Adhesion and Interfacial Failure in Drug Eluting Stents
Cardiovascular disease is the leading cause of death across the world.

It represents about 30% of all deaths.

Stents represent a life saving technology for arteriosclerosis.

Drug Eluting Stents (DES) reduce the possibility of clotting after stent insertion.
Drug-Eluting Stents

AFM Adhesion Pull-Off Force Measurement

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AFM Adhesion Pull-Off Force Measurement

Silane coated tip on Parylene/Silane treated E-polished 316L substrate

Pull-Off Force = 30 nm/div × 1.22 div × 0.9 N/m = 33 nN
AFM Adhesion Pull-Off Force Measurement

Different Tip-Substrate Combination

- stb316e – silane tip on bare 316L
- btb316e – bare tip on bare 316L
- pts316e – parylene tip on silane treated 316L
- sts316e – silane tip on silane treated 316L
- stps316e – silane tip on parylene/silane 316L
- ptp316e – payrlene tip on parylene/silane 316L
Experiments: AFM


Adhesion Force (nN).

- Parylene, Silane: 313
- Silane/Parylene, Silane: 292
- Parylene, Parylene: 207
- Silane/Parylene, Parylene: 118
- Parylene, Bare 316L: 320
- Silane/Parylene, Bare 316L: 257

Surface Pair (Surface 1, Surface 2)

Surface Coating

- EP 316L
- Parylene C

Average Coupon rms Roughness (nm)

- EP 316L: 106
- Parylene C: 370

Coupon STD (nm)

- EP 316L: 42
- Parylene C: 31

Average Radius (nm)
Adhesion Theory

\[ F_{ad} = \overline{F} \pi \gamma R \]

\[ \frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2} \]

\[ \gamma = \gamma_1 + \gamma_2 - \gamma_{12} \]

(a) Hertz

(b) JKR

(c) DMT

(d) Actual


Derjaguin BV, Muller VM, Toporov YP (1975) J. Colloid Interface Sci., 53, 314.

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Adhesion Theory

Johnson–Kendall–Roberts (JKR) model: describes well the contact area when the surface forces are short range in comparison to the elastic deformations they produce (i.e., compliant materials, strong adhesion forces, large tip radii)

\[ F_{JKR} = \frac{3}{2} \pi \gamma R \]

Derjaguin–Muller–Toporov (DMT): applies well in the case of long-range surface forces with an hertzian geometry (i.e., stiff materials, weak adhesion forces, small tip radii)

\[ F_{DMT} = 2\pi \gamma R \]

\[ \lambda = 2\sigma_0 \left( \frac{R}{\pi K^2 \gamma} \right)^{1/3} \]

\[ \lambda = f(\alpha) = -0.913 \ln(1 - 1.018\alpha) \]

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\[ F_{ad} = \overline{F} \pi \gamma R \]

\[ \overline{F} = 0.267\alpha^2 - 0.767\alpha + 2.000 \]

\[ \gamma = \sigma_0 h_0 \]

Typical Force-Displacement Curve

\[ \Delta = 285 \pm 58 \text{ nm} \]
Modeling AFM Adhesion

- **Parylene/316L**
  
  **Adhesion Energy:**

\[ \lambda = 2\sigma_0 \left( \frac{R}{\pi K^2 \gamma} \right)^{1/3} \]

\[ \lambda = f(\alpha) = -0.913 \ln(1 - 1.018\alpha) \]

\[ \overline{F} = 0.267\alpha^2 - 0.767\alpha + 2.000 \]

\[ \gamma = \sigma_0 h_0 \]

\[ R = 370 \text{ nm} \]

\[ F_{ad} = 320 \text{ nN} \]

Lorentz–Berthelot mixing rule:

\[ h_{012} = \frac{1}{2}(h_{01} + h_{02}) \]
Fracture Mechanics

Fracture Mechanics Problem:

- Mode I and Mode II stress intensity factors: $K_I$ and $K_{II}$
- Strain energy release rate:
- Mode mixity:
- Unstable Crack:

Mode I

Mode II

Mode III
Experiments: Brazil nuts

Energy release rate: \[ G = \frac{1}{E} \left( K_I^2 + K_{II}^2 \right) \]

Loading phase: \[ \psi = \tan^{-1} \left( \frac{K_{II}}{K_I} \right) + \omega + \varepsilon \ln \left( \frac{\hat{L}}{h} \right) \]

\[ K_I = f_I \rho^{-1.2} \quad K_{II} = f_{II} \rho^{-1.2} \]


Typical Fracture Surfaces: Parylene/Steel Sample #8

Figure 9 - Flat Not Marked

Figure 10 - Notch Not Marked

Figure 11 – Notch Marked

Figure 12 – Flat Marked

- **Parylene**: Spectra found >1% Cl
- **Glue**: Spectra found Mainly C and O (Indicative of GLUE)
- **Steel**: Spectra found >27% Fe (Indicative of steel)
Comparison of DMT models and Interfacial Fracture Experiments

\[ F_{DMT} = 2\pi \gamma R \]

\[ G = G_0 (1 + \tan \Psi^2) \]

![Graph showing interfacial fracture toughness comparison between DMT and Parylene Brazil Disk models.](image)
Atkinson Model

- Atkinson et al. (1982)

\[ N_I = \frac{K_I}{\sigma_0 \sqrt{\pi a}}, \quad N_{II} = \frac{K_{II}}{\sigma_0 \sqrt{\pi a}} \]

\[ \sigma_0 = \frac{P}{\pi l}. \]

\[ N_I = \sum_{i=1}^{n} T_i \left( \frac{a}{l} \right)^{2i-2} A_i(\theta), \quad N_{II} = 2\sin 2\theta \sum_{i=1}^{n} S_i \left( \frac{a}{l} \right)^{2i-2} B_i(\theta) \]

\[ A_i \text{ and } B_i \text{ are coefficients related to } \theta \]

\[ \hat{\psi} = \tan^{-1} \frac{K_{II}}{K_I} + \omega + \epsilon \ln \left( \frac{L}{h} \right) \]

\[ G = G_I + G_{II} = \frac{K_I^2 + K_{II}^2}{E_1} = \left( N_I^2 + N_{II}^2 \right) \frac{P^2}{E_1 a} \]
Evans and Hutchinson (1982) presented the row model

\[
\frac{\Delta G}{G} = \Sigma(\phi, \beta, \psi, \epsilon)
\]

\[
= + 2h \frac{\cos(\beta - \phi) \tan \psi}{\cos \varphi (1 + \tan^2 \psi)}
\]

\[
- \frac{h^2 (\sin \beta + \cos \beta \tan \psi)^2}{\cos^2 \phi (1 + \tan^2 \psi)}
\]

If \( \phi + \psi < \pi/2 \),

\[
\langle \Delta G \rangle / G = \frac{1}{\pi} \int_{\pi - \psi}^{\pi} \Sigma \, d\beta
\]

If \( \phi + \psi > \pi/2 \),

\[
\langle \Delta G \rangle / G = \frac{1}{\pi} \int_{\pi - \psi}^{3\pi/2 - \psi} \Sigma \, d\beta
\]

\[
+ \left( \frac{\phi + \psi}{\pi} - \frac{1}{2} \right)(1 - \Omega).
\]
Fundamental Mechanism of Interfacial Fracture

- A zone model was proposed for improvement

\[ \alpha = \frac{(L/l)}{\ln[1/\sin(\pi D/2l)]} \]

\[ \alpha_0 = \frac{\pi (EH^2/lG_0)}{32(1 - v^2)\ln[1/\sin(\pi D/2l)]}. \]

\[ \Delta G/G = \frac{\tan^2 \psi \left\{ 1 - k \left[ \alpha_0 (1 + \tan^2 \psi) (\Delta G/G + 1) \right] \right\}}{1 + \tan^2 \psi} \]

\[ G_i = G_0 (1 + \tan^2 \psi). \]
Crack Surface Profile Measurement

- Scanning Electron Microscopy (SEM) Images
## Material and Geometrical Parameters

<table>
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<th>Parylene</th>
<th>Interface</th>
<th>Drug</th>
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Comparison of Model Predictions

![Graph showing comparison of model predictions for Parylene](image-url)
Comparison of Model Predictions

Silane-Parylene

- Brazil Nut (Rahbar)
- AFM (Parylene) (Meng)
- Zone model (Ting)
- Row model (Ting)

G (J/m²)

ψ

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Comparison of Model Predictions

![Graph showing comparison of model predictions for different drug formulations. The graph plots the energy density G (J/m^2) against the parameter Ψ. Different lines and markers represent various models, such as Brazil Nut (Meng), AFM Drug (Meng), Zone model (Ting), and Row model (Ting).]
Summary and Concluding Remarks

- This class presents some examples of the applications of adhesion and fracture mechanics concepts to drug eluting stents.
- Pull-off forces determined from AFM experiments on bi-material pairs (useful for ranking interfaces).
- Brazil disk specimens used to measure mode mixity dependence of interfacial fracture toughness.
- Link established between molecular AFM measurements of pull-off force and surface energy.
- The surface energy estimates are in good agreement with results from Brazil disk tests.
- Trends of mode mixity fracture toughness from row/zone models in agreement with experiments.
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- Juan Meng
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Overview of Course

- Introduction to fatigue crack initiation and propagation
- Empirical fatigue models
- Fundamentals of fracture mechanics
- Toughening mechanisms
- Fundamentals of fracture – brittle/ductile and mechanisms in different classes of materials
- Frontiers of fracture mechanics – dental multilayers and biomedical stents