Nanotribology for Formulation Development

Zhenyu J. Zhang,^{1, #} Mark Moxey,¹ Abdullah Alswieleh,¹ Steven P. Armes,¹ Andrew L. Lewis,² Mark Geoghegan,³ and Graham J. Leggett¹

¹Department of Chemistry, University of Sheffield, Brook Hill, Sheffield, S3 7HF, UK ²Biocompatibles UK Ltd., Chapman House, Farnham Business Park, Weydon Lane, Farnham, Surrey, GU9 8QL, UK and ³Department of Physics and Astronomy, University of Sheffield, Sheffield S3 7RH, UK Present address: [#]School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham B15 2TT, U.K.

Email: z.j.zhang@bham.ac.uk

Friction force microscopy (FFM), a variant of scanning probe microscopy, measures adhesive and frictional forces with nanometre spatial resolution between two surfaces in contact. Unlike other chemical analysis methodologies, such nanotribological approach is a versatile toolbox for the development of complex structural formulation in both ambient and liquid environments. The unique capability of FFM is demonstrated with the following three studies.

1. Performance of detergent formulation

Nanofriction measurements over 1 μ m by 1 μ m area were carried out at different locations of individual cotton fibres treated with various washing processes and detergent formulations.¹ Coefficients of Friction (CoF) were found to increase with the number of wash cycles due to the loss of natural wax layer, but reduced by treatment of fabric conditioner. Such trend is valid in both ambient (controlled humidity) and liquid tested. Furthermore, distribution of CoF as a function of washing cycles effectively reflects the damages caused by the detergents within the yarn.

2. Lubrication characteristics of polymeric coating

To optimise the lubrication characteristics of surface grafted biocompatible polymer, poly(2-(methacryloyloxy)ethyl phosphorylcholine) (PMPC), nanotribological studies were performed considering the following parameters: thickness of the polymer film, solvent quality, and chemical functionality of the surface in contact.^{2,3,4} We have shown that the configuration of molecules at the interface is dependent on their solvation state, which consequently influence the lubrication characteristics and contact mechanics, e.g. osmotic pressure increases in a good solvent and yield a reduced tendency for the polymer layer to deform under applied load.

3. Characterisation of nanostructured objects

To develop design principles for the construction of molecular objects at the nanometre scale, photolithography was utilized to facilitate the growth of polymer brushes that are patterned on different length scales, as shown in the figure below. Using FFM, it was possible to measure the effect of the initiator density on both the heights and the frictional properties of the resulting nanostructured brushes.⁵ The coefficient of friction was found to decline as the brush height increased, with a smooth variation in both parameters being observed as a function of the density of initiator sites, which demonstrates that FFM could be a unique approach to examine polymer brushes with nm-scale spatial arrangement.



Figure 1. SPM image of patterned PMPC polymer brushes with corresponding sectional analysis showing the transition of molecular configuration.

Reference:

- 1. Zhang et al. J. Mater. Chem. 2010 20 8531
- 2. Zhang et al. Langmuir 2011 27 2514
- 3. Zhang et al. Langmuir 2013 29 10684
- 4. Zhang et al. *Langmuir* 2016 **32** 5048
- 5. Zhang et al. *Langmuir* 2017 **33** 706