Polymer Brushes for Silicon Nitride-Steel Contacts: a Colloidal Force Microscopy Study

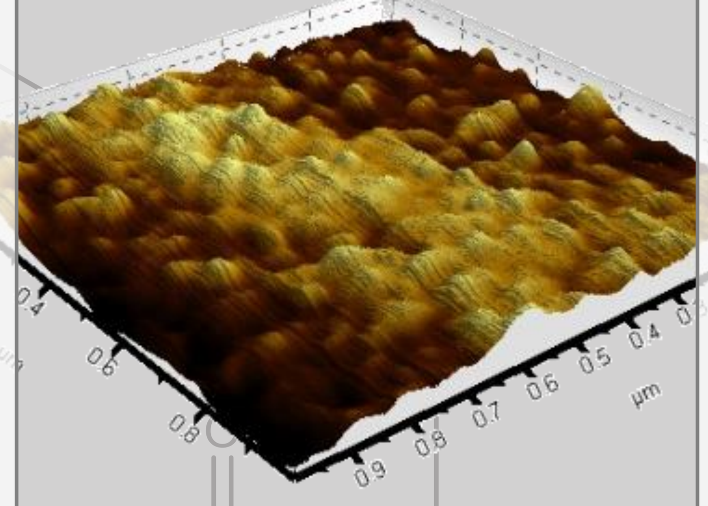
Simon Watson [a], Ling Wang [a], Mengyan Nie [a], Steve Hinder [b], Keith Stokes [a]

[a] National Centre for Advanced Tribology at Southampton (nCATS), University of Southampton, Southampton SO17 1BJ, UK
[b] Department of Mechanical Engineering Sciences, University of Surrey, Guildford, GU2 7XH

UNIVERSITY OF Southampton

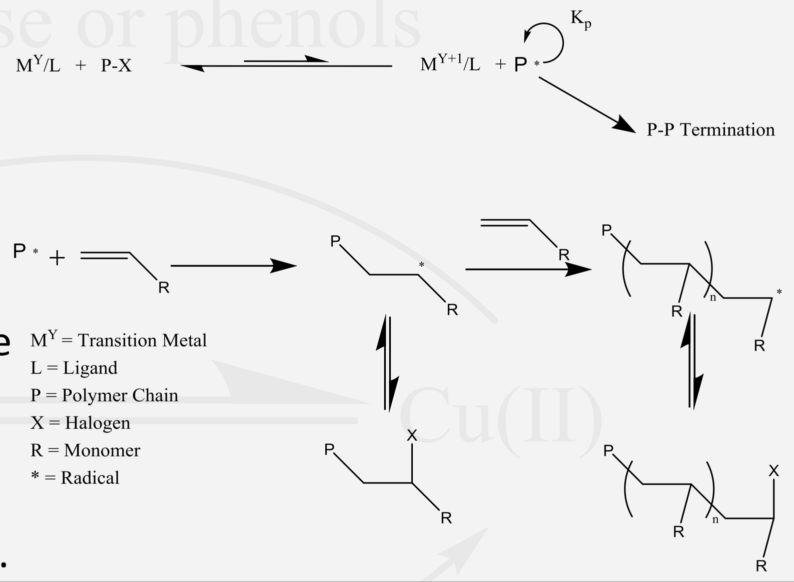
1. Background

- Silicon nitride rolling element bearings have seen great success as hybrid bearing systems in applications including automotive, aerospace, renewables and the railway industry [1].
- Current lubrication and protection solutions are focussed on lubricating metal surfaces thus are not optimised for hybrid contacts.
- 'Grafted from', also known as surface initiated polymerisations (SIP) allow key improvements over 'grafting to'. Primarily that grafting densities can approach 1 chain/nm^2 compared to the 0.05-0.1 chain/nm2 for 'grafting to' strategies
- Although polymer brushes have been extensively studied, great challenges are still present such as withstanding the challenging environment they are to perform in, for example, high pressure and shear. Surviving these conditions under complex operating conditions is also a major challenge.
- Therefore polymer brushes must be optimised for tribological contacts.
- This study aims to develop polymer brush based lubrication solutions that are optimised for silicon nitride-steel contacts through self assembling initiators and subsequent polymerisation techniques.



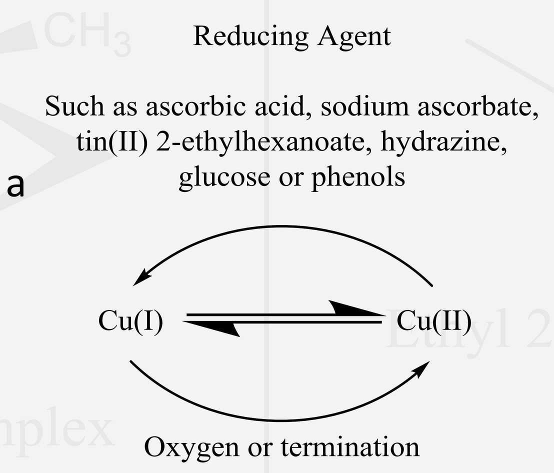
2. Atom Transfer Radical Polymerisation (ATRP)

- ATRP is the most popular type of polymerisation for producing "grafting from" brushes due to the relative robustness of the technique [1].
- For example, unlike the other techniques, rigorously dry working conditions are not needed and reactions are very tolerant of a variety of monomers, ligands and catalysts.
- The catalyst is key to create radicals that propagate resulting in monomer addition.
- A fast deactivation equals a reduction in polymer termination reactions.
- Activation and deactivation of the polymer chain must be very quick to form high quality brushes and minimise termination reactions.



3. Activators Re-Generated by Electron Transfer (ARGET)

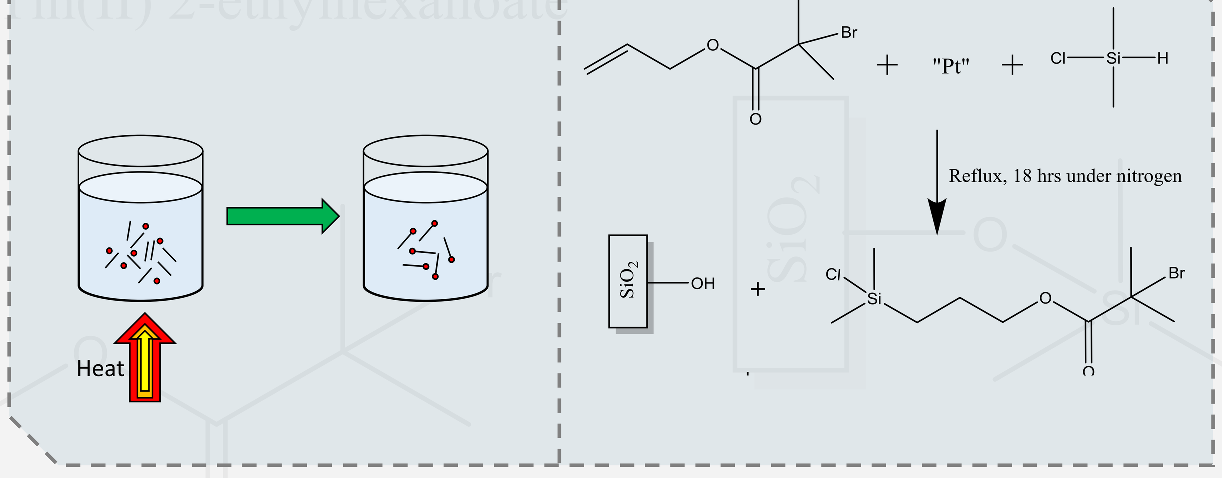
- ARGET is used to reduce the concentration of metal catalysts up to 1000 times to ppm levels [2].
- In ATRP, a small amount of oxygen can result in a large drop in the rate of polymerisation.
- ARGET ATRP overcomes this problem by having a readily available source of a reducing agent, the system can withstand a large excess of reducing agent.
- Therefore any Cu(II) generated is reduced back to the useful Cu(I).



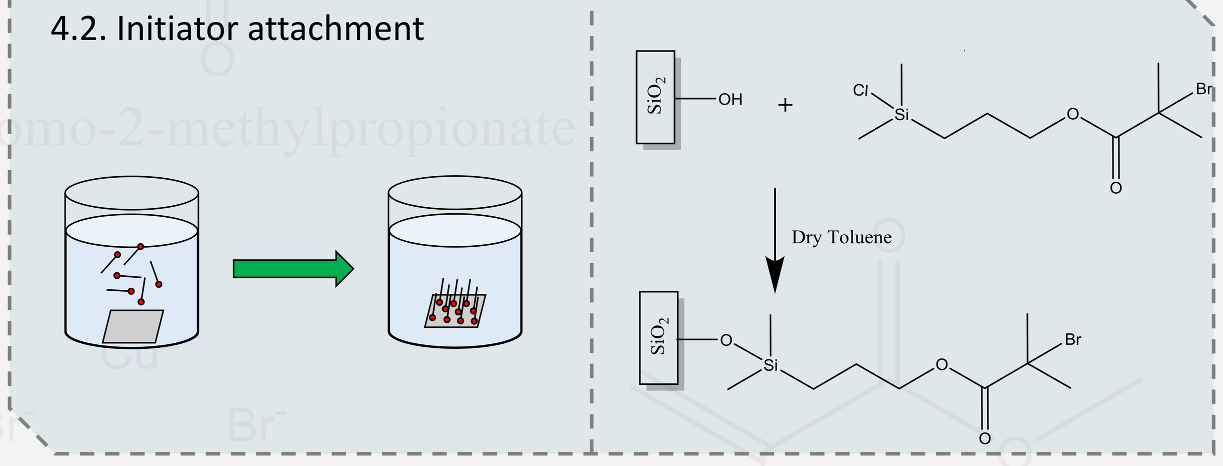
Reproduced from Ref. 1 with permission from the Royal Society of Chemistry.

4. Polymer Brush Synthesis route

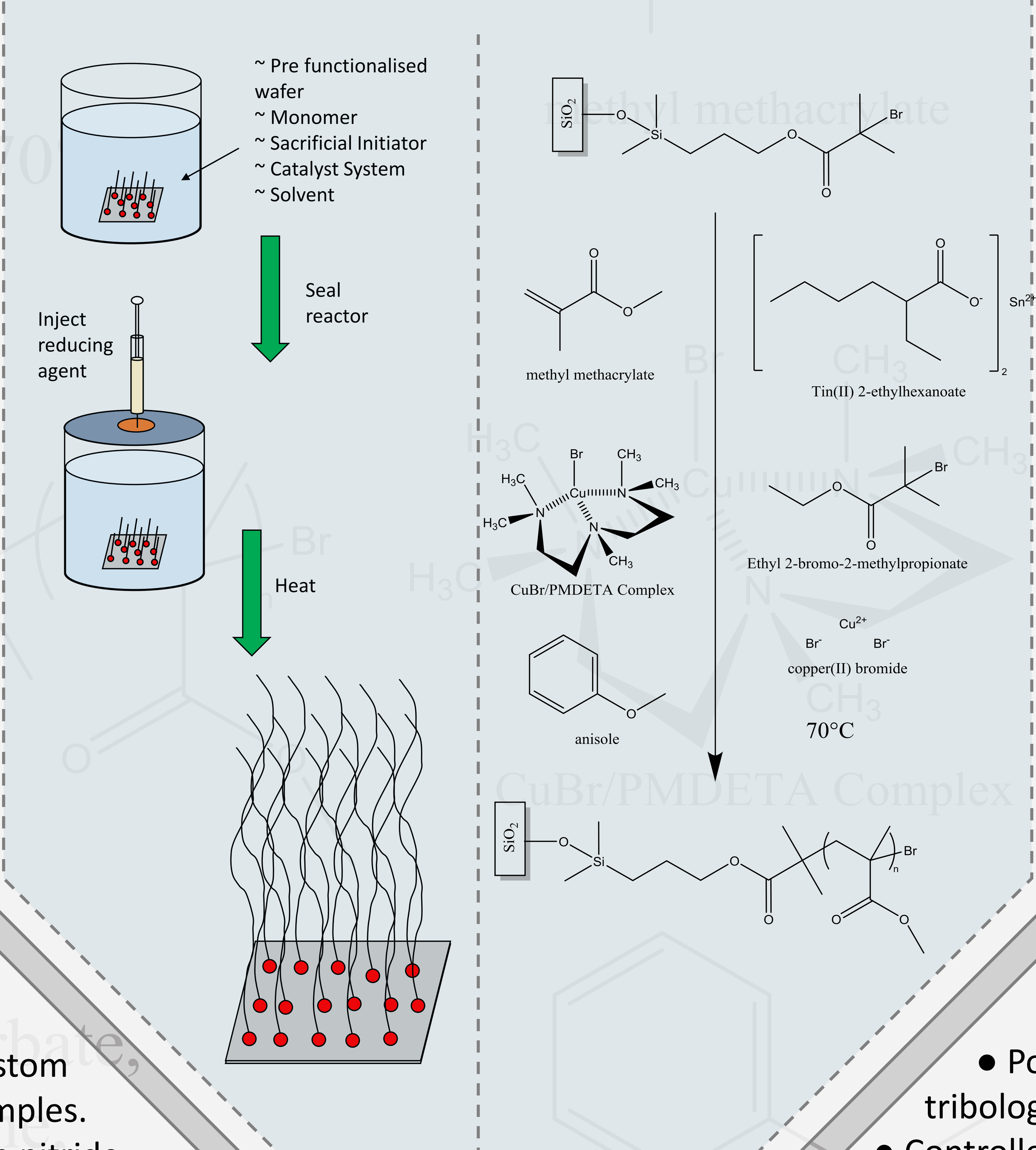
4.1. ATRP initiator synthesis



4.2. Initiator attachment

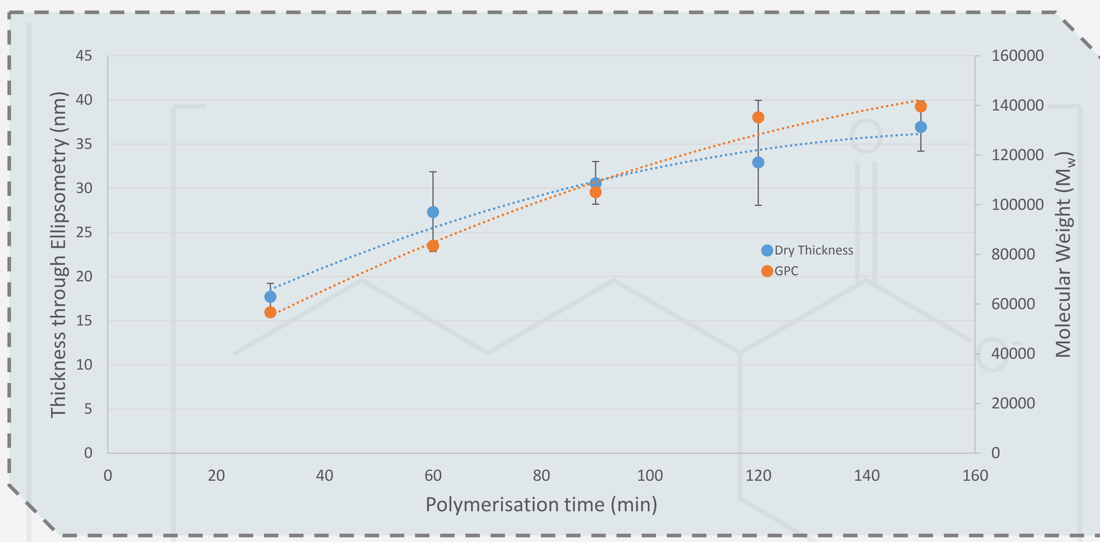


4.2. Surface initiated polymerisation



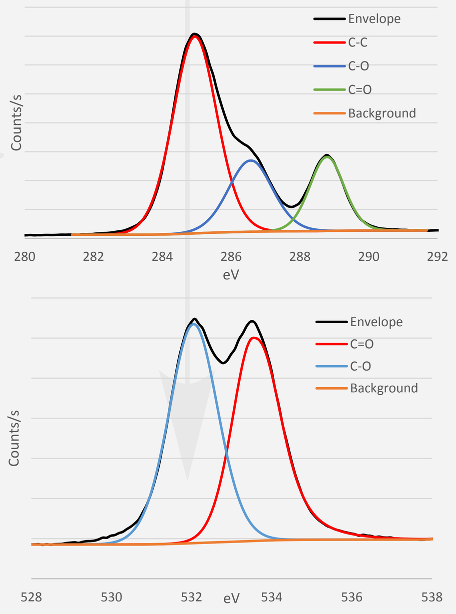
5. Polymer growth

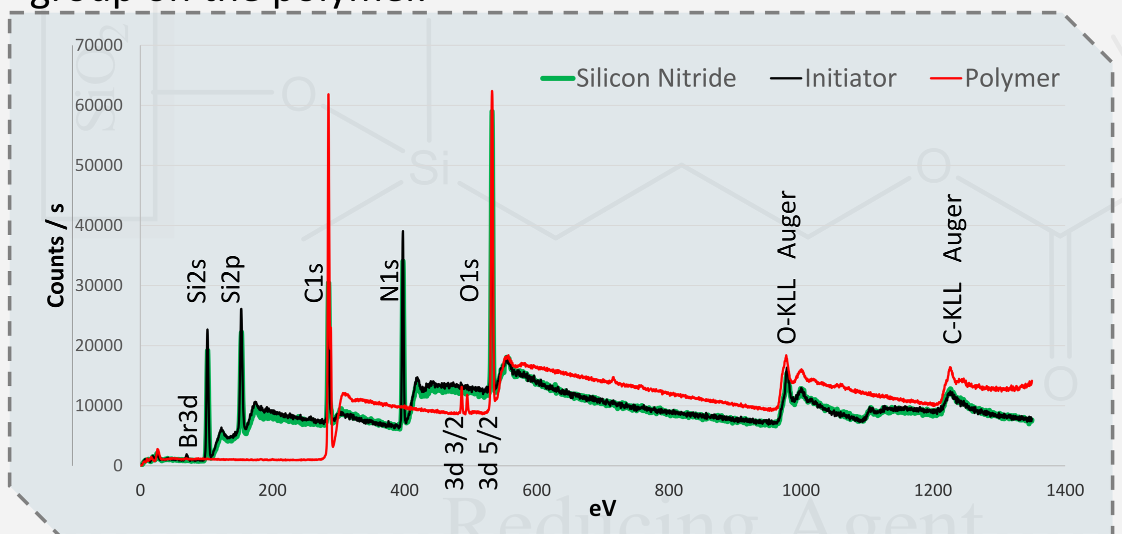
- Polymer growth was investigated through ellipsometry and gel permeation chromatography of the free polymer at five 30 minute intervals until 150 minutes elapsed.
- Thickness of the polymer film grew to a maximum of 37 nm within the 150 minutes.
- The rate of polymerisation plateaus, this is as expected as there is less monomer available.
- In addition, a high rate of polymerisation occurs in the first 30 minutes due to the high availability of monomer.
- Free polymer weights correlate well with polymer analysed on the surface of silicon nitride.



6. Confirmation of Polymer Brush Formation

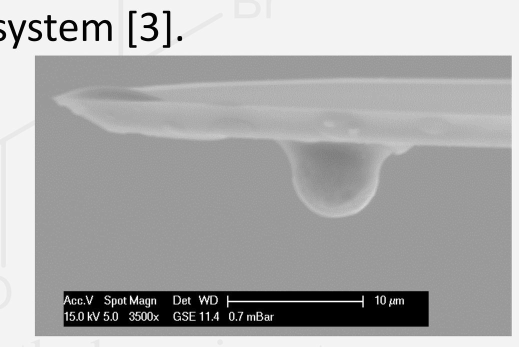
- Key points from XPS are the retention of Br indicating end group functionality has been achieved.
- The lack of Si and N peaks in the polymer indicates full coverage of the silicon nitride by the polymer film.
- High resolution core spectra shows the development of the oxygen and carbon peaks from the simple initiator and oxide to a ester group on the polymer.

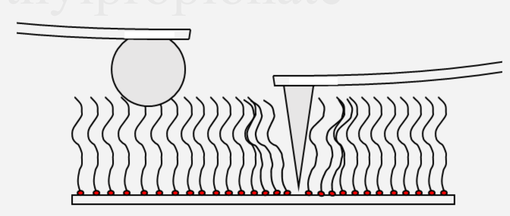




7. Colloidal Probes

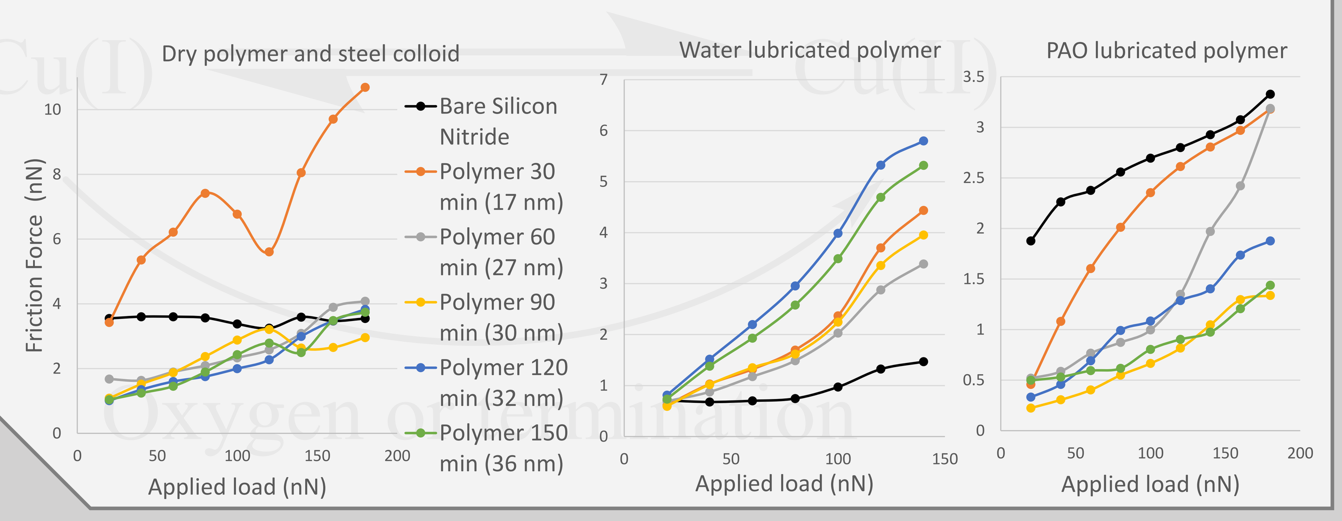
- Although polymer brushes repel interactions from sharp AFM probes, it is likely that the high local pressures will be in excess of what the brush can withstand and result in interpenetration of the brush system resulting in high friction and damage to the brush system [3].
- Using colloidal probes spreads the load across the polymer whilst accurately recording frictional response.
- Custom probes were fabricated by gluing 420L steel spheres to tipless cantilevers with two part epoxy using a micromanipulator under a light microscope [4].





8. Nanotribology

- Polymer brushes were tested via lateral force microscopy with custom colloidal probes. Samples were 20 nN step loaded over 4 x 4 µm samples.
- Dry samples performed much better under lower load than silicon nitride. However, higher loads did not always outperform silicon nitride.
- Silicon nitride outperforms all polymer under aqueous conditions, likely due to the collapsed polymer brush system providing no repulsive forces.
- When lubricated with a polyalphaolefins (PAO) the friction force is reduced over three and a half times at the lowest load in the best case scenario.
- Similarly under the highest load the polymer performs nearly two and a half times better.



9. Conclusions

- Polymer brushes have successfully been formed on silicon nitride and tribologically tested for the first time.
- Controlled ARGET ATRP can form up to 37 nm of PMMA in 150 minutes, confirmed by XPS and ellipsometry
- XPS analysis shows a well defined polymer that retains end group functionality.
- XPS core spectra shows carbon and oxygen signals in expected ratios signifying PMMA is present.
- Nanotribology results show the impact of the polymer film within a hybrid contact for the first time.
- By testing in various fluids the importance of a synergistic solvent is eluted.
- Tribological testing in synergistic solvent such as PAO results in reduced friction forces.
- Swelling effects are clearly related to frictional response
- Friction can be reduced within the hybrid contact between two and a half to three and a half times by using PMMA polymer brushes.

10. Acknowledgements

The authors acknowledge the financial support from the Defence Science and Technology Laboratory (DSTL, DSTLX1000093632), which is part of the UK's Ministry of Defence, from EPSRC (Grant EP/M50662X/1), and to the IMechE Educational Awards Committee for a travel grant to attend STLE 2017.

11. References

[1] S. Watson, M. Nie, L. Wang and K. Stokes, RSC Advances, 2015, 5, 89698-89730.

[2] K. Matyjaszewski, H. Dong, W. Jakubowski, J. Pietrasik and A. Kusumo, *Langmuir*, 2007, **23**, 4528-4531.

[3] R. Bielecki, E. Benetti, D. Kumar and N. Spencer, *Tribology Letters*, 2012, **45**, 477-487.

[4] W. A. Ducker, T. J. Senden and R. M. Pashley, *Nature*, 1991, **353**, 239-241

EPSRC [dstl] Institution of MECHANICAL ENGINEERS

STLE Annual Meeting, May 21-25 2017

stle ATLANTA May 21-25, 2017

Contact: S.Watson@soton.ac.uk