Experimental report

14/02/2017

Proposal: **1-03-34**

Council: 4/2016

Title: Artwork is not forever

Research area: Materials

This proposal is a new proposal

Main proposer: **Bernard CABANE**

Experimental team: Amelie CASTEL
Yahya RHARBI
Bernard CABANE

Local contacts: Philipp GUTFREUND

Samples: Benzyl alcooh

Instrument	Requested days	Allocated days	From	To
D17	2	0		
FIGARO	2	2	19/12/2016	21/12/2016

Abstract:

We propose to measure the solvent penetration of benzyl alcohol into varnish layers as used in the restoration process of artwork by using Neutron Reflectometry.

Report of experiment – Figaro 1-03-34_163

PhD Project: Using neutrons to protect our works of art

A. Castel, P. Gutfreund and Y. Rharbi

The purpose of this Figaro experiment was to observe the penetration and the effects (swelling, dissolution) of benzyl alcohol and D_2O on model varnish films usually used by art restorers. We used neutron reflectometry to determine the depth density profile of the solvent.

<u>Materials / samples:</u>

Laropal® A81 is a condensation product of urea and aliphatic aldehydes. This low molecular weight resin comes in the form of small semi-transparent pellets. Its glass transition temperature (Tg) is 57°C. It is soluble in alcohols, esters, ketones and aromatic hydrocarbons and is very stable to heat.

The resin Laropal®A81 was dissolved in proportions of 40 g/L and 78,8 g/L in Toluene (two samples each). The samples were produced by spin coating the solution on 8x5x1 cm^3 single crystal silicon blocks. The thickness obtained was approximately 100 nm (40 g/L) and 210 nm (80 g/L).

<u>Experiment and results</u>

First, the neutron reflectometry was applied to each sample in air before and after annealing for 30 min at 113 °C.

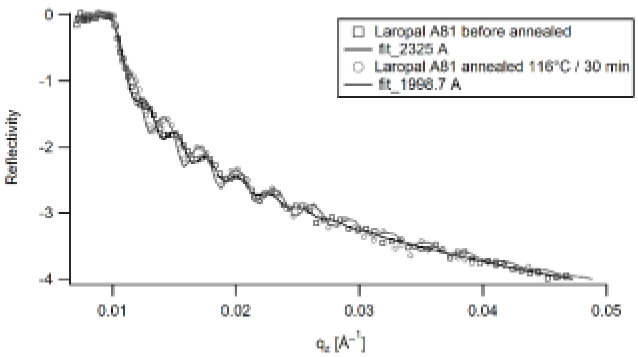

Figure 1: Neutron Reflectivity from a polymer film of Laropal® A81 in air before (rectangles) and after annealing (116°C / 30 min) (circles). Solid lines are fits to the data. Figure produced using Motofit.

As can be seen in Fig. 1 the reflectivity of the polymer layer changes after annealing. The thickness of the varnish is reduced from 2325 Å to 1998,7 Å upon annealing. It could be the solvent that is removed or the polymer that gets compact.

Then, one sample was immersed in D_2O the whole night.

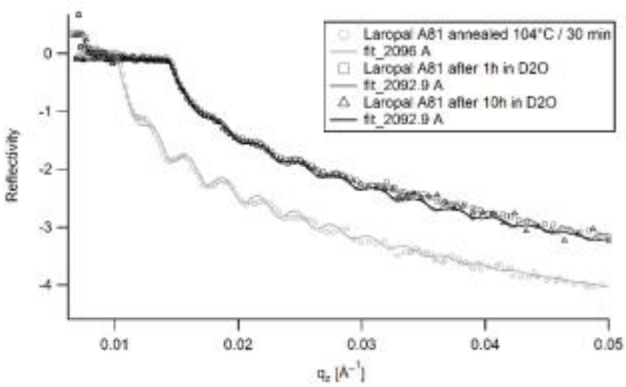

Figure 2: Neutron reflectivity from a polymer film of Laropal® A81 before (circles) and after immersed in D_2O (rectangles and triangles). Figure produced using Motofit.

The results (figure 2) show that D_2O does not significantly swell this synthetic polymer within the sensitivity of 0.5%. After drying the polymer film the initial structure is recovered.

The last step was to observe the influence of benzyl alcohol on the polymer film. Two samples were placed in contact with an increasing concentration of solvent (0%, 0.05%, 0.1%,0.3% and 0.5%) in D_2O.

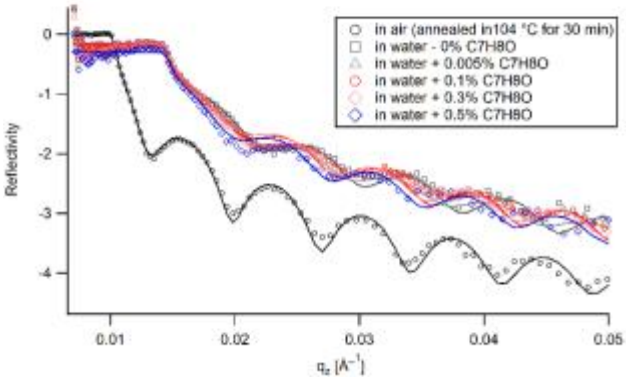

Figure 3: Influence of Benzyl alcohol on a polymer film of Laropal® A81 observed by neutron reflectometry. Figure produced using Motofit.

The film thickness promptly increases with the concentration of benzyl alcohol transferred. At 0,5 % of benzyl alcohol, we observed a change of the film with time; beyond this concentration, there is a radical rupture of the film, we thus estimate 0.5% to be the critical concentration for an irreversible rupture for these thicknesses.

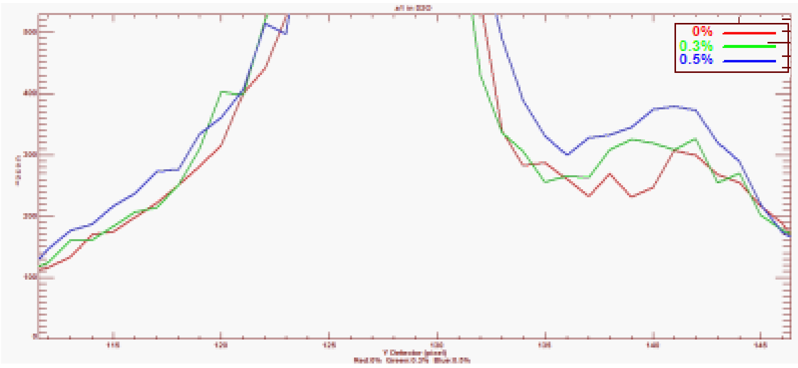

Figure 4: Detector scan of the reflected intensity [a.u.] of the polymer subjected to three concentrations of benzyl alcohol in water (0%, 0.3% and 0.5%).

Immerged in benzyl alcohol up to 0.5%, the film swells linearly with the quantity of solvent in D_2O. That means benzyl alcohol has been transferred to the polymer since water does not swell the film (figure 2). It should be noted that the swelling was accompanied by an increase in off-specular (Yoneda) scattering as can be seen in Fig.4. This points towards in-plane heterogeneities that are amplified during swelling until film rupture follows. This is in harsh contrast with the homogeneous normal swelling of the varnish, which is reflected in a very smooth polymer/water interface (< 5 Å) up until the film rupture.

<u>Conclusion</u>

This first approach allowed to verify the viability of our protocol.

The results obtained showed that:

- Laropal® A81 is not sensitive to D_2O after annealing and it does not swell at its contact
- benzyl alcohol is a good solvent to dissolve Laropal® A81 and the quantity of solvent transferred in the varnish layer depends on the quantity of solvent added into the D_2O. Beyond a certain concentration the film breaks
- inhomogeneous swelling (e.g. through cracks) could be the reason of the film rupture

This experiment gives results which appear promising even though the varnish films showed some macroscopic thickness variations. We expect to have higher resolution results with perfectly homogeneous films in the near future.