Experimental report

01/03/2023

Proposal: 9-11-1975 **Council:** 10/2019

Title: Study of water uptake and failure modes in protective polymer coatings

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: C15H16O2
C6H4(CH2NH2)2

Instrument	Requested days	Allocated days	From	To
D17	3	1	07/06/2021	09/06/2021

Abstract:

Polymer based barrier coatings are important, as they are effective at inhibiting corrosion. In this proposal we plan to study the water transport and distribution in thin planar epoxy inorganic interface layers analogous to the polymer particle interfaces present in actual epoxy network composites..

We want to depth profile the water volume fraction in these polymer layers using neutron reflectivity kinetically using D2O uptake and then subsequent exchange with H2O. To ascertain the solvent exchange kinetics along with any difference in water distribution in these films. We will be able to quantify water enrichment/depletion at the polymer layer/substrate interface. This study will enable us to understand the importance of the many polymer/inorganic interfaces which are present in fully formulated coatings, which have additives of micro and nanoparticles, and so lots of interface. Also knowing the polymer solvated volume fractions and dynamics will allow us to produce accurate simulations which will help us to generate important predictions and insight.

NOTE: This experiment was performed during the Covid-19 pandemic. As a result, the experiment was simplified considerably to reduce workload on the beamline staff. The experimental days were combined with experiment 9-11-1988.

Introduction: This experiment aimed to use neutron reflectivity to examine the uptake and distribution of water in in thin films of model epoxy networks as a proxy for coatings used in the anti-corrosion industry. This type of epoxy coatings fail when a conduction pathway is formed, and ions come into contact with the metal surface, leading to corrosion. These pathways are typically formed as a result of the uptake of water in the coating, as such precisely understanding the overall uptake for a film, and if the water preferentially sits at the surface as well as the diffusion time can help us design better and more longer lasting industrial coatings.

Experimental Details:

Sample preparation: All 5 samples, detailed in Table 1, were prepared in Sheffield and shipped to the ILL prior to the start of the experiment. Each sample was spin coated onto silicon blocks with a native oxide layer and annealed under inert gas in the oven for 5 hours at temperatures greater than 30°C above the glass transition temperature to remove residual solvent. Samples labelled DER331 are cross-linked systems of liquid epoxy resign and m-Xylylenediamine (MXDA). The reagents were mixed in a 1:1 stoichiometric ratio and allowed to cure at room temperature until sufficient molecular weight was achieved to film form before being dissolved in 2-Methyltetrahydrofuran (m-THF) and spin coated. The samples labelled Araldite 6099 are a high molecular weight uncross-linked epoxy, which was spin coated from 1,4-Dioxane. The sample labelled PS was a film of polystyrene spin coated from Toluene, this was used as a hydrophobic control sample to see how it compared to the hydrophilic epoxy samples.

Sample #	Block label	Sample Type	Layer 1 (nm)	Layer 2 (nm)
1	B1	DER331	SiO2=1.51	avg≈33.2
2	B2	DER331	SiO2=1.33	avg≈159.7
3	B3	Araldite6099	SiO2=1.38	avg≈146.5
4	B4	Araldite6099	SiO2=1.26	avg≈30.6
5	B5	PS	SiO2=1.47	avg≈29.6
6	Au1	Araldite6099	Au≈602	avg≈24.6

Table 1: Sample details and pre characterisation of layer thickness from ellipsometry

Neutron Reflectivity Measurements: Each sample was first measured dry in air. Two angles were used to give a qz range of .008- 0.3 $Å^{-1}$. D17 was used in time-of-flight (TOF) mode and the specular neutron reflectivity curves were extracted from the raw incident and reflected neutron beams using the COSMOS data reduction program. Samples were then mounted in solid-liquid cells. Dynamics data for a single angle in 1 min time slices were collected for samples 2 and 3 the first 60 minutes in D20. Full q-range measurements at two angles were then taken for the completely saturated samples 2 hours after the cells were filled with D20. Dynamic scans were then collected again during the exchange from D20 to H20 and full q-range measurements at two angles were then taken for the completely statured in

H20 (~2 hrs post exchange). Samples 1, 4,5, and 6 were all measured without kinetic data just with a full profile in H20 and then D20 at two angles.

Results:

Sample 6, which has a thick layer of evaporated gold on it to provide a different in surface chemistry as compared to the native silicon oxide which we expected to have hydrogen bonding with the epoxy was unfortunately returned to Sheffield completely de-wetted and ripped up. As we are unsure when this happened, likely in the first filling in the liquid cell, this data was discarded. Furthermore, the in D20 the fringes were completely lost in samples 2 and 3 on immersion in D20 (Fig 1) due to the film being contrast matched to the silicon.

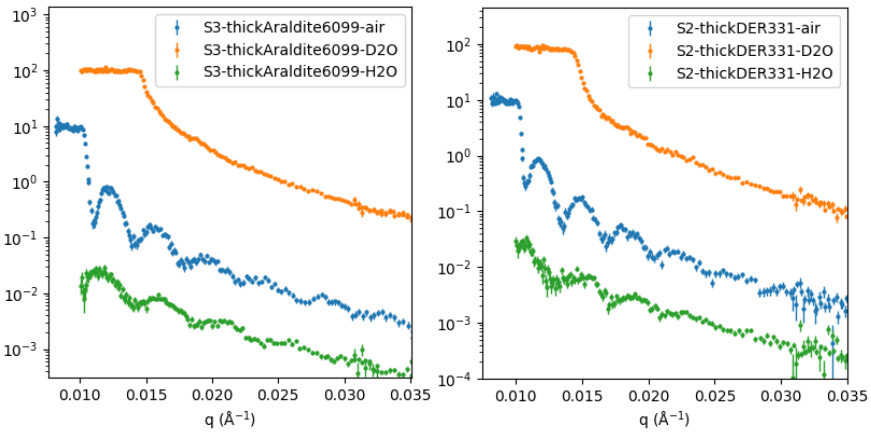

Figure 2: Data for thick films of cross-linked and uncross-linked epoxy in air, D20 and H20. In D20 the films ended up contrast matched to the Silicon resulting in the loss of fringes

Our preliminary uptake study's using ellipsometry indicated a total uptake of less than 1% water a room temperature. In order to contrast match the silicon the films we would have had to uptake more than 2.5% D20 or more than twice what was expected for these films. While a surprising and interesting result, it rendered the D20 data and diffusion kinetics unfitable. Surprisingly this was not the case for the thinner films (Fig 2) which produced the interesting and industrial relevant result that there was a lower concertation of D20 at the buried interface which could explain why these materials are effective corrosion protection coatings.

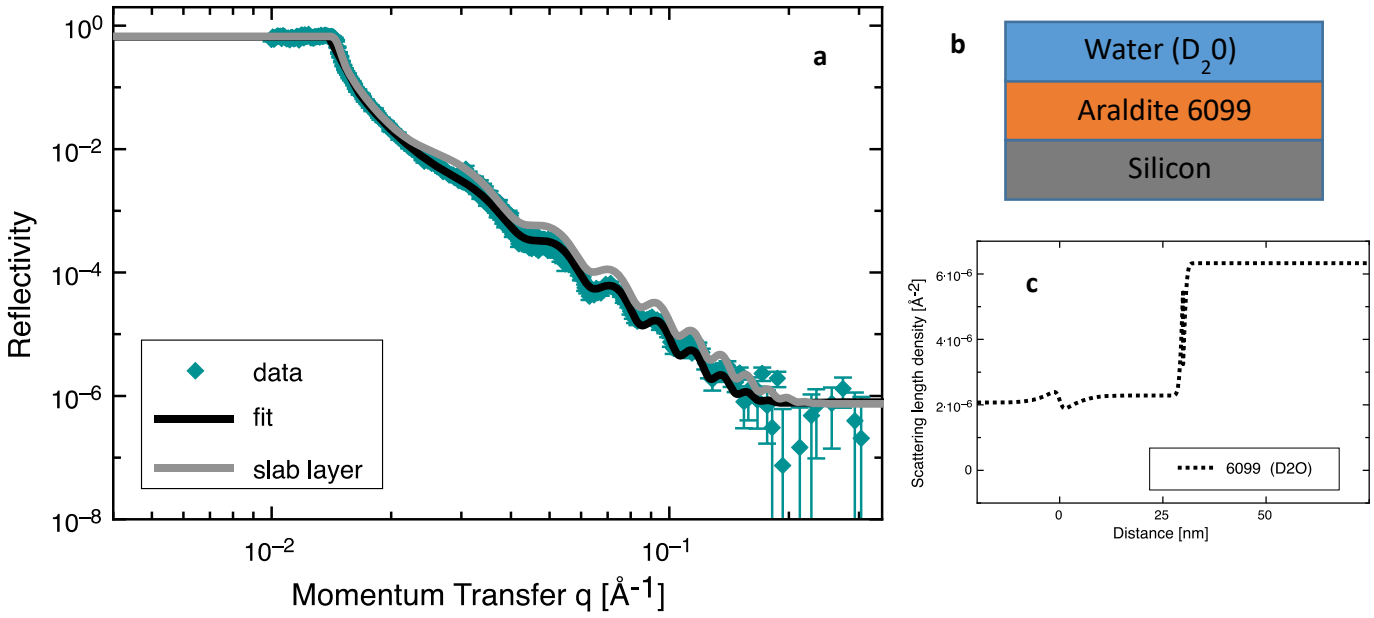

Figure 1: a) Reflectivity data for uncross-linked 6099 epoxy in D20. The included fits are for a slab model which assumes that no D20 enters the film and a fit with a graded layer showing the D20 of profile in the film. b) a diagram which shows the 3 layers used in the fit. c) The SLD profile for the fit showing a depletion layer at the buried interface with a lower concentration of D20.