Centre for Research in
Engineering Surface Technology
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Synthesis and characterisation of polyurethane coatings through nanoscratch and non-contact optical profilometry

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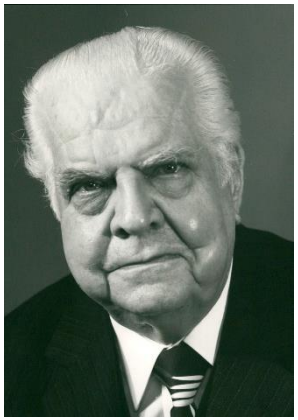
Polyurethane Overview

- Polyurethane was initially discovered by Dr. Otto Bayer in 1937 and was used as an alternative for elastic rubber.[1]

- The simple reaction between a polyol and a diisocyanate allows for rapid polyurethane formation making it very popular during World War II where resources were vital.[1]

- In the modern era, polyurethane has found many applications in industry, from medical devices to aerospace.[1]



Urethane formation

- **Polyurethane is produced through a step growth addition reaction of a hydroxyl and an isocyanate.**

- **The positively charged carbon within the isocyanate group (-N=C=O) undergoes nucleophilic attack from the oxygen of the alcohol group.[2]**

- **The alcohol's active hydrogen is added to the negatively charged nitrogen (nucleophilic addition to C=N bond).[2]**

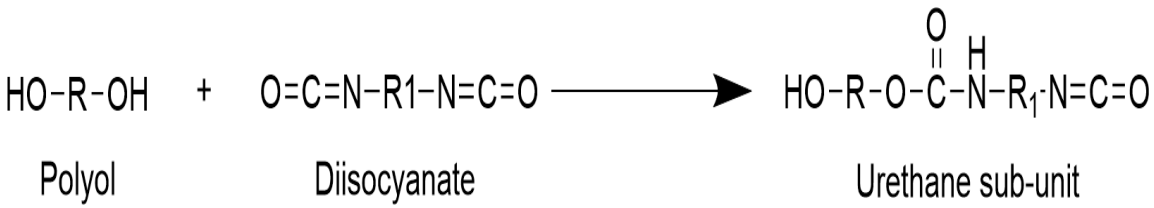


Figure 1: Polyurethane general reaction scheme

Reaction mechanism

- **The reaction proceeds via a four membered transition state including one alcohol group.[2]**

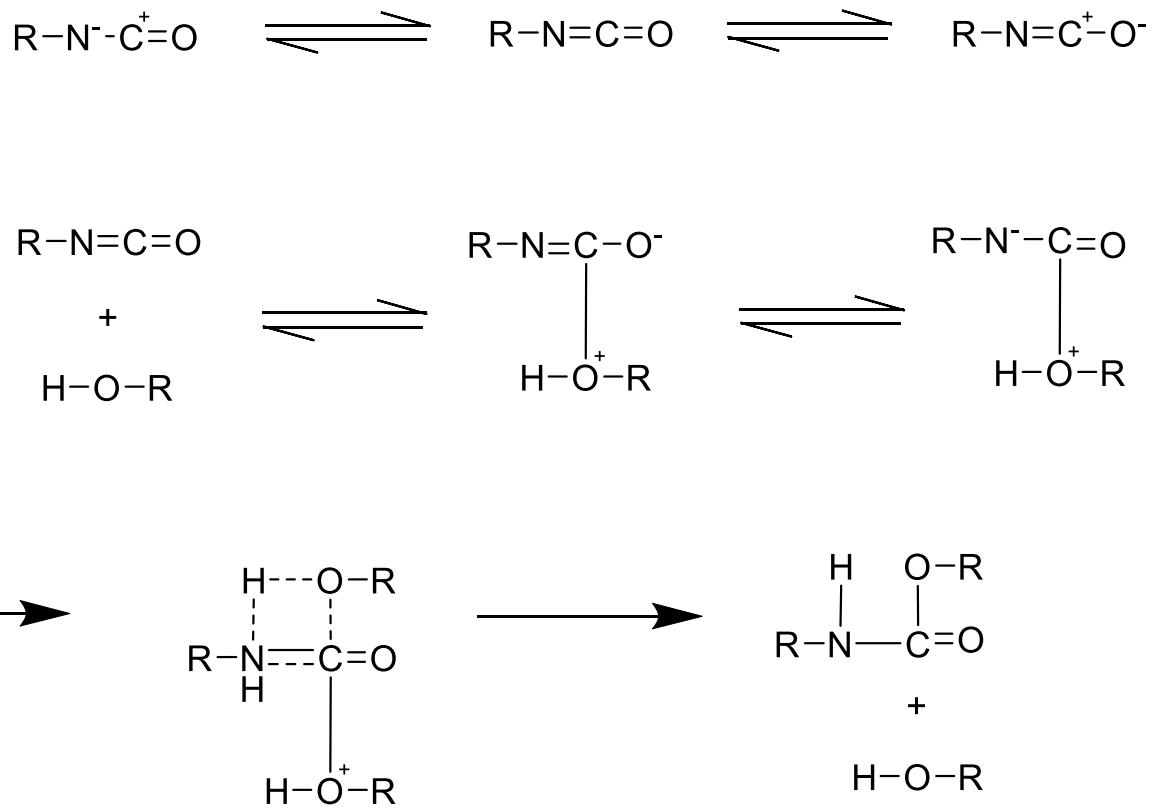


Figure 2: Polyurethane reaction mechanism [2]

Methylene diisocyanate and castor oil polyurethane as an anti microbial coating

- **Methylene diisocyanate (MDI)**
  - Rigid structure may increase durability.
  - The negative charge of the nitrogen can be delocalized into the π electron ring system.[3]
  - Aromatic delocalisation further increases the positive charge on the carbon.[3]
- **Castor oil**
  - Castor oil is environmentally friendly.
  - Branched structure increases crosslinking network and overall durability.

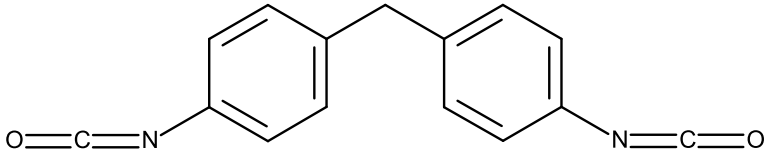


Figure 3: Methylene diisocyanate structure

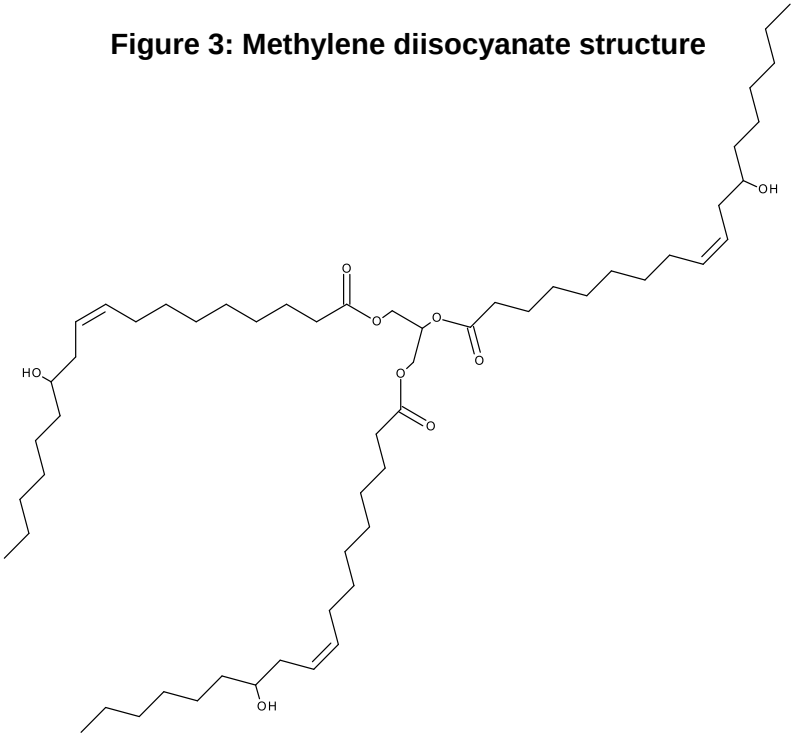
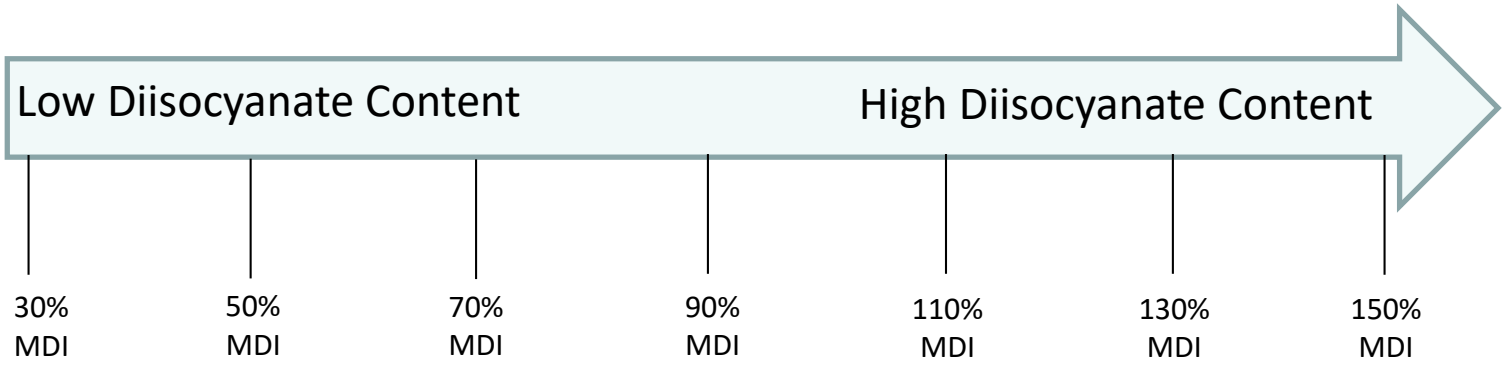


Figure 4: Castor oil structure

Methylene diisocyanate and Castor oil polyurethane - formulation

- Diisocyanate range from 30%-150% w/w
- Curing temperature - 120°C
- Substrate – Aluminium (A-36)
- Dip coated – 1000 mm/min



Spectroscopic analysis of Methylene diisocyanate and Castor oil polyurethane

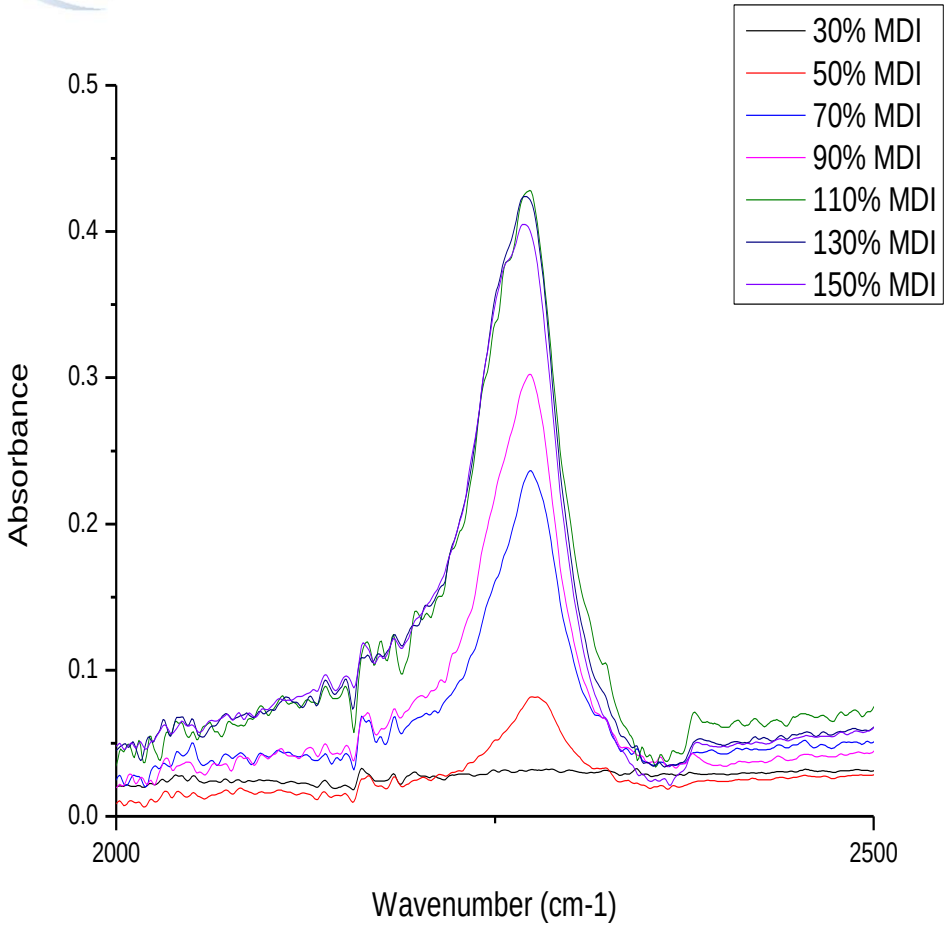


Figure 5: FT-IR analysis (isocyanate peak: 2000cm^{-1} – 2500cm^{-1}) of cured polyurethane samples

- **FT-IR spectra showing diisocyanate peak – 2250cm^{-1}.**
- **Peak increases until 110% MDI as polyurethane system becomes saturated.**
- **Saturation indicates all reaction sites are used up.**

Physical analysis of Methylene diisocyanate and Castor oil polyurethane

- **Nanoscratch**
  - Scratch and indentation are the primary methods of analysis

- **Profilometry**
  - 3D, non-contact, optical profilometer
  - Surface analysis performed through the separation of white light into a vertical range.[4]

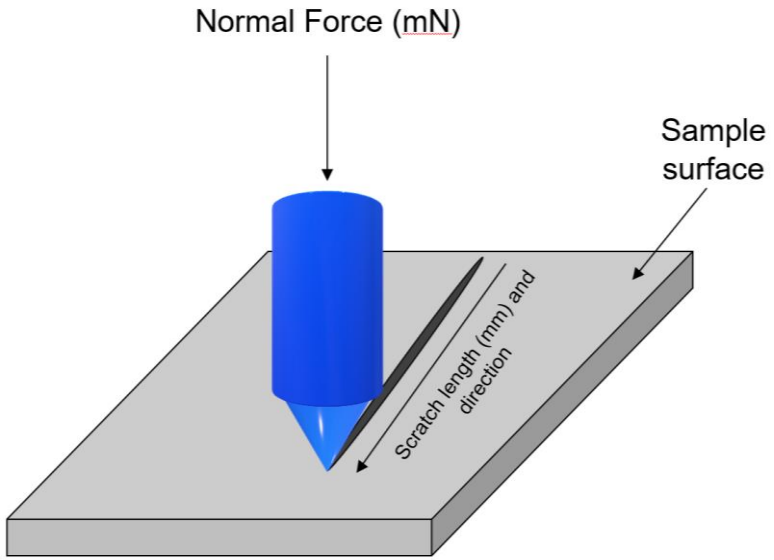


Figure 6: Nanoscratch schematic

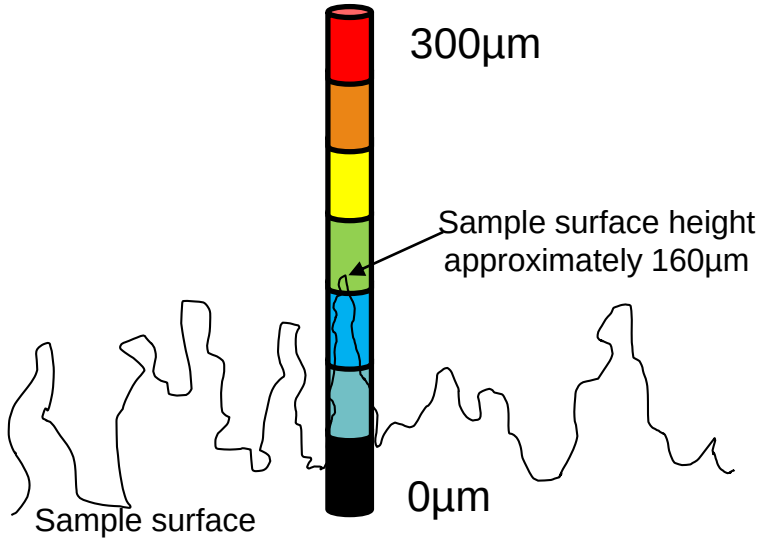


Figure 7: Height analysis through optical profilometry

JR25 Data – Optical profilometry

Table 1: Roughness values of 90% MDI sample surface

X-axis Ra (µm)	Y-axis Ra (µm)	Oblique Ra (µm)	Mean Ra (µm)	Standard Deviation (µm)
0.471	0.365	0.343	0.393	0.068

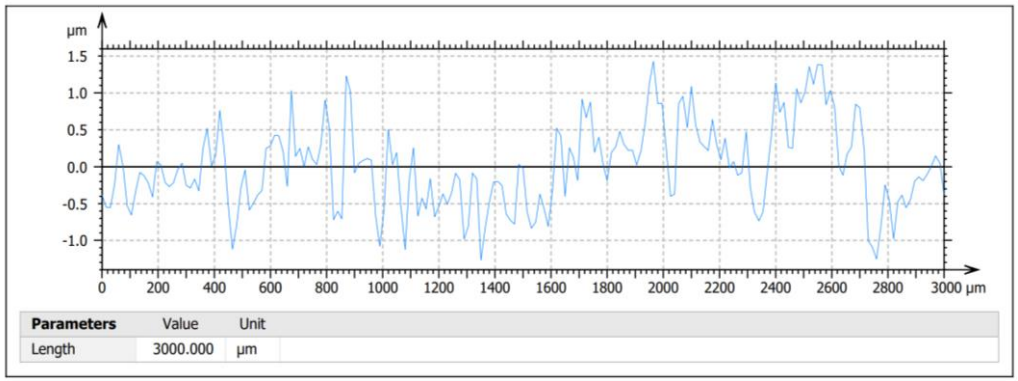


Figure 8: 90% MDI surface profile

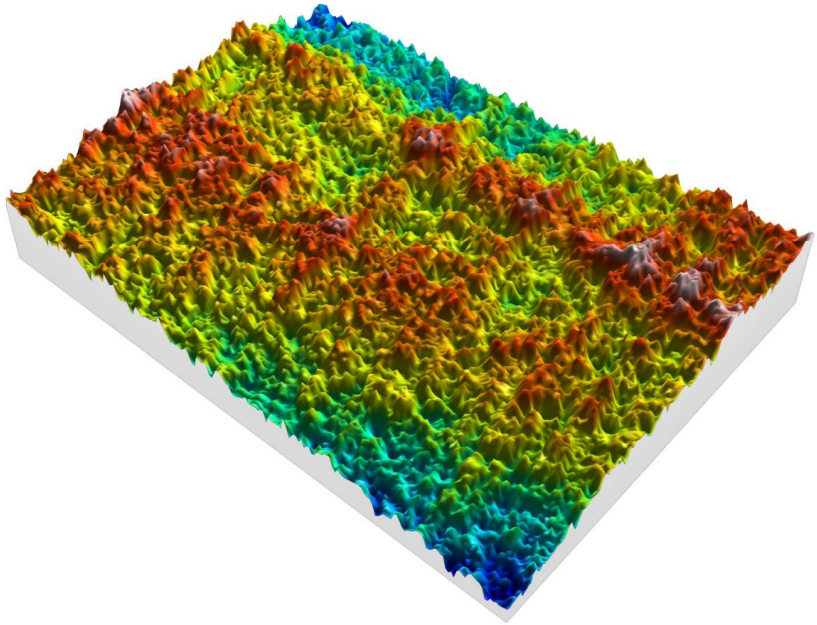


Figure 9: 90% MDI sample 3D visualisation

- **Roughness (Ra)**
  - Average of a set of individual measurements of a surface's peaks and valleys. (µm)
- **3D imaging**
  - Coating surface can be visualised through 3D processing.

CB500 Data - Nanoscratch

- **Adhesion failure force (mN)**
  - Test: 1-300 mN progressive load, 2 mm scratch length

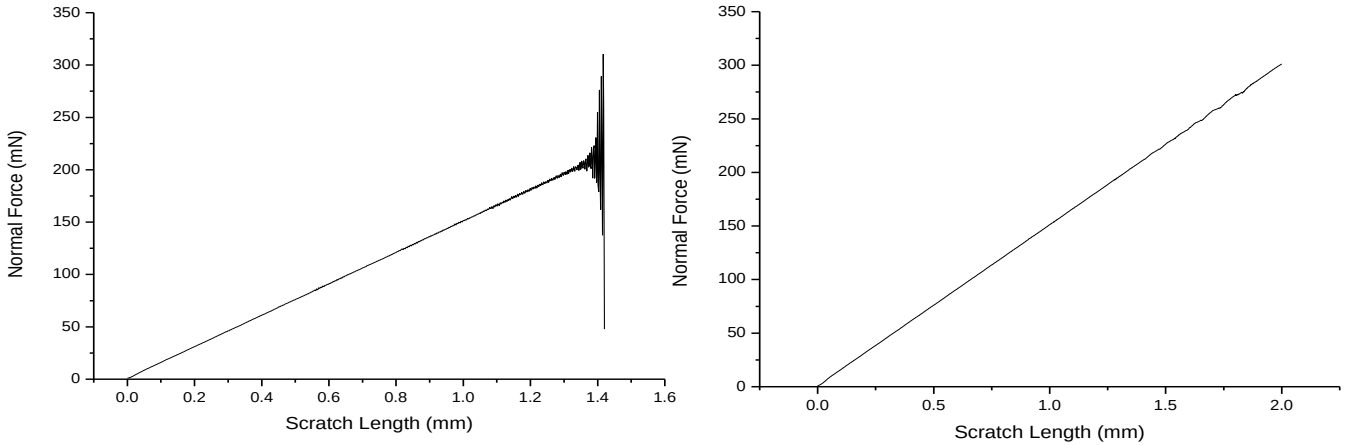


Figure 10: 30% MDI (left) and 90% MDI (right)

- **CoF**
  - Test: 60 mN constant load, 2 mm scratch length

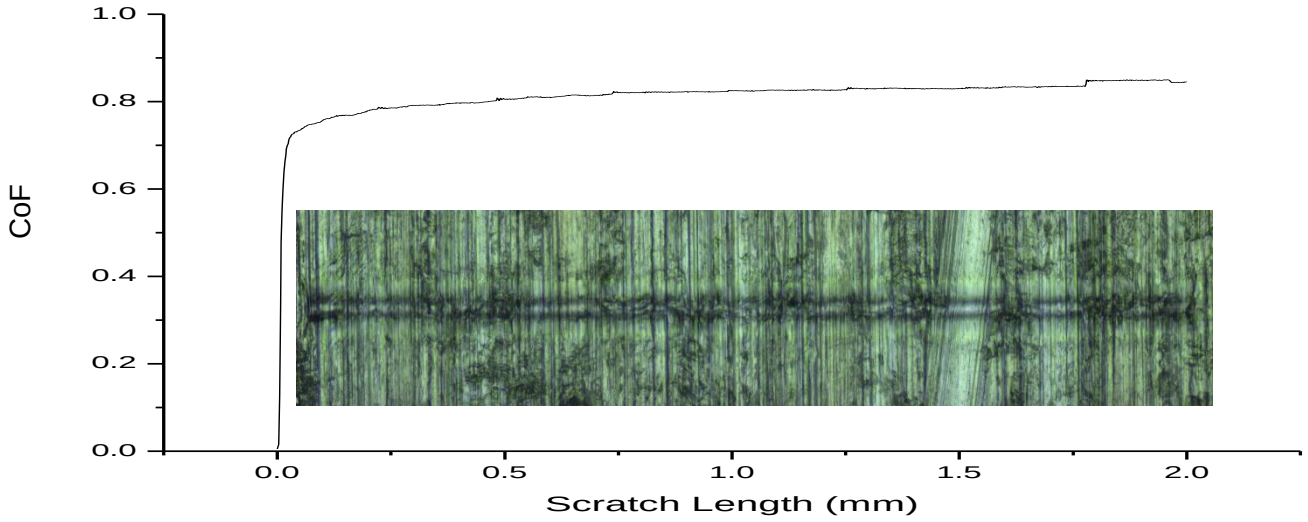


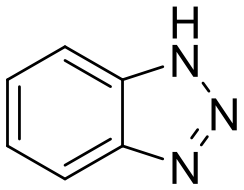
Figure 11:90% MDI CoF with microscopic image correlation

Next step – Addition of antimicrobial compounds

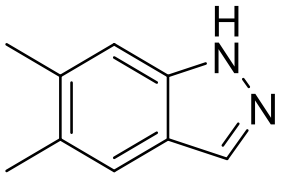
- **Addition of antimicrobial compounds to provide another advantageous characteristic.**
- **Antimicrobial compounds (0-1% w/w) addition**
  - Silvadur

Silver nanoparticles

Benzotriazole



5,6-benzimidazole



- **Bacteria to test coatings against**
  - Escherichia coli
  - Staphylococcus aureus
  - Pseudomonas aeruginosa

CB500 – Commercial use

- **Commercial work has been focused on the medical device industry.**
- **Points of interest:**
  - Particle generation
  - Coating failure mechanism
  - Coefficient of friction analysis

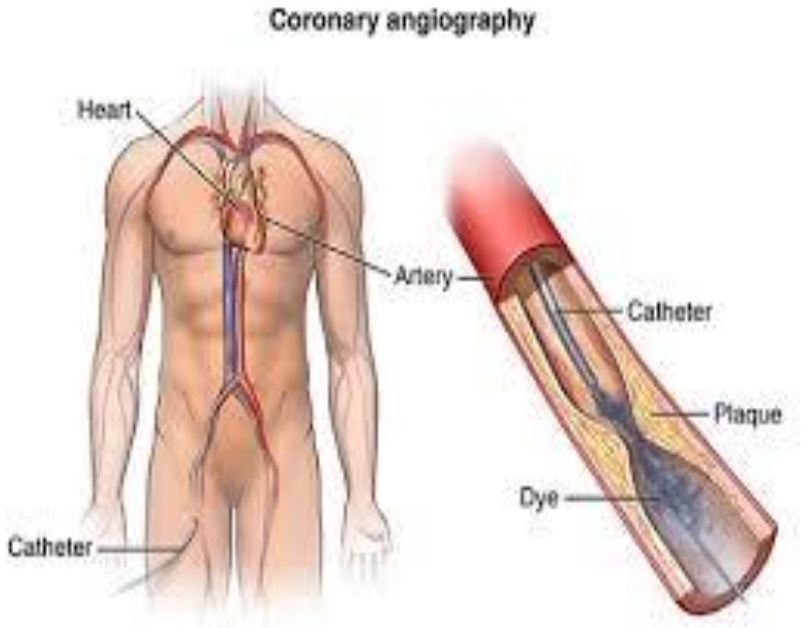


Figure 12: Cardiovascular catheterisation visualisation [7]

Commercial proprietary samples – Nitinol catheter tubing

- **Adhesion failure in wet and dry conditions**
  - Test: Progressive load 1-1000 mN, 2 mm scratch, 2 mm/min
  - Wet test: Sample submerged in PBS for 15 mins @ 37°C prior to analysis

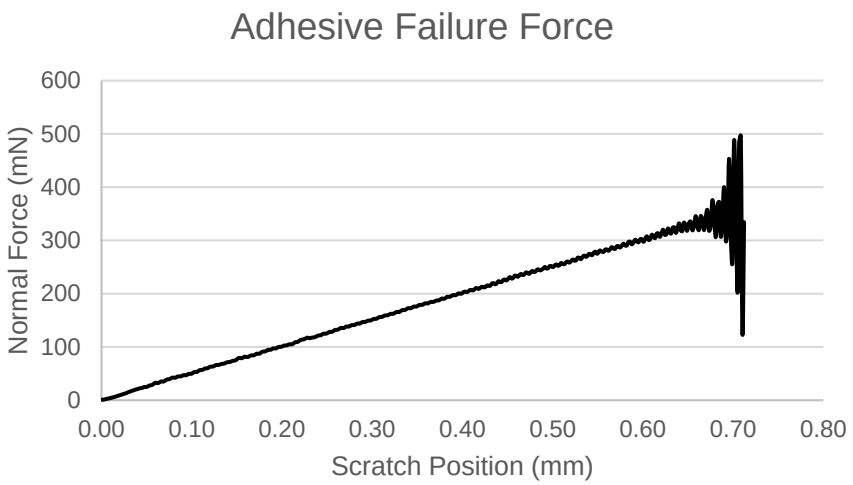


Figure 13: Sample 4 adhesive failure force under DRY conditions

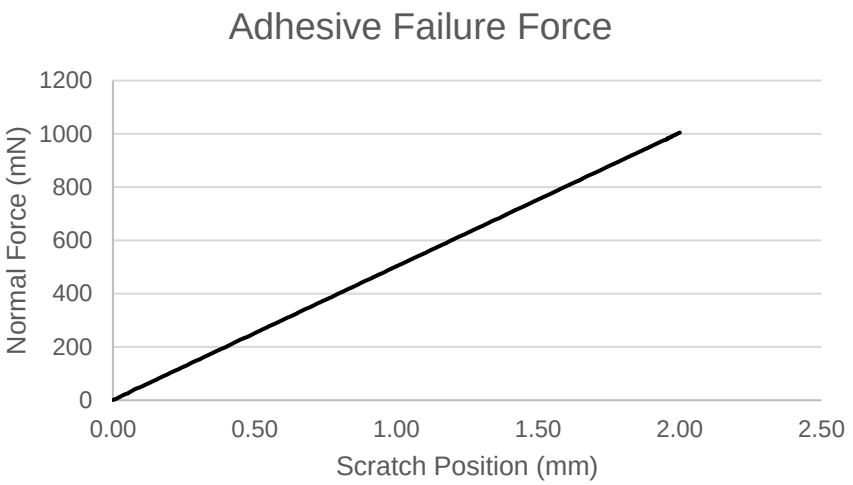


Figure 14: Sample 4 adhesive failure force under WET conditions

Surface failure - dry

Figure 15: Sample 4 coating failure under DRY conditions

Surface failure - wet

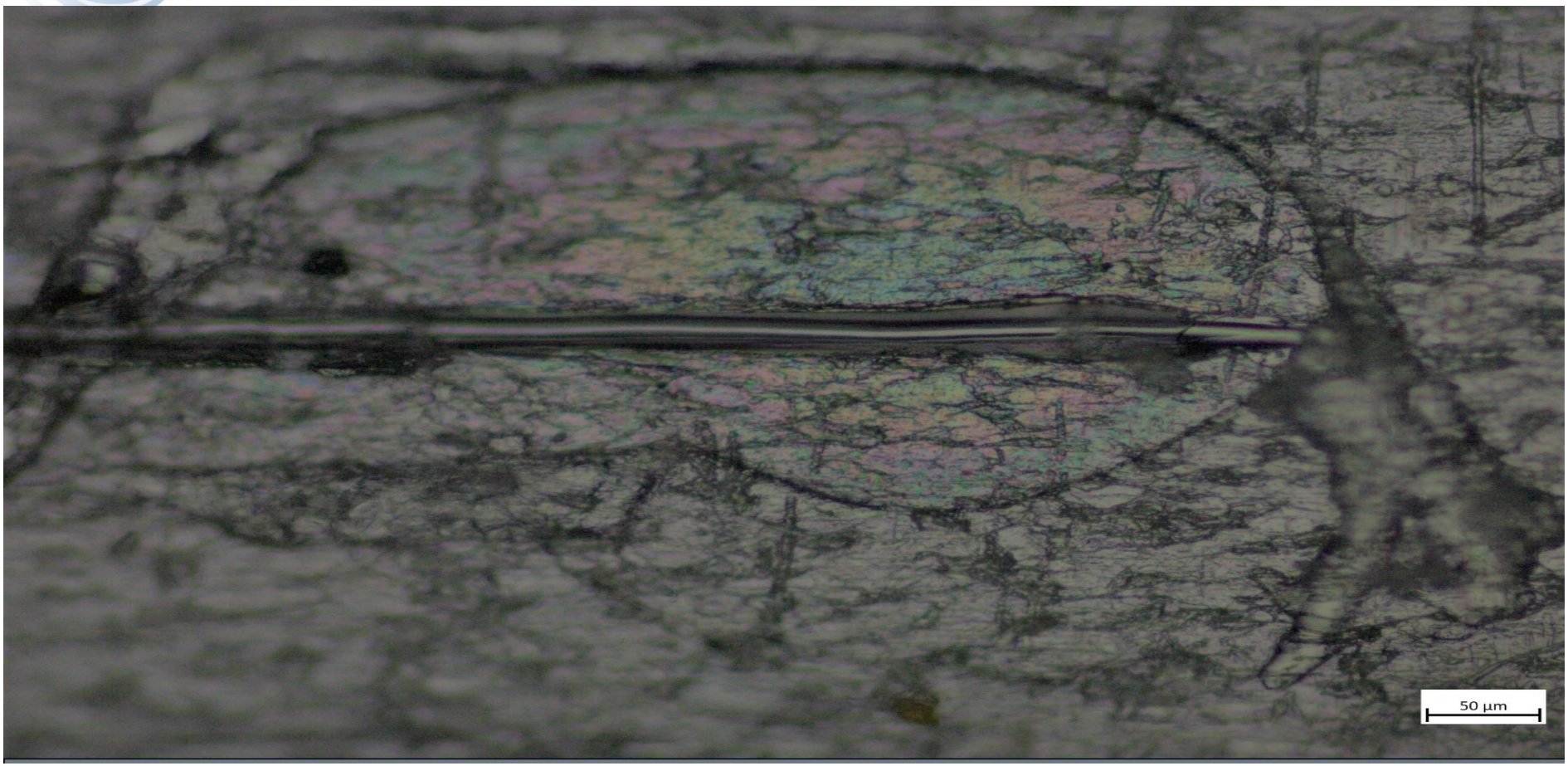


Figure 16: Sample 4 coating failure under WET conditions

Commercial proprietary samples

- **Coefficient of friction wet and dry**
  - Test: Constant load 150 mN, 2 mm scratch, 2 mm/minute
  - Wet test: Sample submerged in PBS for 15 mins @ 37°C prior to analysis

Table 2: Dry vs wet CoF analysis

Sample	Dry Average CoF	Wet Average CoF	Difference
1	0.74	0.50	-0.24
2	0.51	0.37	-0.14
3	0.73	0.55	-0.18
4	1.08	0.32	-0.76
5	1.29	0.34	-0.95

References

- 1) A. Das and P. Mahanwar, A brief discussion on advances in polyurethane applications, *Adv. Ind. Eng. Polym. Res.*, 2020, 3, 93–101.
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- 2) M.F. Sonnenschein, Polyurethanes - Science, Technology, Markets, and Trends, The Dow Chemical Company, Midland, MI, USA, 2015.
- 3) G. Raspoet, M.T. Nguyen, M. McGarraghy, & A. Hegarty, *J. Org. Chem*., 63, 6878-6885 (1998).
- 4) Nanovea, Confocal Chromatic Profilometry, https://nanovea.com/chromatic-confocal/.
- 5) Cardiac Catheterisation, https://www.hopkinsmedicine.org/health/treatment-tests-and-therapies/cardiac-catheterization.