Characterization of Vacuum Deposited Thin Organic Layers by Phase Shifting Interferometry and FTIR Spectroscopy for Space Contamination Study

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Abstract

Although satellites and spacecrafts are exposed to very small amounts of organic contamination (typically 10^{-9} to 10^{-5} g.cm^{-2} cumulated over their lifetime) from the outgassing of some of their own structural components, fixation and photo-degradation of organic compounds can significantly alter the thermo-optical properties of critical surfaces involved in their passive thermal regulation. The study of surface molecular contamination under conditions representative of space environment is therefore of prime interest in order to define mitigation strategies. The Centre Spatial de Liège has recently initiated research work on this topic and first experimental results are presented here. Organic thin films have been deposited using vacuum thermal evaporation / sublimation and their topology and equivalent surface concentration have been characterized using phase shifting interferometry. Furthermore, FT-IR spectroscopy in reflection configuration have been tested in different conditions in order to monitor the IR signature of contaminated surface samples this in the perspective of implementing an in situ monitoring system on a deposition chamber with UV exposure capability.

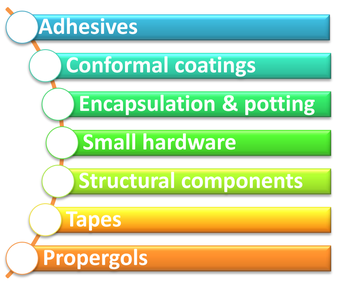
Introduction & scope: spacecraft outgassing contamination & thermo-optical properties

In space vacuum, thermal cycling as well as radiations induce particulate and molecular contamination. The molecular contamination comes from organics materials composing the satellite and propergols. Molecules releases in three mechanisms: desorption, diffusion and decomposition. Depending on satellite geometry and surfaces view factors, the outgassed molecules can either be "lost" in deep space or condensed on spacecraft surfaces. Since the sun irradiates satellite, contamination undergoes irreversible polymerization and photochroism mainly by UV such as the whitening/yellowing of current life polymers. Hence along a satellite lifetime the contamination is growing and also altered.

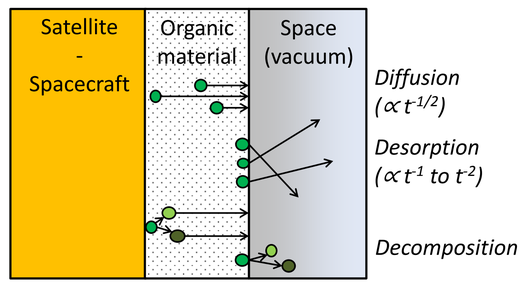
It is an important issue for thermo-optical surfaces aiming at regulating satellite temperature through radiative emission. They are characterized by thermo-optical properties: the solar absorptance α and the emissivity ε. Optical solar reflectors (low α_s and high ε) , the main components in passive thermal regulation, are very sensitive to contamination issues. The end-of-life (EOL) α_s reaches for instance typically twice to thrice its beginning-of-life (BOL) value.

In order to develop mitigation strategies, it is primordial to identify the functional groups and understand contamination mechanisms. However to be representative of space environment measurement must be done in-situ to avoid the contributions of atmospheric species to reactions.

Contamination sources



Outgassing processes

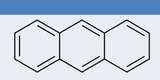
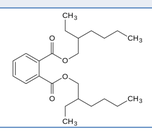


Solar Absorptance: $\alpha_s = 1 - \frac{\int_{250\ nm}^{2500\ nm} R(\lambda)S(\lambda)d\lambda}{\int_{250\ nm}^{2500\ nm} S(\lambda)d\lambda}$ **Emissivity (IR):** $\varepsilon_{IR} = \frac{\int_{3\ \mu m}^{20\ \mu m} A(\lambda)E(\lambda)d\lambda}{\int_{3\ \mu m}^{20\ \mu m} E(\lambda)d\lambda}$

Vacuum deposited organic thin films & contaminated concentration estimation

Deposition characteristics

- Method: Thermal vacuum
- Pressure: ≈ 10^{-5} mbar
- Samples: Glass / Ag (150 nm) / SiO_x (5 nm) by IBS

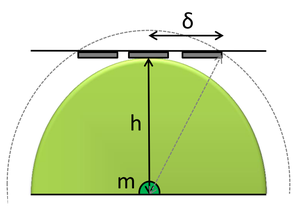
Contaminant *d (g.cm^{-3})	Formula	T_{fusion} (°C)	$T_{crucible}$ (°C)	$P_{sat\text{-}vap.}$ at 25 °C (mbar)
Anthracene * 1.25		+ 217,5	≈ 150	≈ 8x10^{-4}
Bis(2-ethylhexyl) phthalate (DEHP) *0.99		- 50	≈ 100	≈ 10^{-7} – 10^{-8}

Estimation of deposited concentration

Local concentration is estimated according to the known deposited mass and distances using emission characteristics of a surface source according to Knudsen's assumptions for evaporation at low pressures. The law involves the cosine of the emission angle. Hence the surface has directional properties. Finally the thickness e_{moy} is given by:

$$e_{moy} = \frac{mh^2}{\pi\rho(h^2+\delta^2)^2}$$

Schematic representation of vacuum thermal outgassing experiment



$$c = e_{moy}.\rho$$

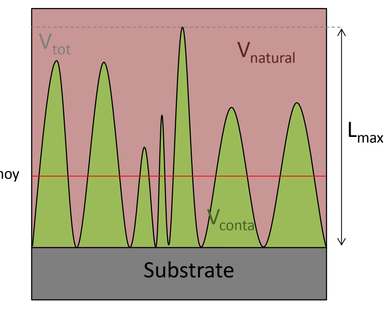
Direct concentration measurement through PSI

Thanks to topology reconstruction from phase shift interferometry, it is possible through volumetric data to go back to concentration deposition and its equivalent thickness when the films display complex topologies (ex. DEHP).

$$V_{conta} = V_{tot} - V_{natural} \qquad c\left(\frac{g}{cm^2}\right) = \rho.\frac{V_{conta}}{S}$$

$$V_{conta} = (L_{max}.S) - V_{natural} \qquad e_{moy} = c/\rho$$

Contaminated surface cross section

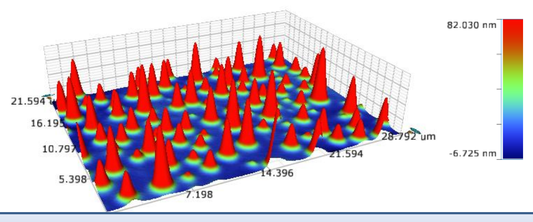


Results : Phase Shift Interferometry quantification

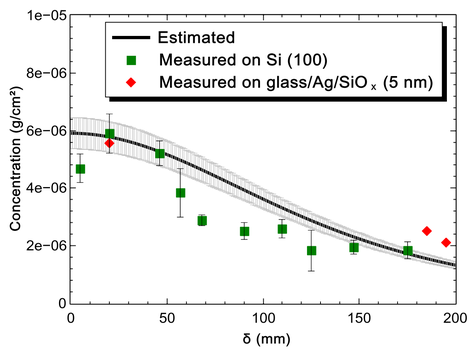
DEHP depositions (h ≈ 18 cm)

- DEHP thin films seem homogeneous at macroscale but are heterogeneous at microscale : several random conical protuberances
- Measured concentration are close to estimations both for Si and SiO_x surfaces
- The surface state evolves with time (not shown)

PSI 3D view of DEHP thin film on SiO_x (c ≈ 3.6x10^{-6} g/cm²)

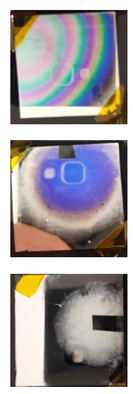


Comparison of estimated vs measured concentration

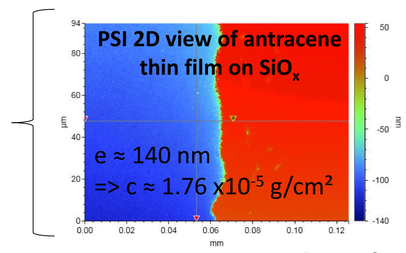


Anthracene depositions (h ≈ 3 cm)

- Anthracene homogeneous films thinner than 90 nm are difficult to deposit or require long exposure time (low sticking coefficient / high reemission) or / and low h distance (meaning low surface coverage and high gradient). It may also be related to crystallization when samples come back to air
- Thin films are dense with a low roughness at the µm scale
- Roughness increases towards borders



e_{max} ≈ 440 nm => c ≈ 5.50x10^{-5} g/cm²
e_{min} ≈ 113 nm => c ≈ 1.41x10^{-5} g/cm²



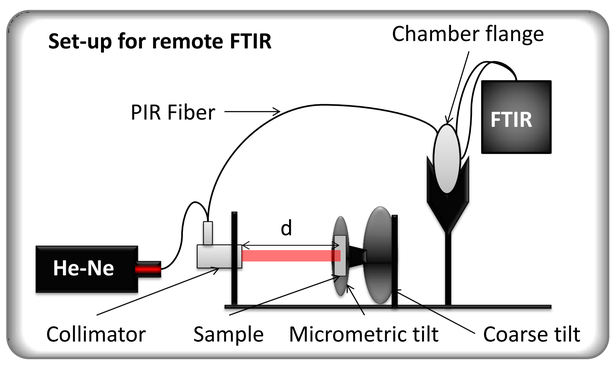
e ≈ 90 nm => c ≈ 1.13 x10^{-5} g/cm²

Results : Remote FTIR analysis

Remote FTIR

- FTIR spectrometer: Excalibur 3100, from Varian
- FTIR parameters: 10 measurements of 900 scans with a resolution of 4 cm^{-1} at a distance d ≈ 9 cm
- Collimator in reflection mode to reduce divergence
- Coarse tilt alignment is done with visible laser light and fine micrometric tilt alignment with IR signal
- PIR (Silver Halide) fiber transmission range ≈ 500 – 2000 cm^{-1}

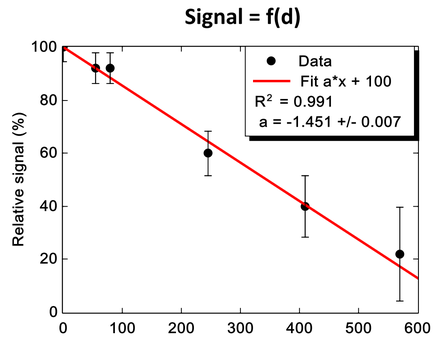
Set-up for remote FTIR



Signal vs distance

- Normalization: Au coating FTIR spectrum
- Maximum signal with PIR fiber ≈ 0.5 % of maximum signal with integrated sphere (before detector saturation)
- Absolute Limit Of Detection (LOD) in the actual configuration is close to d ≈ 700 mm
- An additional loss of signal ≈ 30 % must be expected by using ZnSe window
- Estimation does not fit with measurements, possibly because of reemission and sticking coefficients

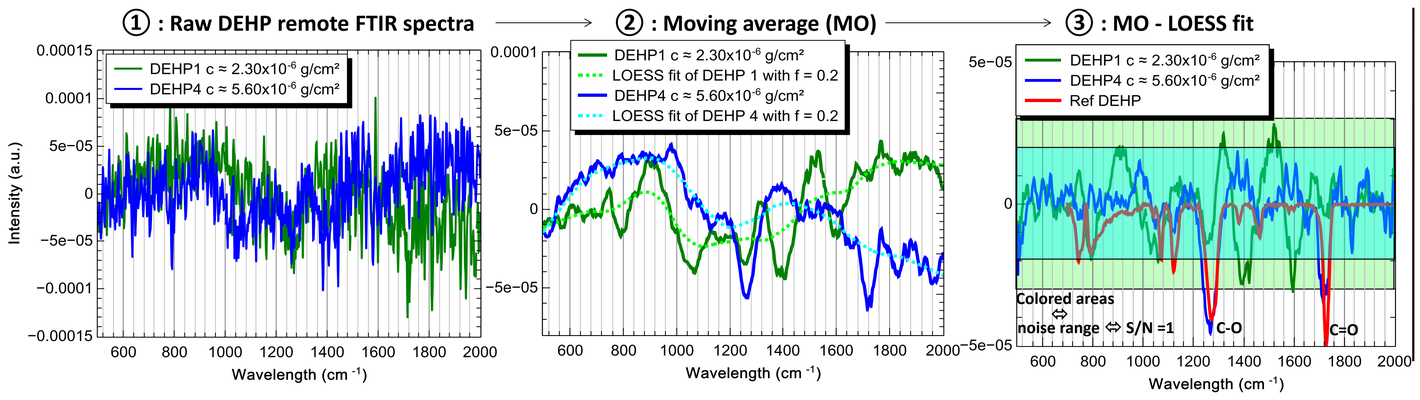
Signal = f(d)



DEHP analysis

- ✓ h ≈ 9 cm
- ✓ At these concentrations, data treatment is required to extract data
- ✓ Characteristic peaks (≈ 1727 cm^{-1} and 1272 cm^{-1}) can then be detected successfully
- ✓ LOD ≈ 3x10^{-6} g/cm²

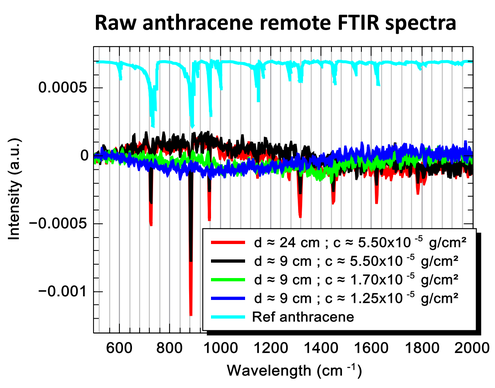
① : Raw DEHP remote FTIR spectra → ② : Moving average (MO) → ③ : MO - LOESS fit



Anthracene analysis

- ✓ Well defined peaks
- ✓ Peak intensity decreases proportionally with the signal loss induced by increasing the distance d
- ✓ LOD ≈ 3x10^{-5} g/cm²

Raw anthracene remote FTIR spectra



Conclusion

Organic thin films of DEHP and anthracene were deposited by thermal vacuum evaporation / sublimation successfully on Si and reflector surfaces. Their concentration can be estimated through a simple approach and be measured with an optical profilometer in PSI mode. A set-up allowing remote measurement of samples at several centimeters have been built with PIR fiber, a reflector collimator and sample tilt-adjustment components. Depending on the contaminant, it have been detected successfully as low as 5x10^{-5} to 5.10^{-6} g/cm². These results validate the concept of remote FTIR in reflection in order to detect IR signatures in the perspective of implementing an in situ monitoring system on a deposition chamber with UV exposure capability. Set-up improvement such as increasing source power or reducing optical fiber losses should increase sensitivity and allow a true IR monitoring as well as lower LOD. Hence in-situ contamination build-up and UV modifications could be monitored in a vacuum environment. Latest experiments conducted with an integrating sphere coupled with a parabolic mirror demonstrate significant improvement both by increasing FTIR signal and by bringing the LOD lower than 10^{-6} g/cm² for the DEHP.