balance: $V_o$ – voltage, $e$ – charge, $a$ – thread radius, $h$ - distance pipette-collector

Kinematic condition for thread velocity $v$

Non-dimensional length of the thread as a function of electrostatic potential

Nanofibres – basic setup

Diagram showing a setup with a liquid jet, camera, high voltage, and high voltage source. The liquid jet is directed towards the camera, which is connected to a high voltage source.
Nanofibres – howto?

1. Viscoelastic fluid:
   Dilute solution (4 – 6)% of polyethylene oxide (molar weight $4 \cdot 10^5$ g/mol), in 40% ethanol – water solvent

2. Electrostatic field
   - high voltage power supply (5-30kV)
   - plastic syringe
   - metal grid to collect fibres

3. Visualization
   - high speed camera (4000 – 40000 fps)
   - high resolution “PIV” camera (1280x1024 pixels)
   - CW Argon laser, double pulse Nd:Yag laser, projection lens
Nanofibres – basic setup
Nanofibres collection
Nanofibres collection
Electrospinning observed at 30fps

Average velocity of the fibres: 2 m/s

Average velocity of the fibres: 2 m/s
Electrospinning observed at 4500fps
Electrospinning observed at 4500fps

Average velocity of the fibre: 2 m/s
Electrospinning

Collected nanofibres

Syringe
Pendant Drop
Envelope Cone
Flat Ground Collector
Secondary Bending Instability
Electron microscopy

PEO nanofibres
Failure modes
Parametric study

Model validation varying following parameters:

- $L$ – length of the rectilinear part
- $\Omega$ – angle of the envelope cone (image analysis)
- $U$ – velocity of the fibre by PIV method
- $a$ – fibre diameter (image analysis)
- structure of collected woven (failure modes)
- elongation strength of single fibre measured by air jet

Effect of

- Electrostatic potential $V$
- Distance pipette-collector $H$
- Solution concentration $c$
- Distance from the pipette $x$
Parametric study

- concentration of PEO: 3%
- Voltage: 8 kV
- H = 215 mm
- polymer solution with the addition of fluorescent particles (0.3μm polymer microspheres)
- light source: Nd:Yag laser

Δt = 500 μs

Average velocity of the fibres: 2 m/s
## Tested polymers

<table>
<thead>
<tr>
<th>Test</th>
<th>Polymer</th>
<th>Solvent</th>
<th>Concentration</th>
<th>Voltage [kV]</th>
<th>Electrospinning</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td><strong>PEO</strong> Polyethylene-oxide</td>
<td>40% water – ethanol solution</td>
<td>3 – 4 %</td>
<td>3 – 12</td>
<td>good and stable process for voltage up to 10kV</td>
</tr>
<tr>
<td>II</td>
<td><strong>DBC</strong>*</td>
<td>Ethanol</td>
<td>2-29%</td>
<td>6 – 16</td>
<td>fairly good</td>
</tr>
<tr>
<td>III</td>
<td><strong>TAC</strong>*</td>
<td>Ethanol</td>
<td>7-30 %</td>
<td>3 – 30</td>
<td>polymer too viscous</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1-7 %</td>
<td>10 – 30</td>
<td>difficult</td>
</tr>
<tr>
<td>IV</td>
<td><strong>PAN</strong>*</td>
<td>DMF</td>
<td>1-25 %</td>
<td>5 – 25</td>
<td>very good</td>
</tr>
</tbody>
</table>

*Prepared at Technical University of Łódź by dr Anna Błasińska
Parametric study

- Polymer: PEO
- Concentration: c=3%
- Solvent: 40% water-ethanol solution
- H=215mm
- V=8kV

$L(t)$ – instability of length of the rectilinear part
Parametric study

- Polymer: PEO
- Concentration: c=4%
- Solvent: 40% water-ethanol solution
- H=215mm

$L (V)$ – length of the rectilinear part
$\Omega (V)$ – angle of the envelope cone
Parametric study

- Polymer: PEO
- Concentration: c=4%
- Solvent: 40% water-ethanol solution
- H=215mm

U(V) – velocity of the fibre at the rectilinear part
Electrospinning observed at 25fps

- Polymer: DBC
- Concentration: c=9%
- Solvent: ethanol
- H=215mm
- V=6kV

12 cm
Different structure of spinning fibres for DBC polymer

DBC: c=9% H=215mm

U=6kV

U=12kV
Parametric study

- Polymer: DBC
- Concentration: c=9%
- Solvent: ethanol
- H=215mm

$L (V)$ – length of the rectilinear part

$\Omega (V)$ – angle of the envelope cone
Electrospinning observed at 25fps

- Polymer: PAN
- Concentration: c=15%
- Solvent: DMF
- H=215mm
- V=13kV

12 cm
Different structure of spinning fibres for PAN polymer

\[ \text{PAN: } c=15\% \; H=215\text{mm} \]

\[ \text{U}=13\text{kV} \quad \text{U}=19\text{kV} \]
Parametric study

- Polymer: PAN
- Concentration: c=15%
- Solvent: DMF
- H=215mm

L (V) – length of the rectilinear part

Ω (V) – angle of the envelope cone
Comparison of PEO & DBC & PAN polymers

**PEO**

- $L(V)$ – length of the rectilinear part
- $\Omega(V)$ – angle of the envelope cone

**DBC**

**PAN**

Conclusions

Electrostatic elongation of polymer threads allows to produce relatively easily fibres in nano range diameters.

Collection of nano-woven of bio-active polymers, e.g., chitin may have practical application for tissue growth.

Electrospinning of polymer solutions still lacks detailed mathematical model, necessary to perform process optimisation.
We would like to acknowledge the valuable contribution of dr Anna Błasińska from TU of Łódź and Anna Blim from IPPT PAN in the work presented.

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