Plasma-assisted Deposition of Antimicrobial Silver Nanoparticles on Medical Textiles

Dr. Andrea Zille
azille@2c2t.uminho.pt
Introduction

Healthcare-associated infections (HAIs) - statistics

6% of the patients in European hospitals are infected at least 1 HAI

European Centre for Disease Prevention and Control Website Data
Introduction

Healthcare-associated infections (HAIs) - statistics

- Respiratory tract: 26%
- Urinary tract: 21%
- Surgical site: 16%
- Bloodstream: 18%
- Gastrointestinal: 7%
- Skin: 4%
- Other: 8%

European Centre for Disease Prevention and Control Website Data
Introduction

Healthcare-associated infections (HAIs) - main concerns

Health risk

Health costs

Antibacterial resistance

New antibacterial materials are needed
Introduction

Metal Nanoparticles

Ag  Cu  ZnO

Unique Chemical and Physical Properties

Antimicrobial  Antiviral  Anti-inflammatory
Introduction

AgNPs employment - main disadvantages

• The release and fate of silver nanoparticles into the environment
Introduction

AgNPs employment - main disadvantages

- AgNPs can display cytotoxicity and genotoxicity in human body.
Workflow

1. Nanoparticles dispersions
2. Plasma treatment optimization
3. Nanoparticles deposition
4. Antimicrobial and cytotoxicity analyses
Substrates and Plasma

- Nanoparticles dispersion
- Plasma treatment optimization
- Nanoparticles deposition
- Antimicrobial and cytotoxicity analysis

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Nanoparticles dispersion</th>
<th>Plasma treatment optimization</th>
<th>Nanoparticles deposition</th>
<th>Antimicrobial and cytotoxicity analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA66 Woven</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PES Woven</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PES Non woven</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

PVP-AgNPs Dispersions
- Ethanol 70%
- Water
- Water + Alginate (0.25%)
- Water + Chitosan (0.25%)

DBD plasma optimized parameters
- 1 kW, 4 m min\(^{-1}\)
- 2.5 - 5 kW min m\(^{-2}\) of dosage
- 5 - 10 Plasma passages
Deposition Methods

- Ultrasound Tip
  Irregular distribution despite its local good deposition

- Dip Coating
  Low amount of AgNPs and agglomeration

- Spray
  Low amount of AgNPs but low agglomeration

- Exhaustion at 30°C
  The best results for both NPs distribution and reduced agglomeration.

- The spray and exaustion at 30°C was used to continue the work.
# Outlines

<table>
<thead>
<tr>
<th>1. Different approaches for preparation of the 1 mg mL(^{-1}) PVP-AgNPS dispersions and its effect in deposition step</th>
</tr>
</thead>
<tbody>
<tr>
<td>2. pH effect in PVP-AgNPs deposition onto PES</td>
</tr>
<tr>
<td>3. Development of sandwich configurations using HMDSO and chitosan</td>
</tr>
<tr>
<td>4. Synthesis of citrate-capped 20 nm AgNPs and its deposition</td>
</tr>
</tbody>
</table>
PA66 knitted - 1 mg mL⁻¹ PVP-AgNPS
PES woven - 1 mg mL\(^{-1}\) PVP-AgNPS
PES nonwoven- 1 mg mL⁻¹ PVP-AgNPS

Ethanol | Water | Water + Alginate

D | D | D
D | D | D
D | D | D
Specular reflectance

- **PES NW 10 - E**
- **PESNW 5 - E**
- **PESNW 0 - E**
- **PESNW 5 - W - A**
- **PES NW 10 - W - A**
- **PESNW 0 - W - A**
- **PES 0 - E**
- **PES 5 - E**
- **PES 10 - W - A**
- **PES 5 - W - A**
- **PA 10 - W**
- **PES 0 - W - A**
- **PES 10 - E**
- **PA 10 - W - A**
- **PA 5 - W - A**
- **PA 5 - W**
- **PA 0 - W**
- **PA 0 - W - A**
- **PES 5 - W**
- **PESNW 5 - W**
- **PES NW 10 - W**
- **PES 10 - W**
- **PA 0 - E**
- **PA 10 - E**
- **PA 5 - E**
- **PESNW 0 - W**
- **PES 0 - W**

- **PA66**
- **PES**
- **PES NW**
Atomic Absorption Spectroscopy

[PVP-AgNPS] adsorption (%)

- **PA66**
- **PES**
- **PES NW**
# pH effect, PVP-AgNPs onto PES

## PVP-AgNPs Dispersions

<table>
<thead>
<tr>
<th>1 mg mL⁻¹ PVP-AgNPs dispersions</th>
<th>pH 4 – Acetate buffer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH 5 – Acetate buffer</td>
</tr>
<tr>
<td></td>
<td>pH 7 – Phosphate buffer</td>
</tr>
<tr>
<td></td>
<td>pH 9 – Tris buffer</td>
</tr>
</tbody>
</table>

## Textile Substrates

<table>
<thead>
<tr>
<th>PES Woven</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Area density</strong></td>
</tr>
<tr>
<td><strong>Warp density</strong></td>
</tr>
<tr>
<td><strong>Weft density</strong></td>
</tr>
</tbody>
</table>

## DBD plasma optimized parameters:

- **1 kW, 4 m min⁻¹**
- **2.5 - 5 kW min m⁻² of dosage**
- **5 - 10 Plasma passages**

### Deposition method

- Exhaustion at 30°C
pH effect, PVP-AgNPs onto PES
Specular reflectance pH effect, PVP-AgNPs onto PES
Sandwich configurations

<table>
<thead>
<tr>
<th>PVP-AgNPs Dispersion</th>
<th>1 mg mL⁻¹ PVP-AgNPs dispersions in Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Textile Substrates</td>
<td>PA66 Knitted, PES Woven, PES Non woven</td>
</tr>
<tr>
<td>DBD plasma optimized parameters:</td>
<td></td>
</tr>
<tr>
<td>1 kW, 4 m min⁻¹</td>
<td></td>
</tr>
<tr>
<td>5 kW min m² of dosage</td>
<td></td>
</tr>
<tr>
<td>10 Plasma passages</td>
<td></td>
</tr>
<tr>
<td>Deposition method</td>
<td></td>
</tr>
<tr>
<td>Exhaustion at 30°C</td>
<td></td>
</tr>
<tr>
<td>Spray</td>
<td></td>
</tr>
</tbody>
</table>

A - Spray: HMDSO + AgNPs
B - Spray: HMDSO + AgNPs + HMDSO
C - Spray: Chitosan + AgNPs
D - Spray: Chitosan + AgNPs + Chitosan
E - Exhaustion 30°C w/ AgNPs
F - Exhaustion 30°C w/ AgNPs + HMDSO
G - Exhaustion 30°C w/ AgNPs + Chitosan
Specular reflectance – PA66- Layer by layer

Control Ex. 30°C – HMDSO 0P
Control Spray – Chitosan 0P
Control Spray – HMDSO 10P
Control Ex. 30°C – Chitosan 0P
Control Ex. 30°C – EtOH 0P
Control Spray – EtOH 0P
Control Spray – HMDSO OP
Control Ex. 30°C – EtOH 10P
Control Ex. 30°C – HMDSO 10P
Control Ex. 30°C – Chitosan 10P
Control Spray – EtOH 10P
Control Spray – Chitosan 10P
Spray: HMDSO + AgNPs + HMDSO 0P
Spray: Chitosan + AgNPs 0P
Spray: HMDSO + AgNPs + HMDSO 10P
Spray: Chitosan + AgNPs + Chitosan 0P
Spray: Chitosan + AgNPs 10P
Spray: HMDSO + AgNPs 10P
Spray: HMDSO + AgNPs 0P
Spray: Chitosan + AgNPs + Chitosan 10P
Control Spray – AgNPs 0P
Control Spray – AgNPs 10P
Ex. 30°C w/ AgNPs 0P
Ex. 30°C w/ AgNPs 10P
Ex. 30°C w/ AgNPs + Chitosan 0P
Ex. 30°C w/ AgNPs + Chitosan 10P
Ex. 30°C w/ AgNPs + HMDSO 0P
Ex. 30°C w/ AgNPs + HMDSO 10P
Ex. 30°C w/ AgNPs + Chitosan 0P
Specular reflectance – PES W- Layer by layer

- Control Spray – HMDSO 0P
- Control Spray – Chitosan 0P
- Control Spray – EtOH 0P
- Control Ex. 30ºC – HMDSO 0P
- Control Ex. 30ºC – HMDSO 10P
- Control Ex. 30ºC – EtOH 10P
- Control Spray – HMDSO 10P
- Control Spray – EtOH 10P
- Control Ex. 30ºC – EtOH 0P
- Control Ex. 30ºC – Chitosan 0P
- Control Spray – Chitosan 10P
- Control Ex. 30ºC – Chitosan 10P
- Spray: HMDSO + AgNPs + HMDSO 0P
- Spray: HMDSO + AgNPs 10P
- Control Spray – AgNPs 10P
- Spray: HMDSO + AgNPs + HMDSO 10P
- Spray: Chitosan + AgNPs 0P
- Spray: Chitosan + AgNPs 10P
- Spray: HMDSO + AgNPs 0P
- Spray: Chitosan + AgNPs + Chitosan 10P
- Control Spray – AgNPs 0P
- Spray: Chitosan + AgNPs + Chitosan 10P
- Ex. 30ºC w/ AgNPs + HMDSO 0P
- Ex. 30ºC w/ AgNPs + HMDSO 10P
- Ex. 30ºC w/ AgNPs 0P
- Ex. 30ºC w/ AgNPs + Chitosan 0P
- Ex. 30ºC w/ AgNPs + Chitosan 10P
- Ex. 30ºC w/ AgNPs + HMDSO 10P
- Ex. 30ºC w/ AgNPs 10P
- Control Spray – Chitosan 0P
- Control Spray – HMDSO 0P
- Control Spray – EtOH 0P
- Control Ex. 30ºC – HMDSO 0P
- Control Ex. 30ºC – HMDSO 10P
- Control Ex. 30ºC – EtOH 10P
- Control Spray – HMDSO 10P
- Control Spray – EtOH 10P
- Control Ex. 30ºC – EtOH 0P
- Control Ex. 30ºC – Chitosan 0P
- Control Spray – Chitosan 10P
- Control Ex. 30ºC – Chitosan 10P
Specular reflectance – PES NW- Layer by layer

- Control Spray – Chitosan 0P
- Control Ex. 30°C – EtOH 0P
- Control Ex. 30°C – Chitosan 10P
- Control Ex. 30°C – HMDSO 10P
- Control Spray – EtOH 0P
- Control Spray – HMDSO 0P
- Control Ex. 30°C – Chitosan 0P
- Control Ex. 30°C – HMDSO 0P
- Control Spray – EtOH 10P
- Control Spray – Chitosan 10P
- Control Spray – HMDSO 10P
- Control Spray – AgNPs 0P
- Spray: HMDSO + AgNPs + HMDSO 0P
- Control Spray – AgNPs 10P
- Spray: Chitosan + AgNPs 0P
- Spray: HMDSO + AgNPs 10P
- Spray: HMDSO + AgNPs + HMDSO 10P
- Spray: HMDSO + AgNPs 0P
- Spray: Chitosan + AgNPs + Chitosan 0P
- Spray: Chitosan + AgNPs 10P
- Ex. 30°C w/ AgNPs + HMDSO 0P
- Spray: Chitosan + AgNPs + Chitosan 10P
- Ex. 30°C w/ AgNPs + Chitosan 0P
- Ex. 30°C w/ AgNPs + HMDSO 10P
- Ex. 30°C w/ AgNPs + HMDSO 10P
- Ex. 30°C w/ AgNPs 0P
- Ex. 30°C w/ AgNPs 10P
- Ex. 30°C w/ AgNPs + Chitosan 10P

R (%)
# Cytotoxicity analyses PES W

<table>
<thead>
<tr>
<th>Sample</th>
<th>No DBD</th>
<th>DBD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control PESW</td>
<td>32.82 ± 16.80</td>
<td>104.31 ± 8.58</td>
</tr>
<tr>
<td>Control Spray-EtOH</td>
<td>0.53 ± 0.84</td>
<td>82.54 ± 7.69</td>
</tr>
<tr>
<td>Control Spray-AgNPs</td>
<td>5.70 ± 6.15</td>
<td>83.73 ± 9.53</td>
</tr>
<tr>
<td>Control Spray-HMDSO</td>
<td>0.41 ± 0.87</td>
<td>87.00 ± 7.59</td>
</tr>
<tr>
<td>Control Ex. 30°C - EtOH</td>
<td>95.80 ± 9.22</td>
<td>102.47 ± 10.60</td>
</tr>
<tr>
<td>Control Ex. 30°C - HMDSO</td>
<td>99.96 ± 9.22</td>
<td>101.42 ± 3.71</td>
</tr>
<tr>
<td>Spray HMDSO + AgNPs</td>
<td>5.25 ± 8.48</td>
<td>98.67 ± 7.64</td>
</tr>
<tr>
<td>Spray HMDSO + AgNPs + HMDSO</td>
<td>0.09 ± 0.44</td>
<td>97.13 ± 2.67</td>
</tr>
<tr>
<td>Ex. 30°C with AgNPs</td>
<td>83.71 ± 4.70</td>
<td>20.96 ± 4.60</td>
</tr>
<tr>
<td>Ex. 30°C with AgNPs + HMDSO</td>
<td>49.40 ± 7.71</td>
<td>32.31 ± 8.16</td>
</tr>
</tbody>
</table>
## Cytotoxicity analyses PES NW

<table>
<thead>
<tr>
<th>Sample</th>
<th>No DBD</th>
<th>DBD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control PESNW</td>
<td>54.89 ± 5.87</td>
<td>98.99 ± 7.62</td>
</tr>
<tr>
<td>Control Spray-EtOH</td>
<td>20.01 ± 5.80</td>
<td>90.70 ± 6.24</td>
</tr>
<tr>
<td>Control Spray-AgNPs</td>
<td>62.44 ± 3.69</td>
<td>102.61 ± 1.91</td>
</tr>
<tr>
<td>Control Spray-HMDSO</td>
<td>84.47 ± 2.61</td>
<td>91.66 ± 6.18</td>
</tr>
<tr>
<td>Control Ex. 30°C - EtOH</td>
<td>93.51 ± 8.81</td>
<td>88.66 ± 4.18</td>
</tr>
<tr>
<td>Control Ex. 30°C - HMDSO</td>
<td>87.56 ± 6.30</td>
<td>83.49 ± 7.01</td>
</tr>
<tr>
<td>Spray HMDSO + AgNPs</td>
<td>70.32 ± 3.51</td>
<td>96.12 ± 8.64</td>
</tr>
<tr>
<td>Spray HMDSO + AgNPs + HMDSO</td>
<td>62.62 ± 3.94</td>
<td>98.28 ± 7.19</td>
</tr>
<tr>
<td>Ex. 30°C with AgNPs</td>
<td>92.49 ± 5.96</td>
<td>1.67 ± 1.77</td>
</tr>
<tr>
<td>Ex. 30°C with AgNPs + HMDSO</td>
<td>87.05 ± 6.28</td>
<td>0.39 ± 0.81</td>
</tr>
</tbody>
</table>
Specular reflectance – 0, 5 and 10 washing cycles

1 WC = 15 minutes at 75°C
Antimicrobial analyses – 0, 5 and 10 washing cycles

S. aureus

<table>
<thead>
<tr>
<th>Washing Cycles</th>
<th>Bacterial Reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 WC</td>
<td>98.0</td>
</tr>
<tr>
<td>5 WC</td>
<td>98.5</td>
</tr>
<tr>
<td>10 WC</td>
<td>99.0</td>
</tr>
<tr>
<td>0 WC</td>
<td>99.5</td>
</tr>
<tr>
<td>5 WC</td>
<td>100.0</td>
</tr>
</tbody>
</table>

PA66-K

- No DBD
- DBD

PES-W

- No DBD
- DBD
Antimicrobial analyses – 0, 5 and 10 washing cycles

E. Coli

<table>
<thead>
<tr>
<th>Bacterial reduction (%)</th>
<th>0 WC</th>
<th>5 WC</th>
<th>10 WC</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA66-K</td>
<td>🟥</td>
<td>🟥</td>
<td>🟥</td>
</tr>
<tr>
<td>PES-W</td>
<td>🟦</td>
<td>🟦</td>
<td>🟦</td>
</tr>
</tbody>
</table>

No DBD

DBD
Acknowledgments

Andrea Zille acknowledge M-ERA E.U. PLASMATEX project and FCT through the Investigator FCT Research contract (IF/00071/2015) and the project POCI-01-0145-FEDER-007136 and UID/CTM/00264 under the COMPETE and FCT/MCTES (PIDDAC) co-financed by European funds (FEDER) through the PT2020 program.
Thank you for your attention