Predicting Biofilm Resistance of UV-Curable via the Lifshitz–van der Waals/Lewis Acid-Base Approach

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Background

- Biofilm resistant coatings are often used in healthcare to reduce risk of infection related to the use of catheters, coronary stents, and IV delivery systems (Schabrun, 2009, p. 236)

- Majority of patented biofilm resistant coatings use metallic biocidal materials (Sawan, et al, 1998; Zupkas, 1999; Sawan et al, 2000; Sawan, et al, 2001)

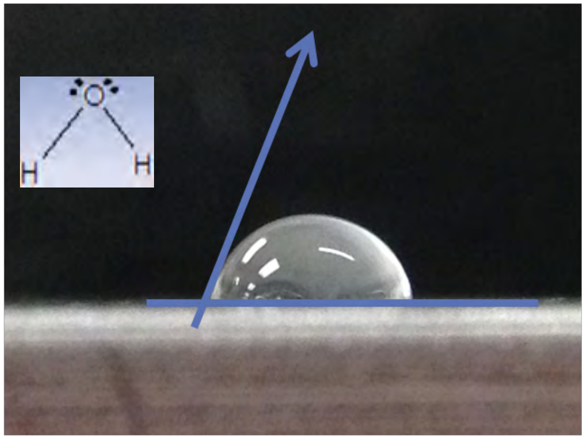
- UV-curable static coatings eliminate leaching and consumption of heavy metals

Goals

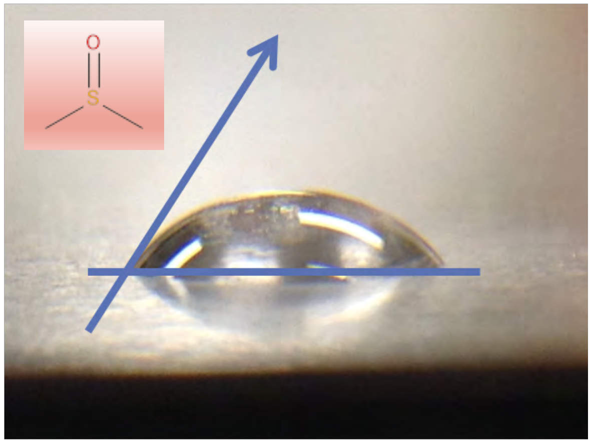
- Demonstrate biofilm resistant characteristics of UV-curable polymer coatings
- Determine surface free energy of bacteria and polymer coatings
- Determine smoothness of polymer coatings
- Evaluate trends for potential design criteria for biofilm resistant UV-curable polymer coatings

Contact Angles and the Sessile Drop Method

- 2 μL solvent drop
- Macro photography (iPad)
- Angle measurement software



Water on Aluminum



DMSO on Cold Rolled Steel

Easy Release Properties

- Surface component interactions with each other more favorable than with solvent / other surface
- Low surface energy due to favorable interactions of coating
- Large contact angle due to strong cohesive forces within the liquid
- Expected to influence interaction of bacteria and polymer coatings

General Reaction Scheme

Pendant groups:

- Phenyl (PA)
- 3-Chlorophenyl (3CPA), 4-Chlorophenyl (4CPA)
- 2,4-Dichlorophenyl (DCPA)
- 4-Bromophenyl (BPA)
- 2,4-Dibromophenyl (DBPA)
- 4-Iodophenyl (IPA)

Application and Curing Process

Automated drawdown application to varying substrates:

- Lenetta charts, glass, plastic, steel
- 100 µm (4 mil)

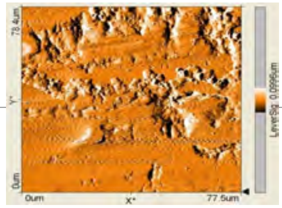
Fusion Lighthammer

Ambient and N_2 purge

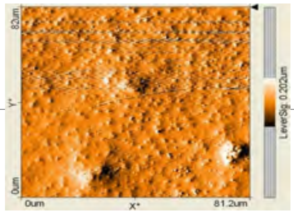
Medium pressure Hg UV source

Cured onto metal, plastic, and glass

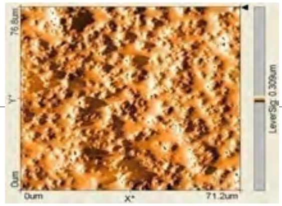
AFM



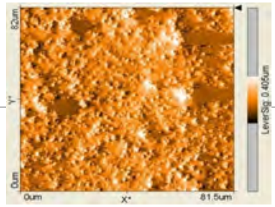
Uncoated



Formulation

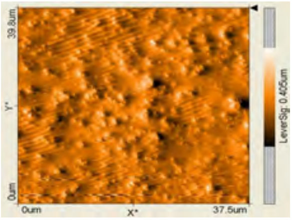


PA (20%)

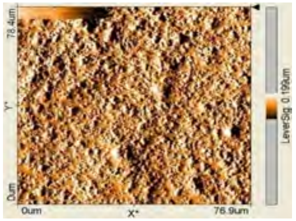


3CPA (20%)

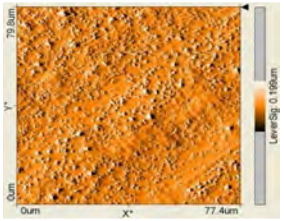
S_y (µm): 0.819 | 0.819 | 5.1233 | 0.8888



DCPA (20%)



BPA (20%)

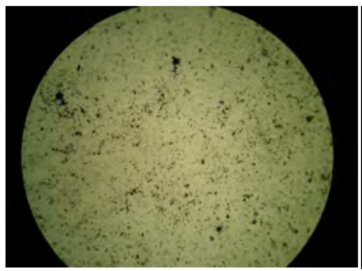
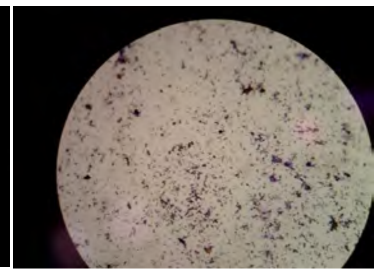
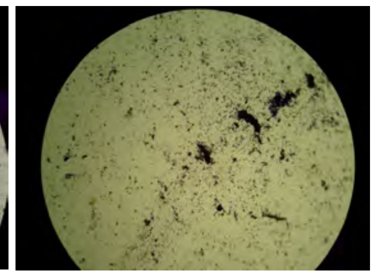
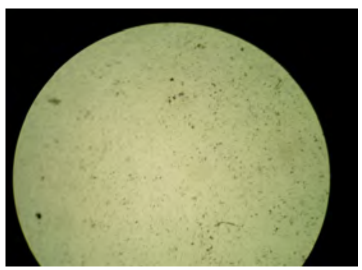
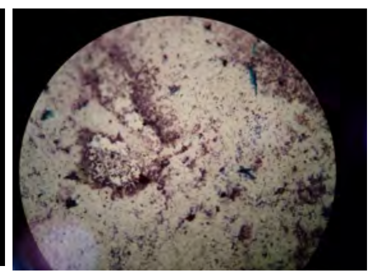
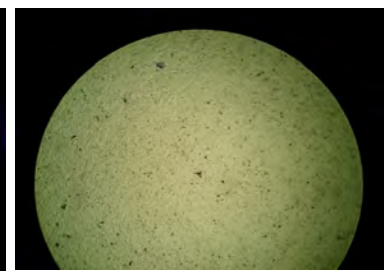


DBPA (20%)

S_y (µm): 0.6703 | 1.5117 | 0.7102

*S_y is a measure of the surface smoothness and the average peak to valley distance approximating 1.0 µm for surgical grade, electropolished steel.

Biological Results

S. aureus	Std. Commercial	20% PA	20% DBPA
Uncoated			
Coated			

Biofilm Formation Results

	E. Coli	*Staph*	*Pseudo*	*Salmon*	*Strep*
Stand.	P	P	F	P	P
PA	S	F	S	S	S
3CPA	S	S	S	S	F
DCPA	F	F	F	F	P
BPA	P	P	S	S	P
DBPA	F	P	P	P	P

P = Pass; less growth than uncoated
S = Same; same growth as uncoated
F = Fail; more growth than uncoated

Modified Young's Equation

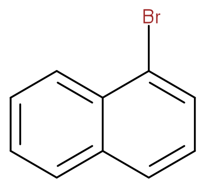
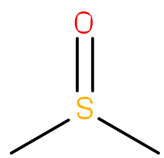
$$(1+\cos\theta_{sl})\gamma_l^{tot} = 2\left(\sqrt{\gamma_s^{LW}\gamma_l^{LW}} + \sqrt{\gamma_s^{+}\gamma_l^{-}} + \sqrt{\gamma_s^{-}\gamma_l^{+}}\right)$$

Lifshitz-van der Waal's γ^{LW}

Dipole-Dipole:

- Lewis Acid γ^{+}
- Lewis Base γ^{-}

Liquid Characterization

Liquid	Structure	γ_l^{tot}	γ_l^{LW}	γ_l^{AB}	γ_l^{+}	γ_l^{-}
Bromonaphthalene		44.4	44.4	0.0	---	---
Dimethylsulfoxide		44	36	8	0.5	32
Water	H_2O	72.8	21.8	51.0	25.5	25.5

Lide, D.R. CRC Handbook of Chemistry Physics, 90th ed,; Boca Raton: Florida, 2009: pp 6-162–6-164.

Order of Application

1.) **Bromonaphthalene**

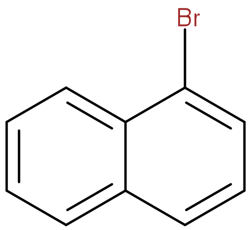
(Apolar solvent)

2.) **DMSO**

(Monopolar Lewis Base)

3.) **Water**

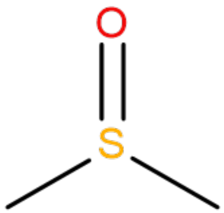
(Lewis Acid and Base Parameter)



1) Bromonaphthalene

- Apolar solvent with negligible values for γ_1^+ and γ_1^-

$$\gamma_s^{LW} = \frac{\left[\frac{1}{2}(1+\cos\theta_{sl})\gamma_l^{tot}\right]^2}{\gamma_l^{LW}}$$



2) Dimethyl sulfoxide (DMSO)

- Solvent with γ_1^+ that can be approximated as zero

$$\gamma_s^+ = \frac{\left[\frac{1}{2}(1+\cos\theta_{sl})\gamma_l^{tot} - \sqrt{\gamma_s^{LW}\gamma_l^{LW}}\right]^2}{\gamma_l^-}$$

H_2O

3) Water

- Any solvent
- Water selected for ease of contact angle analysis

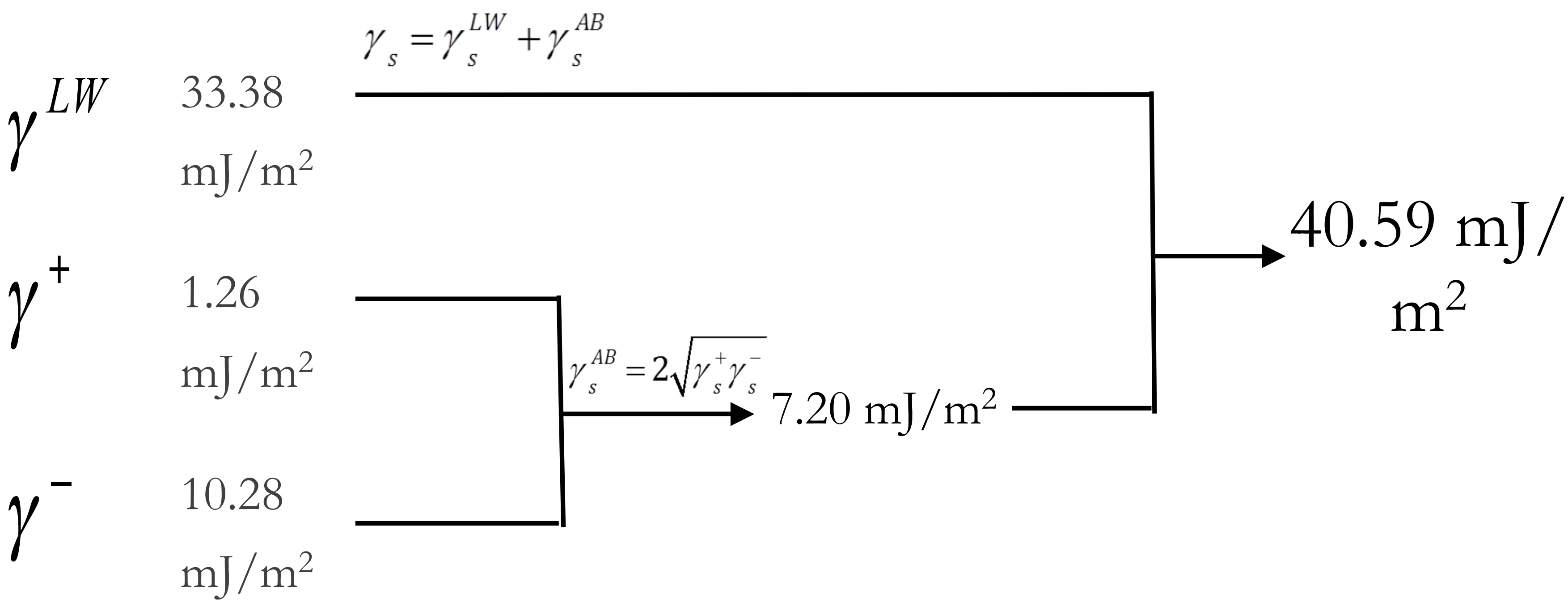
$$\gamma_s^- = \frac{\left[\frac{1}{2}(1+\cos\theta_{sl})\gamma_l^{tot} - \sqrt{\gamma_s^{LW}\gamma_l^{LW}} - \sqrt{\gamma_s^+\gamma_l^-}\right]^2}{\gamma_l^+}$$

Determination of Surface Free Energy

$$\gamma_s^{AB} = 2\sqrt{\gamma_s^+ \gamma_s^-}$$

$$\gamma_s = \gamma_s^{LW} + \gamma_s^{AB}$$

PA


$\gamma_s = \gamma_s^{LW} + \gamma_s^{AB}$
γ^{LW}
33.38 mJ/m^2
γ^{+}
1.26 mJ/m^2
γ^{-}
10.28 mJ/m^2
$\gamma_s^{AB} = 2\sqrt{\gamma_s^{+}\gamma_s^{-}}$
7.20 mJ/m^2
40.59 mJ/m^2

4-BPA

$$\gamma_s = \gamma_s^{LW} + \gamma_s^{AB}$$

γ^{LW} 35.91 mJ/m^2

γ^{+} 0.53 mJ/m^2

γ^{-} 28.16 mJ/m^2

$$\gamma_s^{AB} = 2\sqrt{\gamma_s^{+}\gamma_s^{-}}$$

7.70 mJ/m^2

43.61 mJ/m^2

DBPA

γ^{LW} 37.04 mJ/m^2

γ^{+} 1.37 mJ/m^2

γ^{-} 0.83 mJ/m^2

$\gamma_s^{AB} = 2\sqrt{\gamma_s^{+}\gamma_s^{-}}$ → 2.13 mJ/m^2

$\gamma_s = \gamma_s^{LW} + \gamma_s^{AB}$ → 39.17 mJ/m^2

P. Aeruginosa

$$\gamma_s = \gamma_s^{LW} + \gamma_s^{AB}$$

γ^{LW} 39.57 mJ/m^2

γ^{+} 0.70 mJ/m^2

γ^{-} 56.36 mJ/m^2

$$\gamma_s^{AB} = 2\sqrt{\gamma_s^{+}\gamma_s^{-}}$$

12.59 mJ/m^2

52.16 mJ/m^2

S. Aureus

γ^{LW} 33.54 mJ/m^2

γ^{+} 1.87 mJ/m^2

γ^{-} 51.75 mJ/m^2

$$\gamma_s^{AB} = 2\sqrt{\gamma_s^{+}\gamma_s^{-}}$$

19.67 mJ/m^2

$$\gamma_s = \gamma_s^{LW} + \gamma_s^{AB}$$

53.21 mJ/m^2

Comparison of Experimental Results to Surface Free Energy Determinations

- Greatest Experimental Biofilm Resistance

DBPA > BPA > PA

- Lowest Surface Free Energy
  - DBPA: 39.17 mJ/m^2
  - PA: 40.59 mJ/m^2
  - BPA: 43.61 mJ/m^2

- Smoothness

DBPA: 0.7102 µm

BPA: 1.5117 µm

PA: 5.133 µm

Application to Formulation Design

- Useful in combining resistance to different bacteria (i.e., combine polymer most resistant to *E. coli* with polymer most resistant to *S. aureus*).
- Determine the cosine of the contact angle for each component

$$\cos\theta_{sl} = \frac{2\left(\sqrt{\gamma_s^{LW}\gamma_l^{LW}} + \sqrt{\gamma_s^{+}\gamma_l^{-}} + \sqrt{\gamma_s^{-}\gamma_l^{+}}\right)}{\gamma_l^{tot}} - 1$$

- Apply Cassie's Equation to predict cosine of contact angle of mixture

$$\cos\theta_{tot} = f_1\cos\theta_1 + f_2\cos\theta_2 + \ldots + f_n\cos\theta_n \qquad f_1 + f_2 + \ldots + f_n = 1$$

Drelich, J., Wilbur, J.L., Miller, J.D., & Whitesides, G. M. *Langmuir,* **1996.** *12,* 1913-1922.

Future Work

- Concentration studies (All presented contained 20 wt% halogenated monomers)

- Additional bacteria surface free energy analyses (Clarify trend of surface free energy, biofilm resistance)

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