DEVELOPMENT OF POLYMER BRUSHES FOR THE LUBRICATION OF SILICON NITRIDE–STEEL CONTACTS

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INTRODUCTION

Silicon nitride rolling element bearings have seen great success in hybrid bearing systems, especially applications such as automotive, aerospace, renewables and the railway industry [1]. The key properties are high wear and corrosion resistance, low density of the ball bearing, with a 60% reduction in weight and an 80% reduction in friction compared to classic steel bearings [1]. Compared to steel on steel contacts the coefficient of friction (COF) of hybrid systems is reduced to approximately 0.04-0.09 under oil lubricated conditions and between 0.1-1.0 for dry conditions [2]. Research shows that centrifugal loading on the outer bearing raceway is reduced by a lighter ball bearing. It has also been identified that ceramic bearings perform better under lubricant starvation and hard particle contamination [3]. Silicon nitride is also more resistant to debris created by contact fatigue stresses which are suspended in the lubricant and create secondary wear mechanisms in which the suspended wear particles abrade, scratch and cut the surface creating further damage [2].

Polymer brushes are formed onto surfaces through two methods, named 'grafting to' and 'grafting from' processes [4]. The 'grafting to' method uses prefabricated polymers that can be attached to a surface using physisorption or chemisorption, which is very similar to the way in which self-assembled monolayers (SAMs) are produced [4]. The film thicknesses of polymers produced through the 'grafting to' method are limited by the molecular weights of the preformed polymer in solution [5]. Although this method is relatively easy to carry out as it works much like a SAM, there is steric hindrance that impedes the density of the final film that is formed [6].

In the 'grafting from' techniques, also known as surface initiated polymerisations (SIP), the surface is first modified with a self-assembling initiator layer, which is then exposed to monomeric components with catalyst and, if needed, in an appropriate solvent [5]. This method allows much more control over the final film and the grafting densities can approach 1 chain/nm^2 [7] compared to the 0.05-0.1 chain/nm^2 for 'grafting to' strategies [8]. In comparison to the limit of the films using 'grafted to' methods (<100 nm thickness), the 'grafting from' method can produce much thicker films [5].

Atom Transfer Radical Polymerisation (ATRP) is the most popular type of polymerisation for brushes due to the relative robustness of the technique [9]. 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 [4]. The basic structure for ATRP synthesis of polymer brushes is to have an initiator or monomer, and a catalyst made of a transition metal (e.g. CuBr$_2$) for successful grafting of chains. If the polymer brushes do not all grow at the same rate or time, the shorter chains can be inhibited from growing any further due to steric hindrance. This can be overcome by ensuring there are copious amounts of initiator sites on the substrate. There are two major steps in this polymerisation reaction, namely activation and deactivation. During the activation step, the metal complex breaks the alkyl halogen bond in the initiator, resulting in the formation of radicals. The radicals then propagate with the excess monomer and higher oxidation state metal complex. In the deactivation step, the radicals react with deactivators (e.g. polymer chain or activators) resulting in the formation of halide capped chains or reformed metal complex catalysts. For this to be successful, it is necessary to have a reversible reaction shifted to the dormant species, accompanied by fast initiation and deactivation. This is important as it can reduce the amount of termination steps. Developments of ATRP utilised in this research involve Activators Re-Generated by Electron Transfer (ARGET), this technique is used to reduce the concentration of metal catalysts up to 1000 times to ppm levels [10]. In addition, polymerisations can be completed in limited amounts of air so reactions do not have to be deoxygenated. 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. Therefore any Cu(II) generated is reduced back to the useful Cu(I).

Experimental Section

Chemicals Methyl methacrylate (MMA) (Aldrich, 99%) was passed through a column to remove the inhibitor. Copper(II) bromide (Aldrich, 99%), N,N,N',N'',N''-Pentamethyldiethylenetriamine (PMEDTA) (Aldrich, 99%), (+)-Sodium L-ascorbate (Aldrich, 98%), Anisole (Aldrich, 99%), Ethyl α-bromoisobutyrate (EBIB) (Aldrich, 98%), Sodium sulfate (Aldrich, 99%), 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), were used as received. Silicon wafers (P-Doped [100], Pi-Kem, UK) were cleaved into 1cm^2 pieces,

sonicated in ethanol and water sequentially, dried under a stream of nitrogen before exposure to a PVA TePla 300 plasma asher for 3 minutes. Lateral force mode of atomic force microscope was performed with standard silicon probes (NanoWorld, Switzerland).

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 ^{1}H and ^{13}C NMR. NMR spectra were recorded on a Bruker AVIIIHD500 FT-NMR spectrometer in the indicated solvent at 298 K. Chemical shifts for proton and carbon spectra are reported on the delta scale in ppm and were referenced to residual solvent references or internal tetramethylsilane (TMS) reference. The attachment of the ATRP initiator was completed in toluene or a PAO at concentrations of 1, 2.5 and 5 mM solutions for both 2 and 18 hrs.

^{13}C NMR (CDCl$_3$, 125 MHz): d=171.7 (CO), 67.7 (CH$_2$O), 55.9 (Cter), 30.8 and 22.2 (CH$_3$ and CH$_2$), 14.9 (SiCH$_2$), 1.6 (SiCH$_3$). ^{1}H NMR (CDCl$_3$, 500 MHz): d= 4.14-4.21 (m, 2H, -CH$_2$O-), 1.96 (s, 6H, -CH$_3$-), 1.78-1.88 (m, 2H, -CH$_2$-), 0.89 (m, 2H, -SiCH$_2$-), 0.45 (s, 6H, -Si(CH$_3$)$_2$-).

General Procedure for ARGET ATRP of Methyl Methacrylate. To conduct the SIP a 22 mL vial containing a previously modified silicon wafer with an initiator attached was charged with MMA (15 mL, 150 mmol), CuBr$_2$ (0.0056 g, 0.025 mmol) and PMDETA (0.043 g, 0.25 mmol) in anisole (2 mL) was added in addition to EBIB (0.048 g, 0.25 mmol). The vial was then bubbled with nitrogen for 5 minutes then sealed. A solution of sodium L-ascorbate (0.0495 g, 0.25 mmol) in anisole (2 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 and sonicated in tetrahydrofuran (THF) and dried in nitrogen.

Figure 1. Schematic of polymer brush synthesis

Results and Discussion

As seen in Figure 2, contact angle measurement results demonstrated that a monolayer of the initiator was formed to some degree at various concentrations in both toluene and PAO solvents. As previously reported, high quality self-assembled monolayer of octadecyltrichlorosilane is usually formed on silicon nitride substrate in 2 hrs [1]. However, it took much longer time for the initiator to form a self-assembled monolayer on silicon wafer substrate, as the maximum contact angle was achieved over a longer time. This is due to stearic hindrance of the two methyl groups on the silane and a larger terminal group. The maximum contact angle of 85 degrees was achieved in a 2.5 mM solution of the initiator in toluene in 18 hrs. Using the PAO oil as a solvent, depositions of the initiator monolayer were also carried out the same way as in toluene. Firstly, it is noteworthy that a lower maximum contact angle was achieved for the initiator in PAO solvent than in toluene, as PAO is an imperfect solvent [12]. The polymer brushes of poly methyl methacrylate (PMMA) were successfully formed on the silicon wafer by ARGET ATRP method, and the thickness of all the polymer brushes was measured by a Woolham M-2000 spectroscopic ellipsometer. The data was modelled using a three component model consisting of Si/SiO$_2$/Cauchy. Figure 3 shows that the thickness of polymer film grows almost linearly with respect to time.

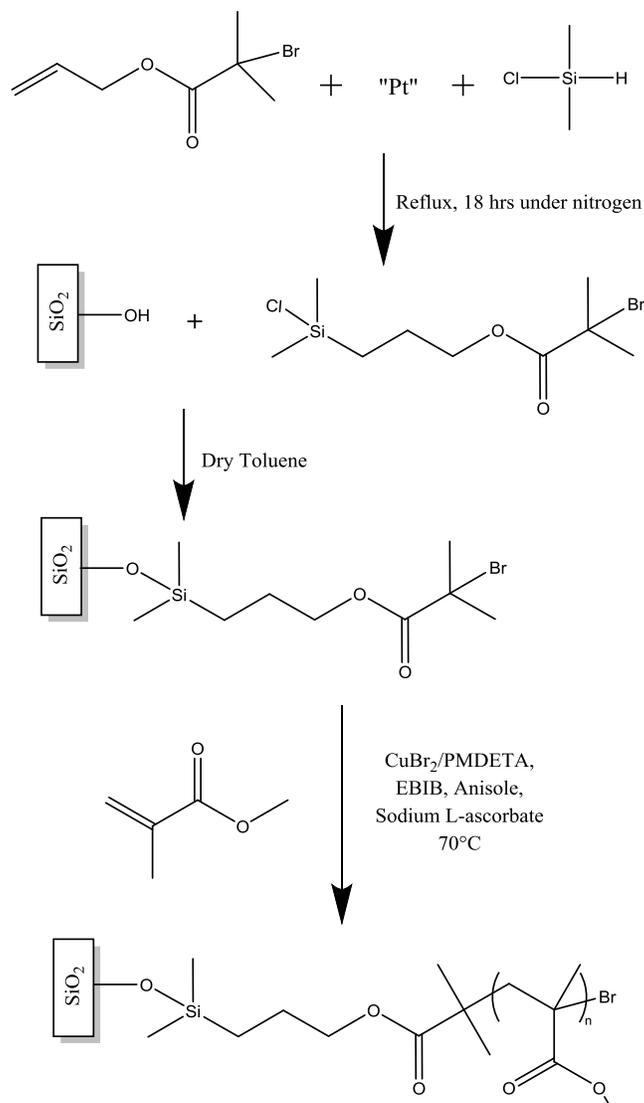Nanotribological performance of as-prepared polymer brushes film was investigated using lateral force mode of atomic force microscope (MAC Mode III, 5500 Scanning Probe Microscopy, Agilent Technologies, USA). Standard force modulation silicon probes with nominal spring constant of 2 N/m and tip radii of 8−10 nm were used. Actual spring constant values for every cantilever were obtained using built-in thermal noise method [11]. The determined constants varied between 1.11 and 1.13 N/m. Normal forces were calibrated by measuring the deflection sensitivity (nm/V) from the slope of the linear part of a force−displacement curve obtained. As seen in figure 4, significant reduction in friction was achieved for all the polymer brushes films under a wide range of loads. However, the influence of the polymer thickness is not obvious or unidirectional, i.e.

Figure 2. Maximum contact angle of ATRP initiator in PAO and toluene

the thicker polymer may not provide a lower friction force. It is surprising that the tribological performance of the thicker polymer brush films at 4 and 6 hrs polymerization is not as good as at 2 hrs polymerization at the nanoscale under higher loads than 20 nN. At higher loads than 60 nN, it is also evident that the thicker polymers reached almost the same friction force as bare silicon nitride. Future work will involve lateral force microscopy work completed in liquids to further understand the swelling effects in which polymer brushes are thought to assist in lubrication.
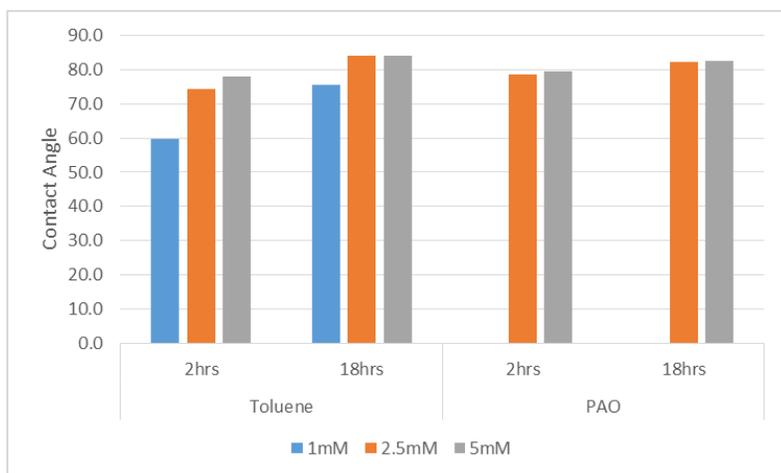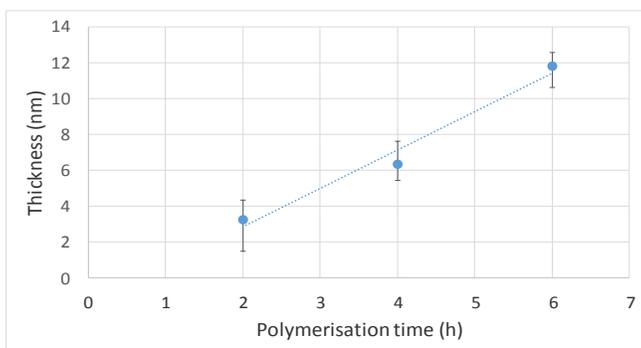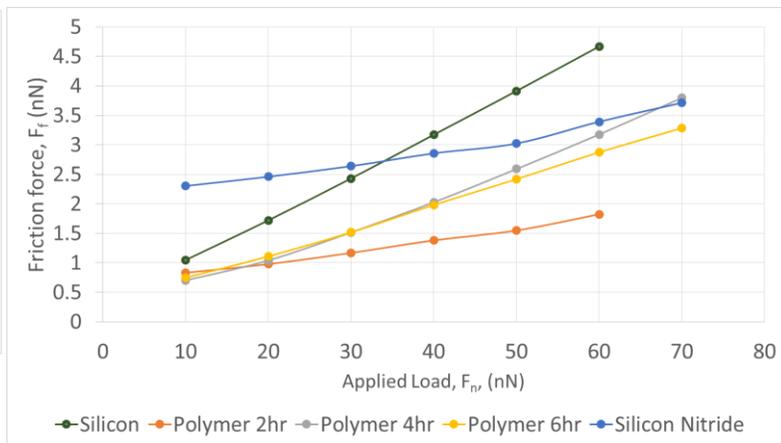

Figure 3, Above. PMMA film thickness with respect to time.
Figure 4, Right. Average results of friction force as a function of load for various thicknesses of polymer with respect to silicon nitride.

Conclusion

Current work has shown that polymer brushes of PMMA were successfully prepared onto the exemplar substrate silicon wafer via ARGET ATRP in a controlled manner, which demonstrates the principle of formation of polymer brushes films onto silicon nitride surface. The grafted structures have the promising characteristic in that they are covalently attached to the surface in question providing a stable coating for tribological contacts. The PMMA brushes have also shown to reduce the frictional force which is promising for future applications.

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