

Project title: The effect of silicone molecular architecture on adhesion, tribology, and lithography

Supervisory team:

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Project Highlights:

- Liquid silicones are used for engineering, ophthalmology, and personal care applications.
- Cyclic, branched, and cubic siloxanes offer novel architectures and new avenues of research beyond the linear chain siloxanes.
- Thin film adhesion and tribology will be investigated for a series of structures.

Project Description:

Silicones are a category of inorganic polymer whose inherent physical and chemical properties impart them with a unique versatility. The global market value in 2016 was estimated at \$13.45 billion, covering construction, electronics, energy, healthcare, and transportation sectors. The annual R&D investment in silicones is \$500 million.

Silicones are modern synthetic products derived from quartz sand, and their uses include:

- Sheen agents in shampoos and conditioners
- Water repellency in paints and coatings
- Sealants for electrical equipment
- Medical grade tubing for fluid handling, e.g. blood

The Si-O bond is stronger than the analogous C-C bond in carbon-based polymers. Hence, the durability of polysiloxane materials is remarkable. Low molecular weight polysiloxanes tend to be liquid at room temperature. They can exhibit rheological complexity, such as shear thinning and viscoelastic behaviour. Polysiloxane liquids are typically used for the purposes of modulating adhesion and friction between contacting surfaces.

The Si-O-Si polysiloxane backbone is highly customisable, which means a range of molecular architectures can be synthesized. **Figure 1** shows that linear, branched, cyclic, and cubic structures are achievable. Each of these has multiple locations for further custom functionalisation.

The adhesive behaviour of linear polysiloxane thin films has been well characterised, with a clear transition between surface tension-dominated and viscosity-dominated force profiles. No comparable data exists for the other molecular architectures. Exposure of linear polysiloxane thin films to electron beams resulted in their crosslinking, forming rubber-like materials, whose Young's modulus could be controlled via the total electron exposure. **Figure 2** shows an example cuboidal structure manufactured in this way. Lithographic patterns were created by controlling the geometry of the exposed regions. Once again, no comparable data exists for the other molecular architectures.

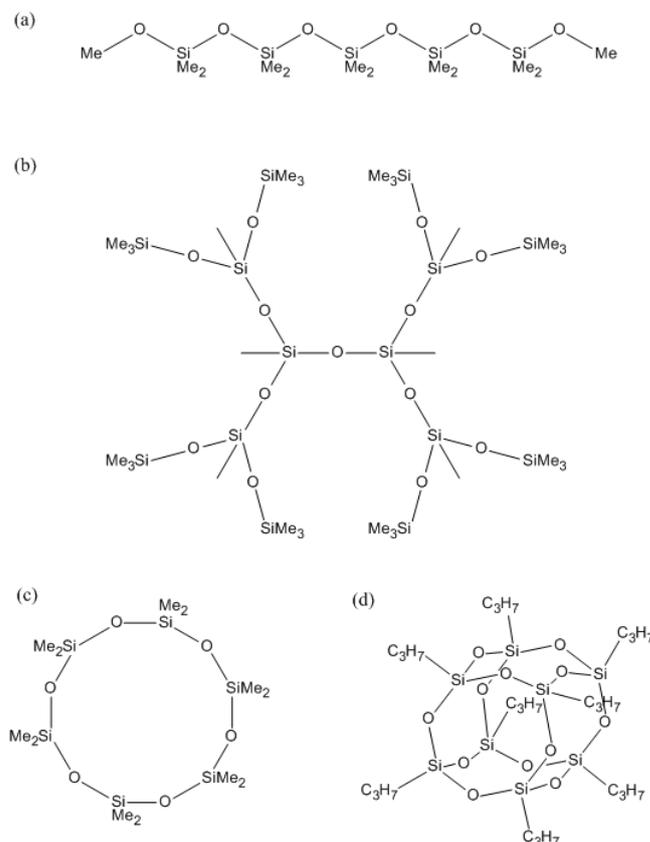


Figure 1. Chemical structures of (a) linear siloxane, (b) branched siloxane, (c) cyclic siloxane, and (d) octahedral silsesquioxane.

Research Methods:

This project will firstly explore the adhesive properties of thin liquid films formed by polysiloxanes with branched, cyclic, and cubic molecular architectures, for comparison with the data already obtained for linear polysiloxanes. Secondly, the project will investigate the tribological behaviour of thin films formed by all four types of polysiloxane. The rheological properties of the liquids will be hugely influential for both the adhesive and tribological behaviour, depending on the propensity for molecules to entangle with, or slide across, each other. Finally, the susceptibility of the four types of polysiloxane to electron beam exposure will be studied. In particular, evidence of crosslinking and solidification will be systematically assessed. Opportunities for nanolithography will be identified.

The results of these studies will be of use to researchers in a range of fields. Specific interest is expected in the fields of ophthalmology, personal care, and micro/nanofabrication.

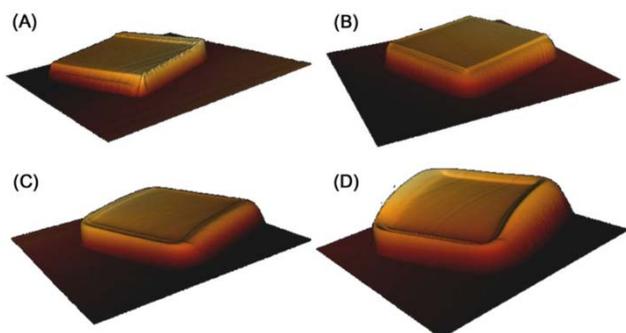


Figure 2. Topography of linear polysiloxane structures post-exposure to electron beam doses of (a) $130 \mu\text{C}/\text{cm}^2$, (b) $542 \mu\text{C}/\text{cm}^2$, (c) $2.26 \text{ mC}/\text{cm}^2$, and (d) $9.39 \text{ mC}/\text{cm}^2$.

Liquid polysiloxanes with branched, cyclic, and octahedral molecular architectures will be identified and procured. These will be subjected to thorough rheological characterisation. Following optimisation of their deposition as thin films via spin coating, their adhesive properties will be studied using atomic force microscopy. The adhesive behaviour of all four types of polysiloxane, when dispensed as liquid bridges between parallel plates, will also be examined. The susceptibility of the thin liquid films to electron beam exposure will then be assessed.

Indication of project timeline:

Year 1: Adhesive properties of silicone films and liquid bridges.

Year 2: Tribological and rheological characterisation.

Year 3: Electron beam susceptibility and nanolithography. Complete thesis write-up.

References

- Heidsieck et al.; *Solar Energy Mater. Solar Cells*, **2017**, *161*, 278-284.
Bowen et al.; *Microelectronic Eng.*, **2012**, *97*, 34-37.
Bowen et al.; *Langmuir*, **2011**, *27*, 11489-11500.
Mark et al., *Inorganic Polymers, Oxford (Oxford, UK)*, **2005**.

Candidate Applications

- 1000 word cover letter outlining how they are equipped in their educational background and expertise to conduct the research project,
- a CV including contact details of two academic references
- An Open University application form, downloadable from: <http://www.open.ac.uk/postgraduate/research-degrees/how-to-apply/mphil-and-phd-application-process> (Note: This is an Advertised studentship and you do not need to submit a proposal).
- IELTS English Language test scores on application. An average of 6.5 and no less than 6 in any one of the four components. Applicant should have these results when applying.

Applications should be sent to

STEM-EI-Research@open.ac.uk by 28 February 2019