INSIGHT INTO THE FUNDAMENTAL BEHAVIOUR OF ORGANIC FRICTION MODIFIERS THROUGH SYNCHROTRON X-RAY EXPERIMENTS

I. Kicior[a,b*], T. Poręba[a], E. A. Willneff[c], J. Frey[a], V. Honkimäki[a], A. Morina[d], P. Dowding[e], S. L. M. Schroeder[b]
*inga.kicior@esrf.fr
[a] European Synchrotron Radiation Facility, 71 Av. des Martyrs, 38043 Grenoble, France
[b] School of Chemical and Process Engineering, University of Leeds, Leeds LS2 9JT, UK
[c] School of Design, University of Leeds, Leeds LS2 9JT, UK
[d] School of Mechanical Engineering, University of Leeds, Leeds LS2 9JT, UK
[e] Infineum UK Ltd., Milton Hill, Abingdon OX13 6BB, UK

KEYWORDS
friction; lubricant additives; experiments in tribology, organic friction modifiers

ABSTRACT
Organic Friction Modifiers (OFMs) are a class of lubricant additives with surfactant-like structure, with usually at least 12 carbon atoms in the hydrophobic chain and a polar head group that change their adsorption behaviour [1]. These additives have been known for a century but became less popular after the discovery of zinc dialkyl dithiophosphates (ZDDPs). ZDDPs are now a subject of sustainability concerns due to the emission of sulphur and phosphorous compounds during their degradation. OFMs do not contain harmful elements, are biodegradable and are therefore studied as a more sustainable alternative. The common theory behind the operation of OFMs is that they adsorb to the surface as a monolayer and physically separate the contact in the boundary lubrication regime. However, recent studies, both simulations and experimental, suggest that OFMs form more complex structures, e.g. clusters of reversed micelles, and their action depends on the friction conditions and presence of other molecules [2,3], especially small polar dopants in the lubricant by design or under vehicle operation conditions. To understand the behaviour of OFMs, structural studies *in situ*/*operando* are required. Important work has been done with neutron techniques [4], but these are relatively slow and may require deuteration to enhance contrast. Therefore, we apply synchrotron X-ray scattering techniques that offer high photon flux, enabling fast measurements and good spatial resolution even for weakly scattering samples. 3 chosen OFMs based on oleyl chain (18 carbon atoms, monounsaturated) have been studied in the model base oil *n*-dodecane, with and without water/acetic acid doping. Mini Traction Machine tests and laboratory XPS (X-ray photoelectron spectroscopy) are compared with *ex situ* SAXS and XRR (small angle X-ray scattering, X-ray reflectivity) and *in situ* XPDF (X-ray pair distribution function) and SAXS in conditions of shear, temperature and pressure.

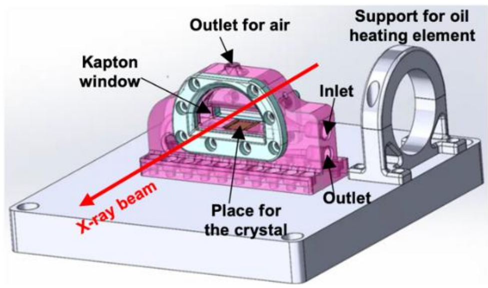

Fig. 1 Schematic of custom-built XRR flow cell that allows for the *in situ* studies of OFM adsorption to the single crystal under flow conditions.

ACKNOWLEDGMENTS
I.K. acknowledges InnovaXN European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement no. 847439) and Infineum UK Ltd. for funding.

REFERENCES
[1] Spikes, H., "Friction Modifier Additives," Tribol. Lett., 60, 5, 2015.
[2] Bradley-Shaw, J., Camp, P., Dowding, P., Lewtas, K., "Molecular Dynamics Simulations of Glycerol Monooleate Confined between Mica Surfaces," Langmuir, 32, 31, 2016, 7707-7718.
[3] Armstrong, A., Apostólo, R., McCoy, T., Allen, F., Doutch, J., Cattoz, B., Dowding, P., Welbourn, R., Routh, A., Camp, P., "Experimental and simulation study of self-assembly and adsorption of glycerol monooleate in *n*-dodecane with varying water content onto iron oxide," Nanoscale, 16, 2024, 1952-1970.
[4] Armstrong, A., McCoy, T., Welbourn, R., Barker, R., Rawle, J., Cattoz, B., Dowding, P., Routh, A., "Towards a neutron and X-ray reflectometry environment for the study of solid-liquid interfaces under shear," Sci. Rep., 11, 2021, 9713.