



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

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Introduction

Polymer brushes have promising characteristics which could lend themselves to the lubrication of hybrid contacts [1]. In this paper the interaction between surface-initiated polymer brushes grown on silicon nitride and a steel counter contact is investigated. The importance of the hybrid contact relies on silicon nitride and its unique material properties which show clear reductions in friction in engineering applications [2]. Although there are many positives for hybrid bearings more can be done, namely that the most lubrication solutions are metal protection driven, and therefore the protection of this contact is usually based on protecting steel. These steel protection mechanisms, such as zinc dialkyldithiophosphates (ZDDPs) and molybdenum dithiocarbamate (MoDTC) contain environmentally unfriendly components such as S and P. The removal of these elements is required due to the effect they have on catalytic converters and increasingly rigorous emissions regulations. Although many polymer brushes have been applied on a variety of surfaces the hybrid contact has not been explored and neither have polymer brushes been applied to silicon nitride for tribological applications. The challenges of testing the hybrid contact in the nanoscale are insuring that a high quality polymer film is created, creating an appropriate steel counter surface, forming brushes in a way that avoids using S and P compounds and forming an appropriate polymer that synergises well with the chosen lubricant. Polymer brushes rely on good solvent to facilitate swelling and therefore better sliding performance.

To form high quality brushes atom transfer radical polymerisation (ATRP) is utilised. ATRP is the most popular type of polymerisation due to the relative robustness of the technique. 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 [3]. However, in ATRP, a small amount of oxygen can result in a large drop in the rate of polymerisation. In order to overcome this problem and to facilitate the growth of polymer brushes, Activators Re-Generated by Electron Transfer (ARGET) is introduced by incorporating a readily available source of a reducing agent [4]. Another benefit of ARGET is this technique can significantly reduce the concentration of metal catalysts up to 1000 times to ppm levels.

Although polymer brushes repel interactions from sharp AFM probes, it is likely that the high contact pressures will be in excess of what the brush can withstand and cause interpenetration of the brush system resulting in high friction and damage to the brush system [5]. To be able to understand the tribological performance of the polymer brushes under operational conditions and without losing the force sensitivity or penetrating the polymer, spherical colloidal probes instead of sharp AFM tips are custom-made and used. One of the benefits of this procedure is that the load is distributed across the sample surface whilst accurately recording the forces therefore making this a ideal technique for the characterisation of the tribological performance of polymer brushes. One of the novelties of this research is nanotribological testing using a steel colloidal probe.

Experimental Details

• Chemicals

Methyl methacrylate (MMA) (Aldrich, 99%) was distilled under reduced pressure to remove the inhibitor. Copper(II) bromide (Aldrich, 99%), N,N,N',N'',N''-Pentamethyldiethylenetriamine (PMEDTA) (Aldrich, 99%), Anisole (Aldrich, 99%), Ethyl α -bromoisobutyrate (EBIB) (Aldrich, 98%), Toluene (Aldrich, 99.8%), Allyl 2-bromo-2-methylpropionate (Aldrich, 98%), 10% Platinum on carbon (Aldrich), Chlorodimethylsilane (Aldrich, 98%), Chloroform-d (Aldrich, ≥ 99.96 atom % D), SpectraSyn 4 poly-alpha-olefin (PAO) fluid (ExxonMobil), Tin(II) 2-ethylhexanoate (Aldrich, 92.5-100.0%) were used as received. Silicon wafers (P-Doped [100], Pi-Kem, UK), Silicon wafers were processed using an Oxford Instruments Plasmalab to deposit silicon nitride via plasma enhanced chemical vapour deposition. Wafers were cleaved into 1 cm² pieces, sonicated in ethanol and water sequentially and dried under a stream of nitrogen prior to use.

• Synthesis and Attachment of 3-[chloro(dimethyl)silyl]propyl 2-bromo-2-methyl-propanoate.

Allyl 2-bromo-2-methylpropionate (1.6 mL), dimethylchlorosilane (10 mL) and platinum on carbon (10 mg) were added to a 25 mL round bottom flask attached to a microscale rig. The system was purged with nitrogen and then the mixture was refluxed under nitrogen for 18 hrs. The excess silane was then distilled off. The resultant solution was quickly filtered over

anhydrous sodium sulfate to produce a colourless oil which was confirmed by ^1H and ^{13}C NMR. NMR spectra were recorded on a Bruker AVIIIHD500 FT-NMR spectrometer in CDCl_3 at 298 K. The attachment of the ATRP initiator was completed in toluene at 5 mM solution for 18 hrs.

• General Procedure for ARGET ATRP of Methyl Methacrylate

To conduct the SIP a 15 mL vial containing a previously modified silicon nitride with an initiator attached was charged with MMA (7 mL, 0.065 mol), CuBr_2 (0.0028 g, 0.0125 mmol), PMDETA (26 μL , 0.125 mmol), EBIB (0.048 g, 0.25 mmol) and 6 mL of anisole as solvent. A solution of Tin(II) 2-ethylhexanoate (130 μL g, 0.125 mmol) in anisole (1 mL) was then syringed through the septum and the vial was placed in a thermostatic water bath at 70°C . The polymerisation was stopped when the vial is unscrewed, thereby exposing the catalyst to air. The modified wafer is then removed, sonicated in tetrahydrofuran (THF) and dried in a stream of nitrogen. The polymer was precipitated by addition to a large amount of petroleum ether. The product was then dissolved and precipitated then dried, this free polymer was then analysed by gel permeation chromatography (GPC).

• Confirmation of Polymer Brushes Film

The thickness of the dry polymer brushes was measured by a Woollam M-2000 spectroscopic ellipsometer at five 30 minute intervals until 150 minutes elapsed. The data was modelled with the corresponding CompleteEASE software using a four component model consisting of Si/SiO₂/Si₃N₄/SiO₂/Cauchy [6]. XPS analyses were performed on a ThermoFisher Scientific (East Grinstead, UK) Theta Probe spectrometer. XPS spectra were acquired using a monochromated Al K α X-ray source ($h\nu = 1486.6$ eV). An X-ray spot of ~ 400 μm radius was employed. Survey spectra were acquired employing a pass energy of 300 eV.

• Custom AFM Colloidal Probes

Colloidal probes were fabricated by attaching a steel ball (6.19-6.49 μm diameter, (US Nanomaterials, USA)) to a tipless cantilever by using two part epoxy [7]. The modified tips actual spring constant was calculated by internal built in thermal noise methods [8].

• Nanotribological Experiments

Samples were investigated using an Agilent AFM5500 with custom made colloidal probes. Scans were performed over 4 μm by 4 μm consisting of 512 lines at a scanning speed of 8 $\mu\text{m/s}$ (1 line/s). Samples were loaded in steps of 20 nN every 0.4 μm ensuring that at least 50 lines were attributed to one load step. At least three scans were performed in different locations for each sample. All samples were tested under ambient conditions, lubricated with water and finally lubricated with PAO4.

Results and Discussion

The initiator functionalised silicon wafer was investigated through sessile drop contact angle (CA). CA can indicate the coverage and quality of a SAM, thereby verifying surface modification progress [1]. The surface modification resulted in an increased contact angle of $83 \pm 3^\circ$ from 27.2° obtained on bare silicon nitride. As seen in figure 2 there is a slight positive trend between polymerisation time and contact angle but the data fall within the expected range. The increasing contact angle is most likely due to the increase in polymer chain length in addition to swelling effects. Figure 3 shows poly methyl methacrylate (PMMA) growth with respect to time. It can be seen that the thickness of the polymer film grew to a maximum of 37 nm within the 150 minutes. It can also be seen that the rate of polymerisation plateaus, this is as expected due to the rate limiting step being the amount of monomer that can be polymerised. Also expected is the high rate of polymerisation during the first 30 minutes. This is due to the high availability of monomer for addition to the polymer chain. Molecular weight of free polymers measured by gel permeation chromatography correlates well to the thickness of the grafted polymer.

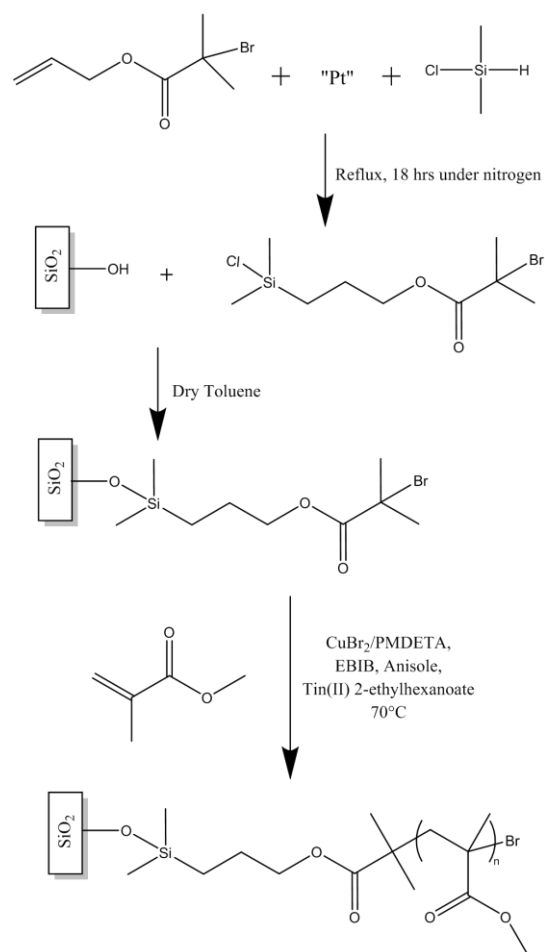


Fig.1. Schematic of polymer brush synthesis.

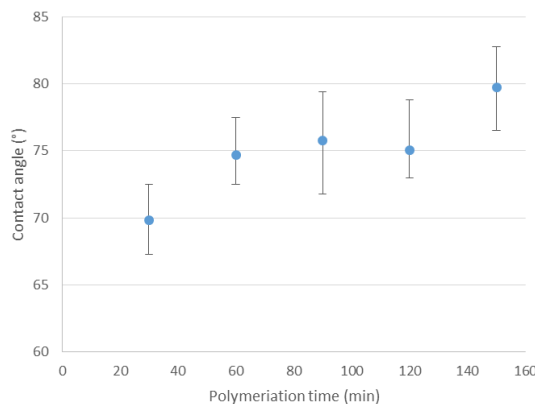


Fig.2. Contact angle vs polymerisation time.

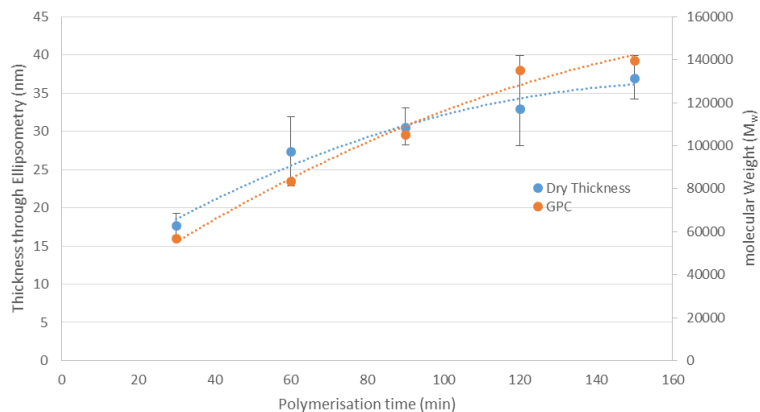


Fig.3. Polymer growth with respect to time.

As shown in figure 4 the silicon nitride and initiator show very similar spectrums, the difference being that the initiator shows a clear Br peak. This indicates that the initiator has successfully anchored onto the substrate. In addition there is clearly no Cl peak meaning that there has been full hydrolysis of the Si-Cl bond. With respect to the polymer the lack of a Si or N signal indicates full coverage of the silicon nitride by the polymer film. High resolution core spectra as seen in figures 5 and 6 show the development of the oxygen and carbon peaks. Three clear peaks make up the spectra of the carbon. This is due to the three different bonding environments that the carbon is in within the polymer. Namely the carbon bonding to oxygen in two separate ways is expected because of the structure of methyl methacrylate, which also explains the similarity in peak size. This is further explored by viewing figure 6, in which the spectra of oxygen in two clear peaks. This cements the successful creation of the polymer film on the surface. Core spectra also shows the presence of Br meaning that end group functionality is retained.

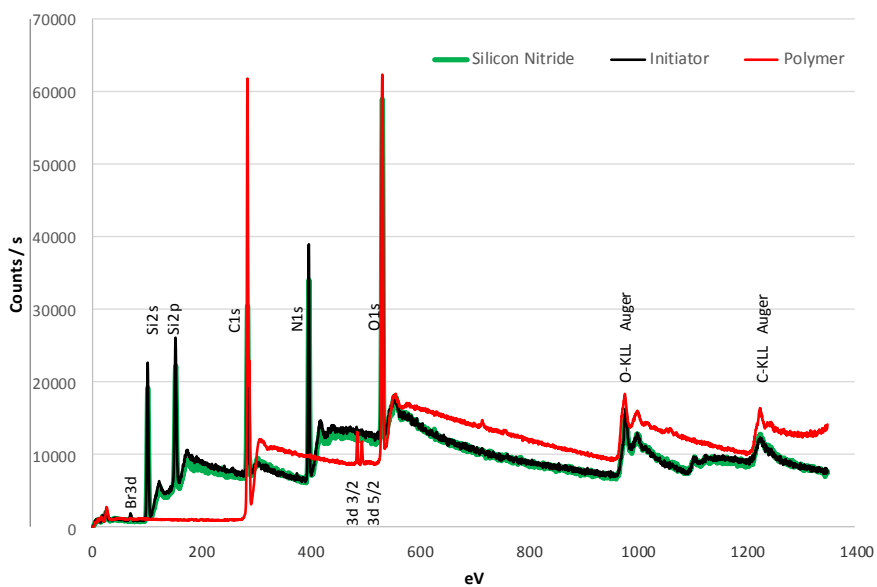


Fig.4. XPS full scan.

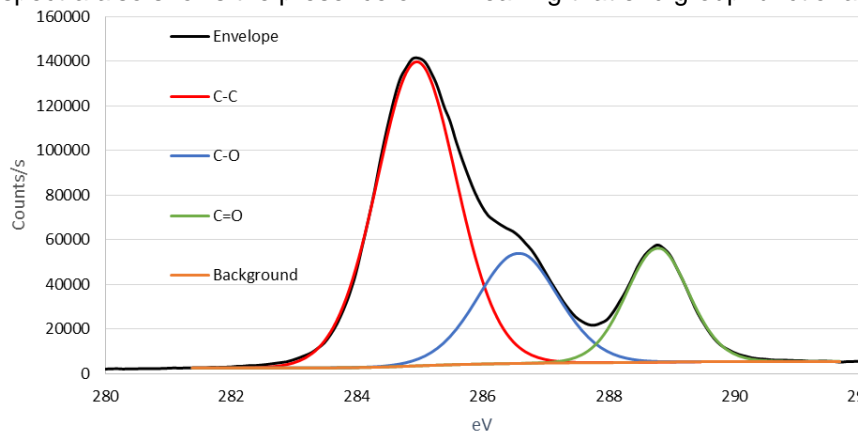


Fig. 5. High resolution core spectra of carbon from the polymer.

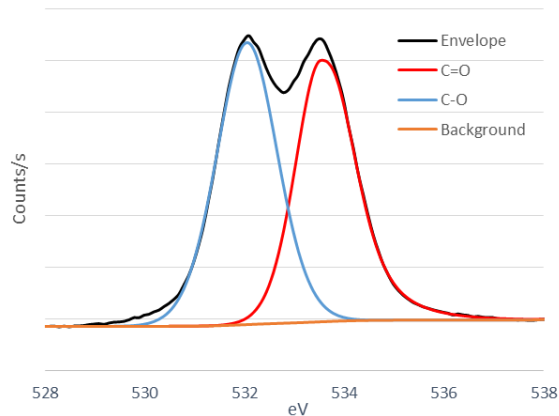


Fig. 6. High resolution core spectra of oxygen from the polymer.

As for tribological performance of dry polymers, all the tested polymers except the 30 minute time point (17 nm thick) outperform bare silicon nitride until loaded above 140 nN. The 30 minute polymer most likely suffers high friction due to the low thickness of the polymer film. Therefore the colloid breaks through the polymer contacting the silicon nitride whilst having to push through all the grafted polymer. When considering the aqueous environment silicon nitride outperforms all polymers under aqueous conditions, likely due to the collapsed polymer brush system providing no repulsive forces. This is expected as the polymer brush system is reliant on a swollen state in a good lubricant to provide friction reducing abilities. When lubricated with a PAO the friction force is significantly 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. It is clear that the polymer brush system is successfully providing a lubricious surface and therefore reducing the friction force. The thicker polymers from 90 minutes onwards perform much better under higher loads. This can be seen by the degradation of the 60 minute polymer above 120 nN. Although the polymer performance degrades with respect to load, it is still better than the bare silicon nitride surface. Most impressively, the polymers around 30-36 nm reduced the friction force of the silicon nitride from 3.32 to 1.33 nN.

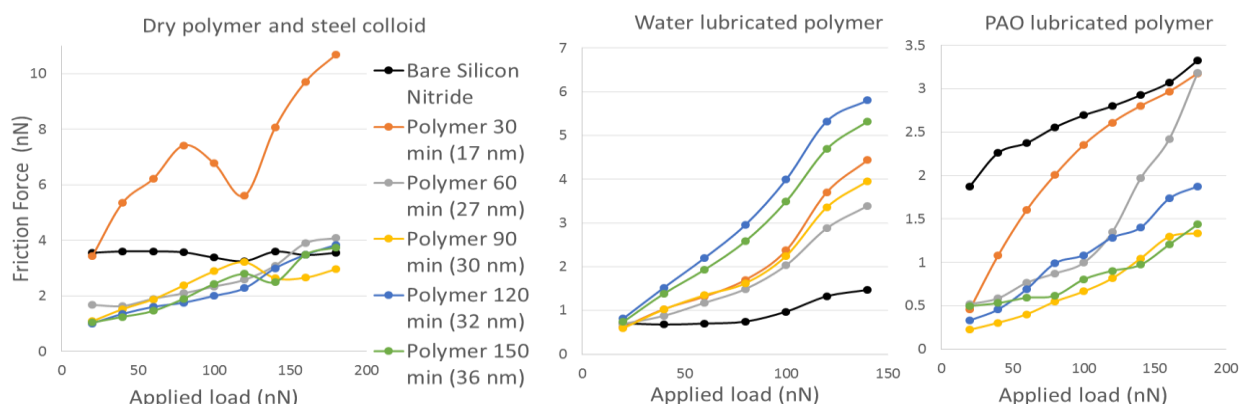


Fig.7. Frictional response of polymer brushes in ambient conditions and in different fluids.

Conclusions

- Polymer brushes have been successfully formed on silicon nitride and tribologically tested for the first time.
- Controlled ARGET ATRP can form up to 37 nm thick PMMA in 150 minutes, confirmed by contact angle, XPS and ellipsometry measurements.
- XPS analysis shows the polymers are well-defined and retain end group functionality. Further XPS core spectra show carbon and oxygen elements exist in different bonding forms and their contributions into each elemental signal are in expected ratios as in PMMA stoichiometry.
- Nanotribological tests with colloidal probes accurately demonstrated the impact of the polymer film within a hybrid contact under simulated machinery operational conditions for the first time.
- Tribological testing in PAO results in a solvated brush system resulting in reduced friction forces indicating the importance of a synergistic solvent. 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.

Acknowledgments and References

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