Experimental report

17/02/2020

Proposal: **9-11-1927**

Council: 4/2019

Title: Studying the nature of surface reconstruction in foul release coatings and their effect on coating performance.

Research area: Soft condensed matter

This proposal is a new proposal

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Local contacts: Philipp GUTFREUND

Samples:
PFPE PDMS Blend
PFPE thin films
PFPE monolayer

Instrument	Requested days	Allocated days	From	To
FIGARO	0	0		
D17	3	3	24/01/2020	27/01/2020

Abstract:

We propose a series of air and liquid neutron reflectivity experiments of monolayer and thin film perfluoropolyether-polyethylene oxide block co-polymer coatings. The objective of this experiment is to determine the chemical nature of PFPE-PEO surfaces in liquid and to study surface reconstruction effects with changing interface. This experiment will further our understanding of the anti-fouling properties of these polymers in water, identifying the properties required for effective foul-release materials thus, enabling the design of improved systems for resisting biofouling.

ILL Experimental report
9-11-27 on D17 24th-27th January 2020

The objective of this experiment was to assess the chemical and structural nature of coatings incorporating amphiphilic, oligomeric perfluoropolyether's (PFPE-PEO) when exposed to a liquid phase. These molecules have a central perfluoropolyether block capped by short polyethylene glycol blocks and have been shown to be very deft at resisting bio-fouling, with coatings incorporating these molecules showing effective resistance against even particularly challenging biofouling such as protein fouling and the development of bio-slimes.
Contact angle studies of water droplets on surfaces incorporating these molecules have shown transitions from partial to fully wetted after a few seconds suggesting some rapid shift in the hydrophobicity of the surface; a chemical and structural surface reconstruction. This was the motivation for utilising neutron reflectivity as one of the few techniques capable of probing any changes in the surface chemistry in liquid environment.

Materials and coating design: All films were formed on 50x50x10mm Silicon substrates (Crystran). Hydroxy terminated Polydimethylsiloxane 3100Cst (sigma) was dissolved in hexane and mixed with TES 40 (~10% wt of PDMS) ethyl silicate crosslinker and an amino propyl terminated PDMS as Catalyst (~1%) and spin coated onto the silicon substrates.

PFPE-PEO was dissolved in either methanol or ethanol at various concentrations (2.5% and 5% in methanol 10% in ethanol).

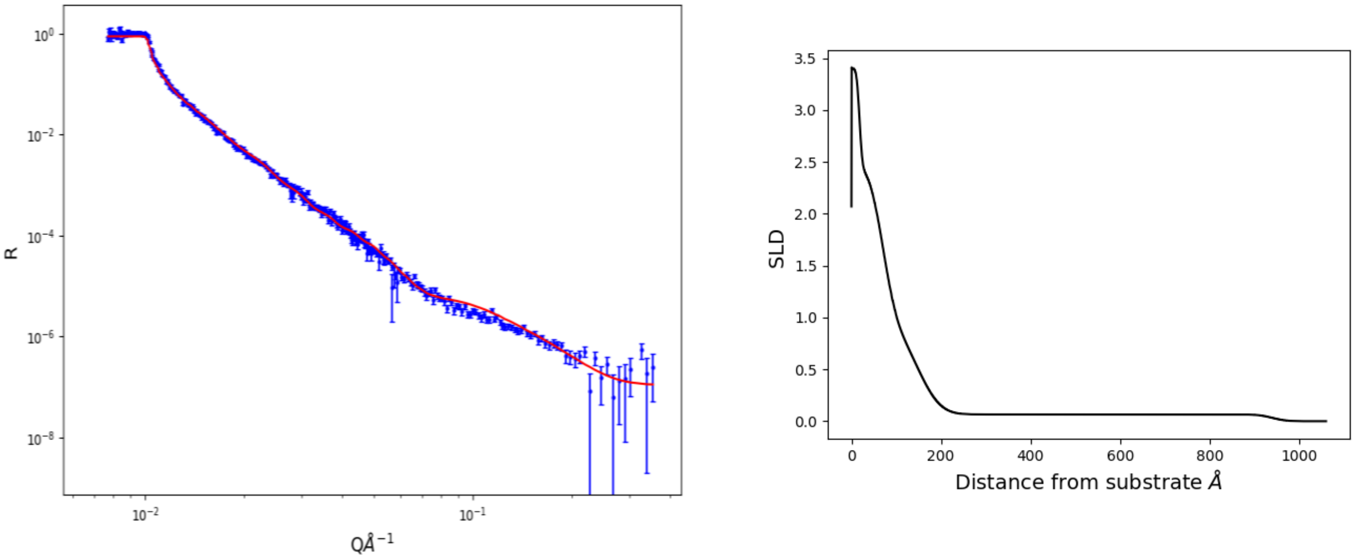
The coatings studied consisted of a thin de-wetted layer of PFPE-PEO spin coated on top of a pre-cured PDMS. This material was chosen as a base film because the favourable mechanical properties and low surface energy of PDMS make it a staple of many foul-release coatings, studying the behaviour of PFPE-PEO at this solid-liquid interface would be particularly pertinent to advancing foul release coating technology. Prior experiments have been attempted by spin coating these molecules together with the pre cure PDMS in a single blended solution however it has proven impossible to incorporate sufficient PFPE-PEO into the solution and maintain coherent thin film coatings. Such blended samples show interesting topographical behaviour, but a previous experiment had shown they don't exhibit surface reorganisation which we attribute to insufficient PFPE-PEO at the surface in these blends to spread as a full layer.

Neutron Reflectivity Experiment:

All samples were measured in air prior to being loaded into solid/liquid cells and filled with water. All samples were measured in D2O, silicon matched water (SLD 2.07) and H2O. The primary data set consisted of a pure PDMS film and 3 films formed of the same PDMS solution with varying amounts of PFPE-PEO spun on top forming macro de- wetted droplets on the order of microns in air.

Results:

Air fits for the data set were consistent with each other and with Base PDMS sample T2, this was as expected and indicated that the PFPE-PEO layer had de-wetted from the PDMS surface and there was no covering layer in air. However, samples did have more structure than might be expected of a pure PDMS film (SLD~$0.065x10^{-6}A^{-2}$) this is a result of silicon dioxide formed in the cured PDMS; the crosslinking reaction of TES 40 results in as much as 40% silica formation which appears to form a diffuse enriched layer near the buried silicon interface.



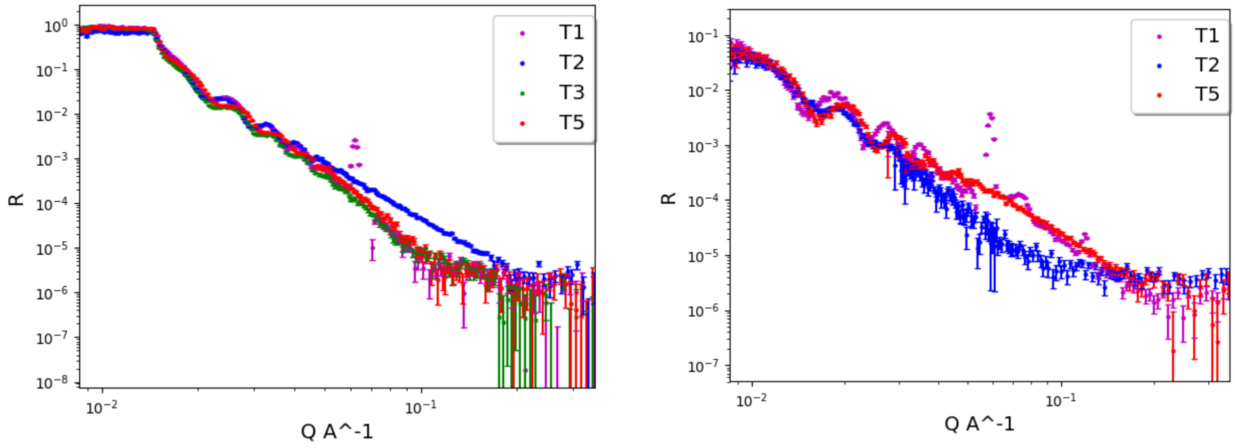
1a. **1b.**

Figure 1A and 1B: Air reflectivity fit for PDMS thin film sample T2 and the SLD profile of fit indicating enriched buried layer near silicon substrate.

Fitting the fit from this sample was used as the basis for the enriched layer in all other samples.

Results evidence of surface reconstruction:

Samples incorporating a PFPE layer exhibited notably different reflectivity profiles in D2O:



2a **2b**

Figure 2a and 2b: Neutron Reflectivity for samples in D2O(a) and H2O(b); T1 PDMS film with PFPE-PEO layer from 11% solution in ethanol, T2: base PDMS, T3: PDMS with PFPE-PEO layer 5% from methanol, T5: PDMS with PFPE-PEO layer 2.5% from methanol.

Fitting and analysis: Fits at this stage are preliminary and ongoing (at time of writing, the experiment concluded **precisely 3 weeks ago**). However, fits in D2O indicate for samples T3 and T5 there is a surface reconstruction due to water and an interfacial layer covering the

liquid/solid surface forms with SLD~3.4x10^{-6} Å^{-2} and a thickness of 25Å. This vindicates the theory that the PFPE-PEO spreads to form a first order wetting (probably molecularly thin) layer on the surface in liquid. This insight significantly improves our understanding of how this material functions in liquid and how effective it could be at resisting biofouling. It is extremely surface active with even the very small amounts of PFPE-PEO deposited on sample T5 being sufficient to create this wetting layer.
The spectra from T1 is similar but has features indicating an advanced structure that we were not anticipating; Bragg sheet formation.

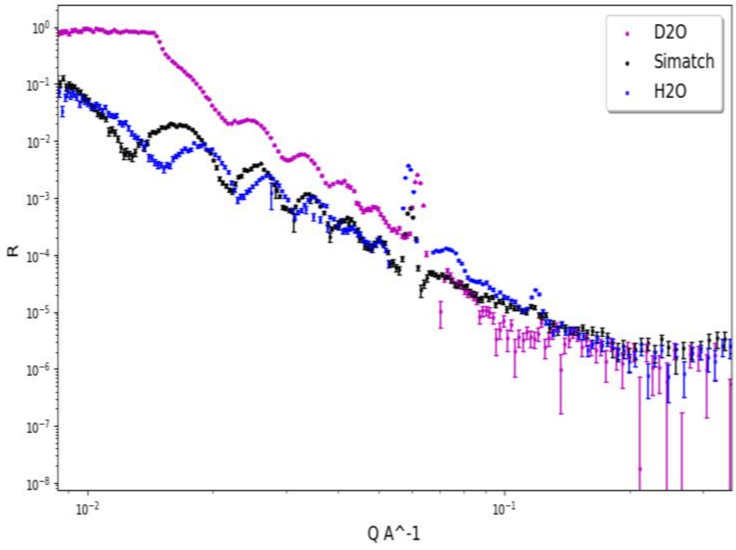


Figure 3: T1 in D2O H2O and silicon matched water.

This sample had by far the largest quantity of PFPE-PEO deposited on the PDMS (equivalent to a more stable 330nm layer when deposited on a PMMA surface) and in water layers of the amphiphilic PFPE-PEO appear to have developed into a more complex lamellar structure based on the hydrophobic fluorinated Block and swollen hydrophilic PEG end Blocks. The primary peaks seen in **Figure 3** indicates an overall length-scale for this feature of **~10nm**, much larger than the wetting layer found in the other samples. A secondary feature is apparent in the Si and H2O contrasts but not the D2O contrast that indicates a further length scale of **~5nm.** This gives some indication of the structure's size and the sharp nature of the feature suggests the structure repeats many times but fitting a precise model to this Bragg Sheet is still ongoing.

Our Local Contact for this experiment was Dr Phillip Gutfreund whose assistance and professionalism were greatly appreciated throughout the experiment. Once we have a viable specular model for the Bragg Peaks exhibited by Sample T1 (seen in **Figure 3**) Phillip has offered to apply models developed in his research group to fit and interpret the corresponding off-specular feature, this is something we don't have the expertise to do ourselves and will improve our overall understanding of the surface structure formed.
The technical Staff at D17 were also excellent providing us with the assistance we needed to set up and align our samples as quickly and seamlessly as possible.

Unfortunately, there was a technical issue with the liquid exchanging pump we found that one line was inoperable and pumped air into the system meaning an intended contrast measurement had to be scrapped and on a couple of occasions contrast exchange failed and a measurement had to be repeated resulting in fewer samples being measured overall than initially intended. This problem was reported with a recommendation that the D17 HPLC pump be serviced as soon as possible.