Sprayable Antibacterial Film: a Nanosilver Composite

Nathan Cloeter, Luis Correa, Benjamin Lee, Matt Reilly, Mercedes Valero

Materials Science and Engineering
Senior Capstone Design
Spring 2014
Overview

1. Introduction
   • Motivation
   • Design Goals
2. Technical Approach
3. Design
   • Film design
   • Solution design
4. Experimental Processes and Data
5. Prototype Process
6. Design Conclusions
7. Project Summary
Motivation

- Nanoparticles and medicine
  - Tailorability
  - Particle distribution
  - High surface area
- Nanoparticle-Polymer composites
  - Release-killing and capture-killing mechanisms
  - Coatings and films

2,700 to 4,200 bacterial units*

* - Wall Street Journal Study, 2012
Chitosan-Nanosilver Composite

Chitosan
• Simple polysaccharide
• Heavily researched for antibacterial properties
• Can synthesize nanosilver *in situ*
• Nanoparticle dispersion

Nanosilver
• Broad-spectrum antibacterial capabilities
• Tailor size and distribution
• Multiple simple synthesis methods
Design Goals

1. Film that adheres to $\text{Al}_2\text{O}_3$ – the iPhone surface
2. Maximum 50µm thickness
3. Spray application
4. Overnight drying
5. Maximum colony forming units of $5 \times 10^5$/ml
Technical Approach - Solution

- Chitosan solubility
  - Soluble in acetic acid
  - Easy to dissolve – no heat and minimal stirring
- Viscosity increases with added chitosan
  - Needs to be experimentally determined
  - Sprayable liquid – viscosity max. 200 cps (non-pressurized)
  - Assume nanoparticles are too small to affect viscosity
- Nanoparticle settling (Stoke’s law)

\[ V_0 = \frac{d^2(\rho_s - \rho) g}{18\mu} \]
Technical Approach - Nanoparticles

• Synthesis

Step A: The adsorption of silver ions onto chitosan.

\[ R{-}\text{NH}_2 + H^+ \rightarrow R{-}\text{NH}_3^+ \]
\[ R{-}\text{NH}_2 + Ag^{+} \rightarrow R{-}\text{NH}_2Ag^{+} \]
\[ R{-}\text{NH}_3^+ + Ag^{+} \rightarrow R{-}\text{NH}_2Ag^{+} + H^+ \]
\[ R{-}\text{NH}_2Ag^{+} + H_2O \rightarrow AgOH + R{-}\text{NH}_3^+ \]

Step B: The formation of silver NPs–chitosan bioconjugates.

\[ 2AgOH \rightarrow 2Ag^{+} + 2OH^- \rightarrow Ag_2O + H_2O \]
\[ Ag_2O + R’CH_2OH \rightarrow R’CHO + 2Ag + 2H_2O \]
\[ Ag_2O + R’CHO \rightarrow R’COO^- + 2Ag + 2H_2O \]

• Chitosan allows for good dispersion due to complexing

![Chitosan molecule diagram]
Technical Approach - Nanoparticles

• Silver ions are the means for antibacterial activity
  • Greater concentrations of silver nitrate
  • Greater surface area allows for greater interaction

• Tradeoff: Gibbs-Thomson

\[ r^* = \frac{2\gamma \ln(C/C_0)}{k_b T} \]

• Changes in temperature also affect particle size

Experimentally analyze both temperature and concentration for particle size and antibacterial efficacy
Antibacterial Nature of Silver

In aqueous environment

\[ 4\text{Ag}(0) + \text{O}_2 \rightarrow 2\text{Ag}_2\text{O} \]

\[ 2\text{Ag}_2\text{O} + 4\text{H}^+ \rightarrow 4\text{Ag}^+ + 2\text{H}_2\text{O} \]
Film Design

- e. coli Bacteria
- Chitosan Chain
- Silver NPs
- Al₂O₃ Layer
Critical Design Aspects

• Adhesion
  • Depends on the Al$_2$O$_3$ surface topography
  • Addition of levan to samples

• Antibacterial efficacy
  • Movement of silver ions
    • Aqueous solution
    • Hydration with PEG (polyethylene glycol)
    • Dispersion, near the surface of the film
  • Relation to nanoparticle size
    • Design for size control
Film Design

- Chitosan
  - Even arrangement, non-agglomerating

- Adhesion: van der Waals forces

\[
A = \pi^2 C Q_1 Q_2 \\
W = \frac{A}{12\pi D^2} \\
F = \frac{A}{6\pi D^3}
\]

(\sim 10^{-19} - 10^{-20} \text{ J})
Film Design

• Adhesion:
  • Mechanical adhesion
  • AFM analysis of iPhone – increased surface roughness promotes mechanical adhesion
Solution Design

• Viscosity
  • Maximum sprayable viscosity: \(200\text{cp}\)
  • Settling during drying:
    • Design: 50µm, nanoparticles \(~50\text{nm}\)
    • Wet thickness: 63µm
    • Maximum settling velocity: 13µm/8hr = 1.625µm/hr

\[
V_0 = \frac{d^2(\rho_s - \rho) g}{18 \mu}
\]

• Ideal settling viscosity: 113cp

\[
\mu_{solution} = 0.8\mu_{spray} + 0.2\mu_{settle} = 182.6\text{cp}
\]
Experimental Procedures

1. Synthesize nanoparticles (26mM and 52mM, 25°C – 95°C)

2. Make films
Solution Testing

Dynamic Light Scattering (ZetaSizer)
Solution Testing

Viscosity measurements (centipoise)
Synthesized with 10mg chitosan in 1% acetic acid

<table>
<thead>
<tr>
<th>Sample</th>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>26 mM #1</td>
<td>124.3</td>
<td>123.8</td>
<td>123.7</td>
</tr>
<tr>
<td>52 mM #1</td>
<td>120</td>
<td>119.1</td>
<td>119.6</td>
</tr>
<tr>
<td>26 mM #2</td>
<td>155.5</td>
<td>154</td>
<td>154.2</td>
</tr>
<tr>
<td>52 mM #2</td>
<td>158.8</td>
<td>161.2</td>
<td>159.2</td>
</tr>
<tr>
<td>26 mM #3</td>
<td>174.6</td>
<td>175</td>
<td>174.7</td>
</tr>
<tr>
<td>52 mM #3</td>
<td>158.5</td>
<td>158.2</td>
<td>157.7</td>
</tr>
</tbody>
</table>

Viscometer
3. Grow bacteria solution

4. Add bacterial agar to film (0h and 24h)

5. Place film in broth and grow bacteria from film
6. Spread bacteria on agar film

7. Grow and count bacteria cultures
Antibacterial Data

• Agar slurry: ~3x10^6 cells/ml
• Dilutions: (10µl of agar/600µl broth)
  - 4.9x10^4 cells/ml, 806 cells/ml, 13 cells/ml

Colony Counts - 95°C synthesized nanoparticle film
Antibacterial Efficacy

Percent reduction:
Chitosan – 100%
26mM – 95.7%
52mM – 97.9%
Experimental Obstacles

• UV sensitivity: some solution samples ruined before film development
• Film development depleted solution quantities for viscosity measurements
• Limitations with laboratory equipment and time
  • Limited amount of nanoparticle solution synthesized
  • Week-long antibacterial testing process
• Antibacterial testing is not always perfect
  • Some samples exhibited no bacterial cultures in the 0h control, indicating lack of initial bacteria in agar slurry
Prototyping

- Film that adheres to $\text{Al}_2\text{O}_3$ – the iPhone surface
- Maximum 50µm thickness
- Spray application
- Overnight drying
- Maximum colony forming units of $5 \times 10^5$/ml
Prototyping

Adhesion

Adhered to aluminum foil

Thickness: avg. 66.5µm

Thin, but not as thin as design goal
Prototyping

**Spray Application**

- Good spray dispersion

**Overnight Drying**

- All films were made overnight and all showed proper drying

Improper wetting: $\text{Al}_2\text{O}_3$ surface tension
Design Conclusions

- 10mg chitosan in 1% acetic acid is a sprayable solution
- Regardless of nanoparticle concentration
- **Stirring of synthesis solution** decreases viscosity
  - Could add more chitosan to solutions for increased efficiency

![Graph showing viscosity comparison](image-url)
Design Conclusions

• Nanoparticle sizing
  • Shows some relation to Gibbs-Thomson
  • Not enough data to correlate to antibacterial properties

Nanoparticle size based on Gibbs-Thomson effect

\[ r^* = \frac{2\gamma \ln(C/C_0)}{k_b T} \]
Design Conclusions

• Spray application
  • Surface energy of Al₂O₃ is too high – poor wetting
    • Design for another surface (commercial polymers have lower surface energies) → coating plastic cases
    • design another application method → aerosols or manual spreading via solution
Project Summary

• Technical approach
  • Gibbs-Thomson effect
  • Solution viscosity
  • Nanoparticle size, distribution, ionization

• Experimental approach
  • Viscosity measurements
  • DLS measurements
  • Antibacterial efficacy

• Prototype
  • Accomplished film development and antibacterial properties
  • Film application method was not as designed
Thank You

Department of Materials Science and Engineering

Capstone ENMA490 2014