

Project title:	The effect of silicone molecular architecture on adhesion, tribology, and lithography
Discipline	Materials Engineering; Nanotechnology
Key words:	Biocompatibility; friction; nanofabrication
Supervisory team:	James Bowen (E&I); Peter G Taylor (LHCS); Salih Gungor (E&I)
URL for lead supervisor's OU profile	http://www.open.ac.uk/people/jb36559

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 molecular structures.

Overview:

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

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.

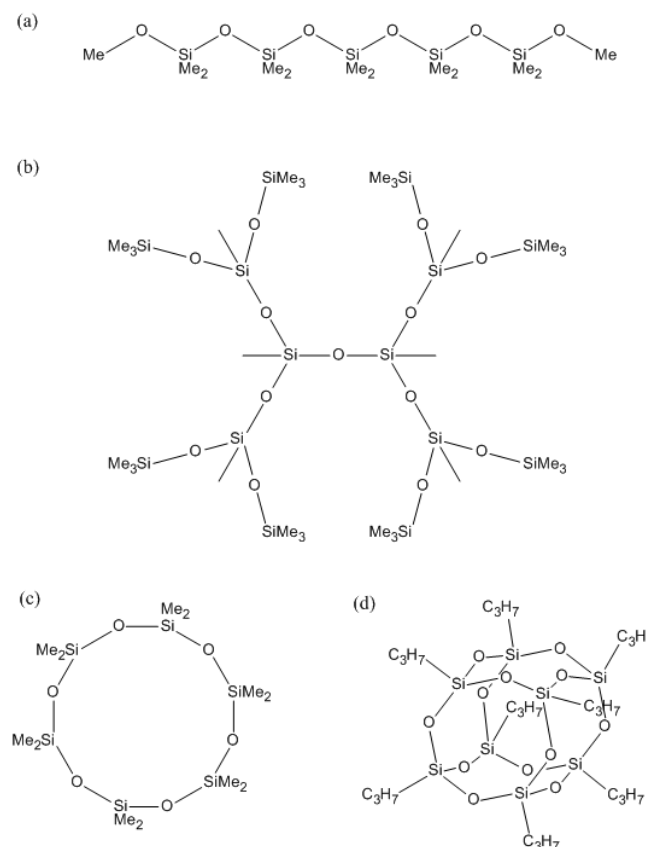


Figure 1. Chemical structures of (a) linear siloxane, (b) branched siloxane, (c) cyclic siloxane, and (d) octahedral silsesquioxane

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.

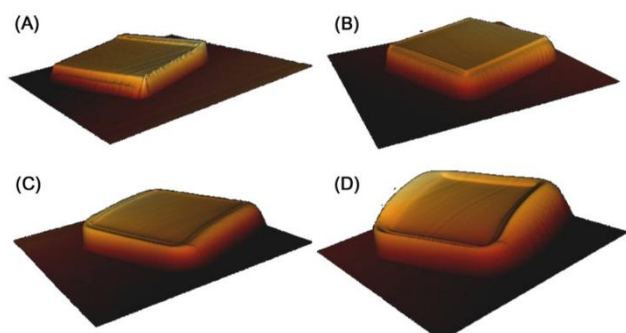


Figure 2. Topography of linear polysiloxane structures post-exposure to electron beam doses of (a) $130 \mu\text{C}/\text{cm}^2$, (b) $542 \mu\text{C}/\text{cm}^2$, (c) $2.26 \text{ mC}/\text{cm}^2$, and (d) $9.39 \text{ mC}/\text{cm}^2$

Methodology:

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 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. Evidence of crosslinking and solidification will be systematically assessed, identifying opportunities for nanolithography.

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. 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.

Proposed timeline

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

Year 2: Tribological and rheological characterisation.

Year 3: Electron beam susceptibility and nanolithography.

Further reading:

Bowen and Taylor's publications:

Langmuir, **2011**, 27, 11489-11500

Microelectronic Eng., **2012**, 97, 34-37

Langmuir, **2012**, 28, 17273-17286

Soft Matter, **2013**, 9, 344-358

Colloid. Surface. A, **2013**, 418, 112-116

Surf. Topogr.: Metrol. Prop., **2016**, 4, 024008

RSC Adv., **2017**, 7, 37474-37477

Mater. Sci. Eng. C, **2018**, 92, 565-574

Other relevant publications:

Solar Energy Mater. Solar Cells, **2017**, 161, 278-284.

Mark et al., *Inorganic Polymers, Oxford (Oxford, UK)*, **2005**.

Further details:

Students should have a strong background in materials, chemistry, engineering, or physics, coupled with an enthusiasm for discovery and innovative thinking. The student will join a well-established group which explores fundamentals and applications of materials engineering at the Open University. Please contact **James Bowen** for further information (james.bowen@open.ac.uk).

Applications should include:

- A 1000 word cover letter outlining why the project is of interest to you and how your skills match those required.
- An academic CV containing contact details of three 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>
- IELTS test scores where English is an additional language.

Applications should be sent to

STEM-EI-PhD@open.ac.uk by **05.03.2021**.