

High Resolution Studies of Interfacial Polymer Physisorption and its Mediation by Surfactant

Introduction

Dual Polarisation Interferometry (DPI) is an essential tool for the clear understanding of interfacial physisorption processes⁽¹⁾. This application note describes the use of DPI for quantitative analysis in real time of the physisorption of an amphiphilic polymer and a non-ionic surfactant at the solid–liquid interface, and the mediating effect exerted by the surfactant on the polymer sorption process.

We were interested in understanding the differences in the structure of the physisorbed polymer as a consequence of differing polymer solution composition in the presence and absence of surfactant. These types of measurements are of particular value to surface scientists and to those developing or assessing the efficacy of surface cleaning products.

Experimental

The DPI experiments were performed on a Farfield **AnaLight**[®] instrument. The surface used was a native unmodified silicon oxynitride **AnaChip**[™], washed with Decon[®] 90. The temperature of the samples was controlled throughout to 20°C. Reagents were analytical grade or higher, water was HPLC grade and degassed prior to use. Nonionic surfactant and amphiphilic polymer samples were used as provided. Solutions were degassed prior to use.

An unmodified **AnaChip**[™] was loaded into the **AnaLight**[®] with water as the ‘running buffer’ and washed *in situ* with 10% (v/v) Decon[®] 90 for 2 minutes. The **AnaChip**[™] was then calibrated with an 80%(w/w) ethanol/water solution, which also served to ensure that any residual Decon[®] 90 was removed. Polymer (0.1% and 0.5%) and surfactant (5%) solutions were passed over the **AnaChip**[™] as single or double injections of 10 minutes, each one followed by a 10 minute water rinse. After each sample measurement, the surface was cleaned with Decon[®] 90 and recalibrated before the next sample was injected.

Results and Discussion

Figure 1 shows the data acquired after rinsing for the different polymer and surfactant samples. In the absence of surfactant, the data shows clearly that polymer sorption is concentration dependent, with concentrated (0.5%) solutions depositing thicker and more diffuse layers at the interface than less concentrated solutions (0.1%).

In the presence of surfactant this concentration dependence is eliminated. The presence of the surfactant results in less polymer mass being deposited within a thinner and significantly denser film structure. These observations have been confirmed by the supplier as the trend expected for these samples.

Event	Density (RI units)	Thickness (nm)	Mass Coverage (ngmm ⁻²)
5% Surfactant (during rinse)	1.3924	5.880	1.866
5% Surfactant (post rinse)	1.4333	0.485	0.262
0.1% Polymer	1.4314	2.254	1.193
0.5% Polymer	1.4248	2.837	1.401
0.1% Polymer + 5% Surfactant	1.4476	1.831	1.128
0.5% Polymer + 5% Surfactant	1.4497	1.831	1.149

Figure 1: Quantitative layer values after sample physisorption for 10 minutes followed by 10 minutes rinse (except for ‘surfactant during rinse’ which was taken after 1 minute)

Figure 2 shows the real time data associated with the 0.5% polymer sorption process. Interestingly, it can be seen that on the first sample injection, the film structure is still changing even when the physisorbed mass is constant. The second sample injection also shows quite different behaviour from the first, indicating multilayer formation rather than a simple continuation of the first adsorption process.

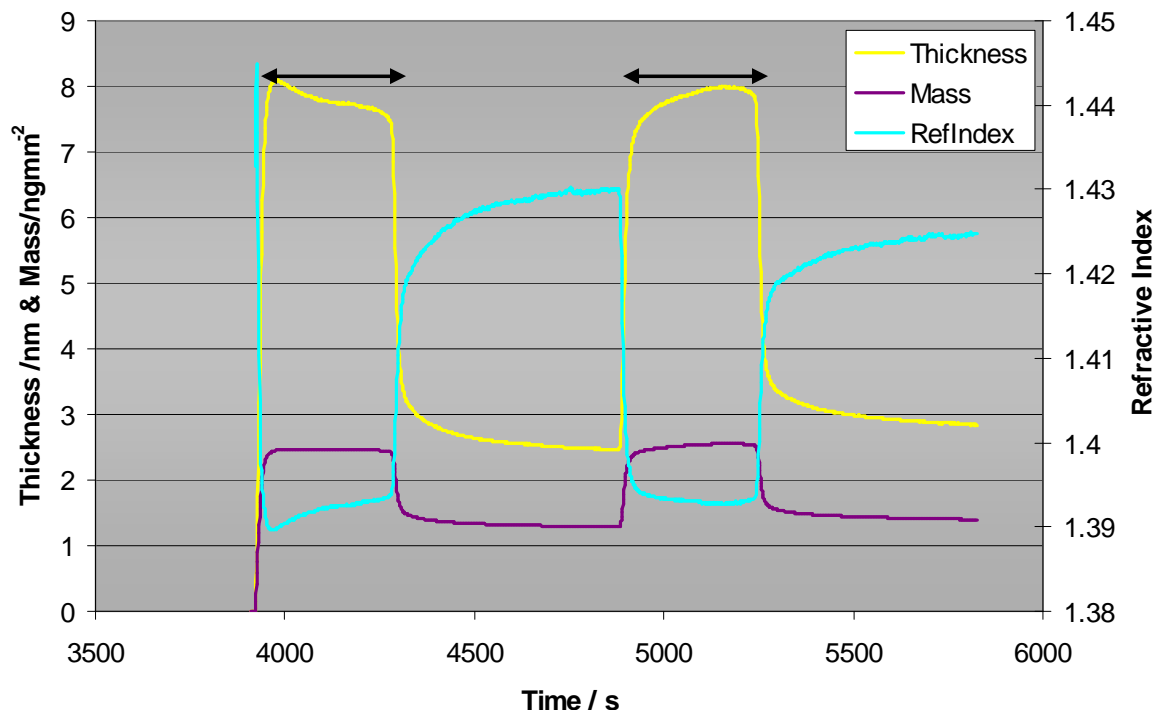


Figure 2: Real-time mass, thickness and density (Refractive Index) changes for the physisorption of 0.5% polymer. The arrows indicate the two sample injection steps, during which time the data has been 'resolved' including the bulk sample Refractive Index change and so includes an offset due to this effect

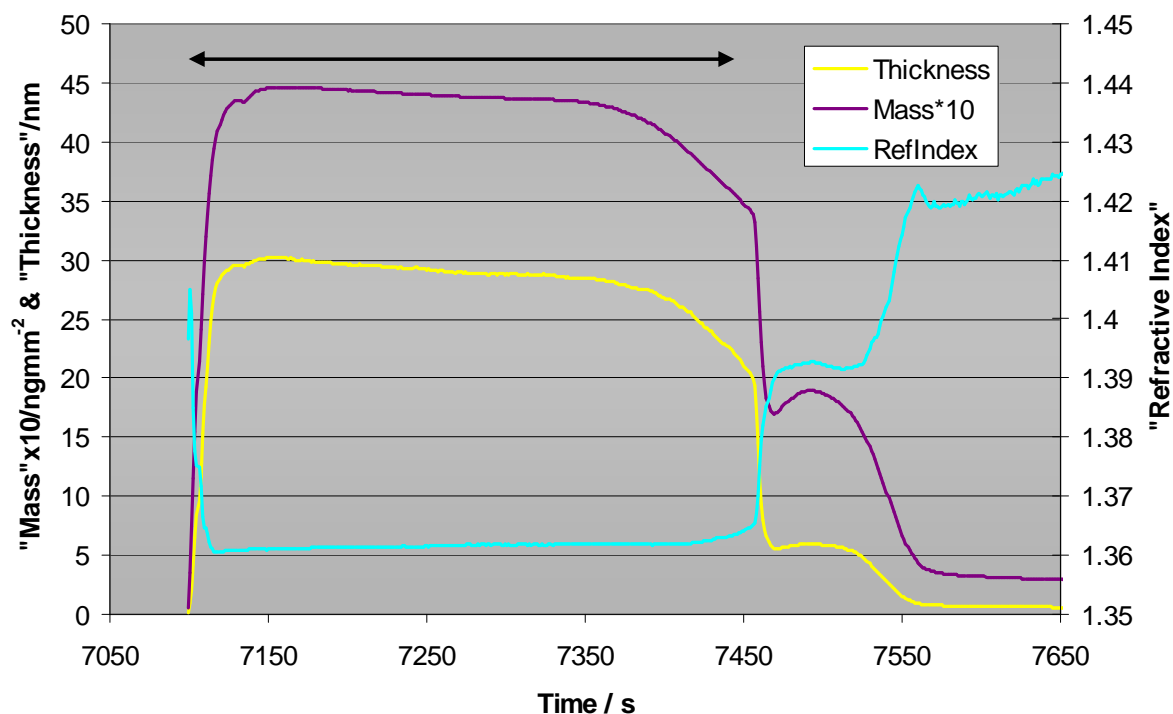


Figure 3: Real-time mass, thickness and density (Refractive Index) changes for the physisorption of 5% non-ionic surfactant. The arrow indicates the sample injection step, during which time the data has been 'resolved' including the bulk sample Refractive Index change and so includes an offset due to this effect

Figure 3 shows the real time data associated with the 5% surfactant sorption and rinse process. Most striking is the mass gain 'shoulder' around 7500 seconds, which is after rinsing has started and most of the surfactant solution has been removed from the **AnaChip™** surface. At this point, the thickness of the layer is ~6nm and RI 1.393. This corresponds to a layer of 44% coverage (taking an RI for the surfactant of 1.468). This, in conjunction with the fact that the layer thickness corresponds to approximately twice the surfactant molecule length, is consistent with the formation of a layer of **micelles** on the surface of the **AnaChip™** as the surfactant concentration drops towards the CMC on rinsing (see schematic in **Figure 5**). This layer is removed as the concentration drops below the CMC with further rinsing.

It should also be noted that a similar micelle layer formation can be concluded in the early stages of introducing polymer samples containing surfactant to the **AnaChip™** (see **Figure 4** below).

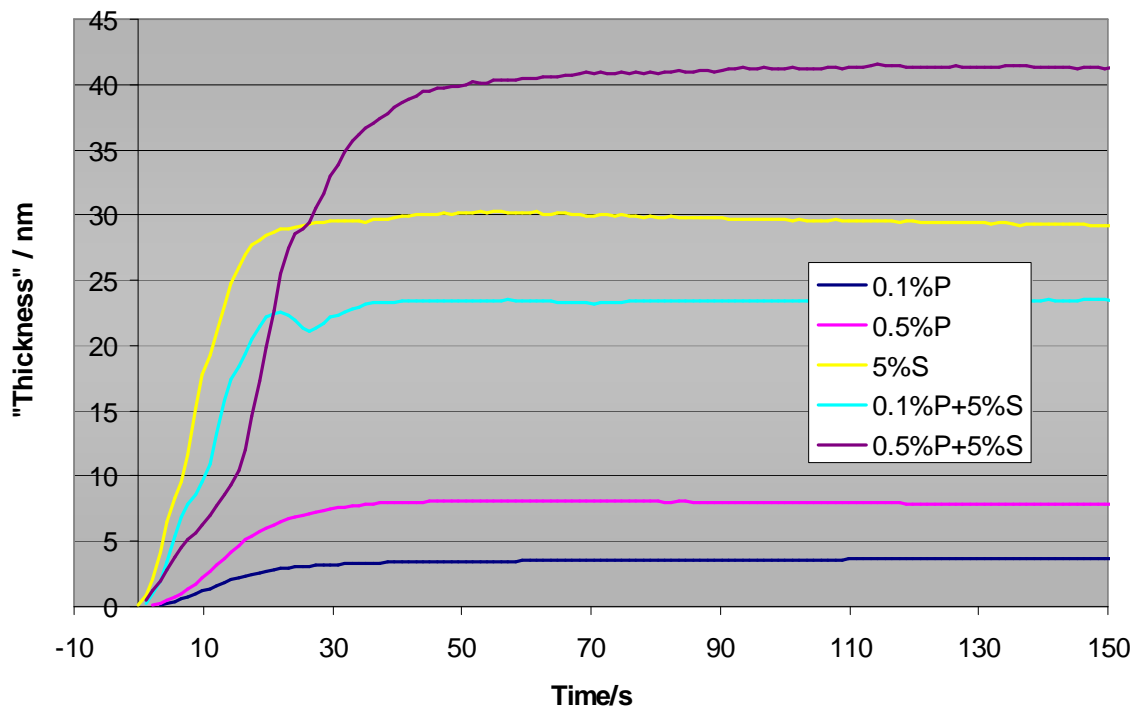


Figure 4: Real-time thickness changes for the physisorption of polymer (P) and surfactant (S) samples (including bulk RI)

Figure 4 shows the real time thickness data for the initial sorption for all samples studied. The polymer samples without surfactant can be seen to adsorb slowly in a straightforward process. The samples containing polymer and surfactant are more complex, showing multiple adsorption steps taking place. The initial surfactant micellar layer formation can be identified in all surfactant-containing samples after a matter of seconds.

The dip in the thickness for the 0.1% polymer/5% surfactant sample around 25 seconds suggests a mechanism for the surfactant mediation of the polymer sorption process. Initially, surfactant and surfactant/polymer complexes are formed at the **AnaChip™** surface. These are displaced as the polymer rearranges itself and slowly physisorbs more strongly onto the **AnaChip™** surface. This observation is supported by the mass and density data (not shown).

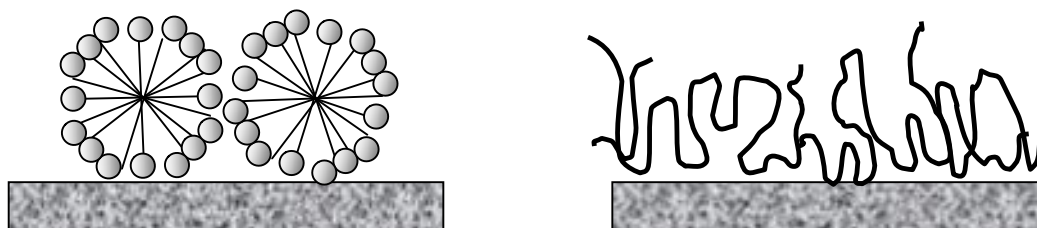


Figure 5: Visual schematic of the surfactant micellar and polymer coated surface structures

Conclusions and Benefits

DPI enables the study of the interfacial behaviour and structure of a diverse range of molecular systems. These experiments show DPI can be applied to the study of the polymer physisorption and its mediation by surfactants.

Crucially, the structural information obtained for the polymer physisorption process highlights the mechanistic effect of the presence of the surfactant. This will also enable the differing properties of the polymer-modified surface (as subsequently determined) to be related to its structure and method of formation. The **AnaLight**[®] instrument range and associated experimental protocols give the researcher a unique combination of high-resolution data in real time on thickness, refractive index (density) and surface coverage in a benchtop, easy to use technique. The **AnaLight**[®] is an important enabling tool for surface scientists giving them the ability to:

- Clearly understand the molecular mechanisms involved in polymer layer and multilayer formation and subsequent interactions
- Quantify the rate of layer formation, rinsing and rinse stability
- Understand of the influence of concentration, additive composition, temperature, pH, salt etc. on layer formation, integrity and structure
- Tailor polymer formulations to optimise applications benefits
- Avoid the limitations and ambiguities that are inherent in other techniques for such studies, and provide the final results and analysis rapidly

References

This work was carried out with samples provided by one of the world's largest manufacturers of personal care products. Farfield would like to thank them for their help and useful discussions.

For further applications information contact: applications@farfield-scientific.com or Telephone the applications team on +44 (0) 870 950 9717

⁽¹⁾ G. Cross, A. Reeves, S. Brand, M. Swann, L. Peel, N. Freeman & J. Lu; *J. Phys. D: Appl. Phys.* **37** (2004) 74-80