Using Ion Beam Analysis to Study the Surfactant Distribution in Cross-Linked Colloidal Polymer Films

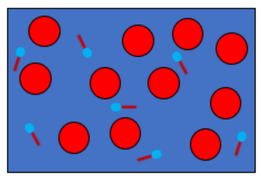
T.R. Palmer[1], K.Greiner[2], M.Duewel[2], R.W. Smith[3], H.M. van der Kooij[4], J. Sprakel[4],J.L. Keddie[1]

[1] University of Surrey, Guildford, UK, [2]Synthomer, Marl, Germany, [3]Surrey Ion Beam Centre, Guildford, UK, [4]Wageningen University, Wageningen, The Netherlands

1. Introduction

Pressure-Sensitive Adhesives (PSAs) adhere to almost any surface following the application of light pressure. Surfactant accumulation at the surface of PSAs is known to cause detrimental effects on their properties [1], hence the ability to control migration of surfactant during the drying stage is of great interest. In this work, we have studied the effect of particle deformation on the migration of surfactant and its final distribution within colloidal polymer films. Particle deformation has been controlled via cross-linking of the polymer chains within particles at differing amounts, from 0 mol% cross-linking up to a maximum of 35 mol% cross-linking. Poly (Butyl Acrylate) films synthesized via emulsion polymerization with SDS surfactant and EGDMA cross-linker [2] have been studied using a combination of Rutherford Backscattering Spectrometry (RBS) and Atomic Force Microscopy (AFM) in order to establish a picture of the surfactant accumulation both on the top surface of films, as well as depth profiles in the top several hundred nanometers of the films.

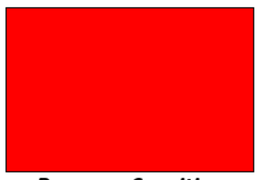
2. Film Formation & Cross-Linking



Polymer dispersed in water

Film Formation

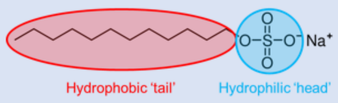
Water Loss → *Polymer Deformation* → *Coalescence*



Pressure Sensitive Adhesive (PSA) Film

Surfactants

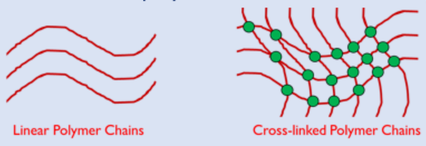
Necessary to aid the stability of the polymer dispersion



Known to migrate to the surface, where it can cause detrimental effects to adhesion & optical clarity

Cross-Linking

Deformation is being controlled by changing the cross-linking of the polymer chains



Cross-links are bonds which join one polymer chain to another

The effect of this on surfactant distribution is being studied

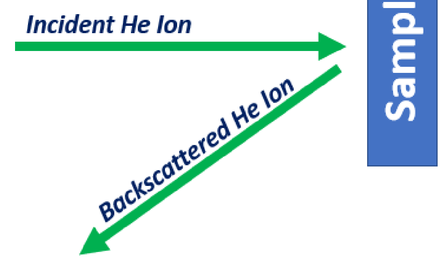
PSAs

PSAs adhere to nearly any surface under the application of light pressure.

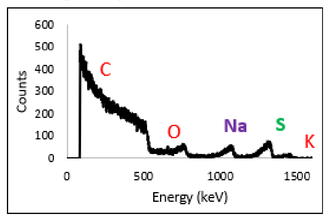
They have wide ranging applications, including tapes, labels & plasters.

3. Rutherford Backscattering Spectrometry

- Helium **RBS** provides depth profiles of hydrogen and deuterium in the top several hundred nm of a film.
- The film surface is bombarded with a **He⁺ ion beam**.
- The beam may collide with **Na** or **S** causing it the incident He to be **backscattered** towards the detector.
- The mass of the elements in the film determines the energies of the backscattered He ions.
- Technique tells us *what* is in the sample, *how much* of it there is, and *where* it is.



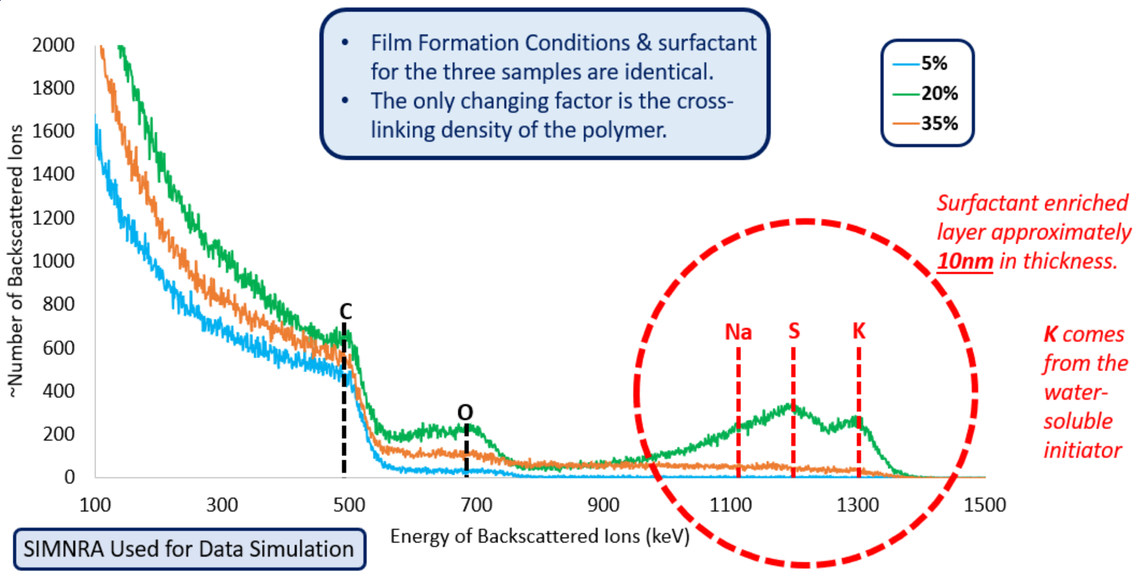
Example Spectrum



- The **energy** on the spectrum tells us **what element** is being found.
- The number of **counts** tells us **how much** of each element we are seeing.
- The **peak widths** are used to work out the **depth profiles**.

4. *Results:* RBS

- Film Formation Conditions & surfactant for the three samples are identical.
- The only changing factor is the cross-linking density of the polymer.

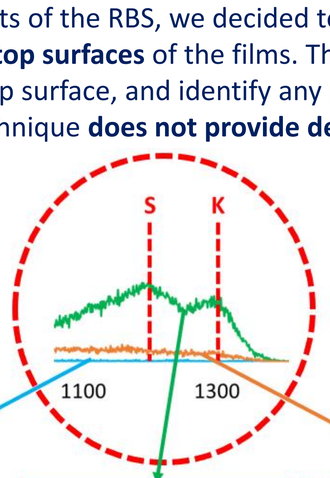


- Inside the red region of interest, we can see spectra for films with **low** (5%), **medium** (20%) and **high** (35%) levels of polymer cross-linking.
- What we see is that for only the green, intermediate level of cross-linking are there significant amounts of **Na** & **S**, indicative of **surfactant at the surface**.
- These results suggest that **surfactant is only accumulating at the surface of films with intermediate levels of cross-linking.**

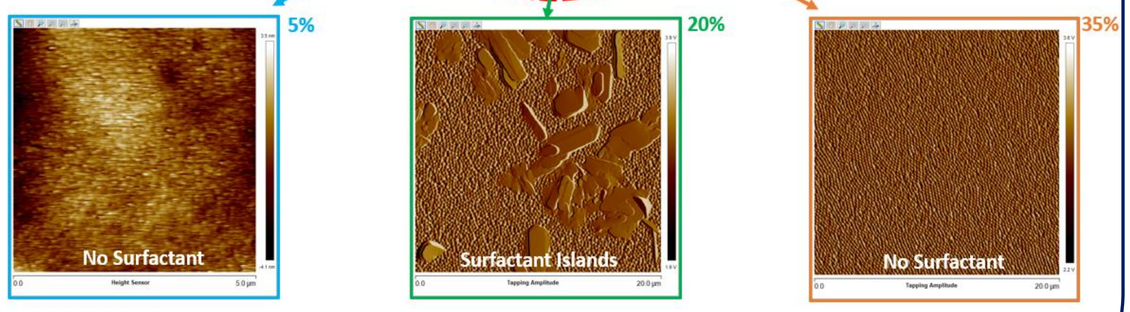
5. *Results:* AFM

In order to verify the results of the RBS, we decided to perform **Atomic Force Microscopy (AFM)** on the **top surfaces** of the films. This **qualitative technique** enabled us to visualise the top surface, and identify any potential surfactant on the surface. This technique **does not provide depth profiling**.

RBS results have been confirmed by imaging the surfaces using **Atomic Force Microscopy**



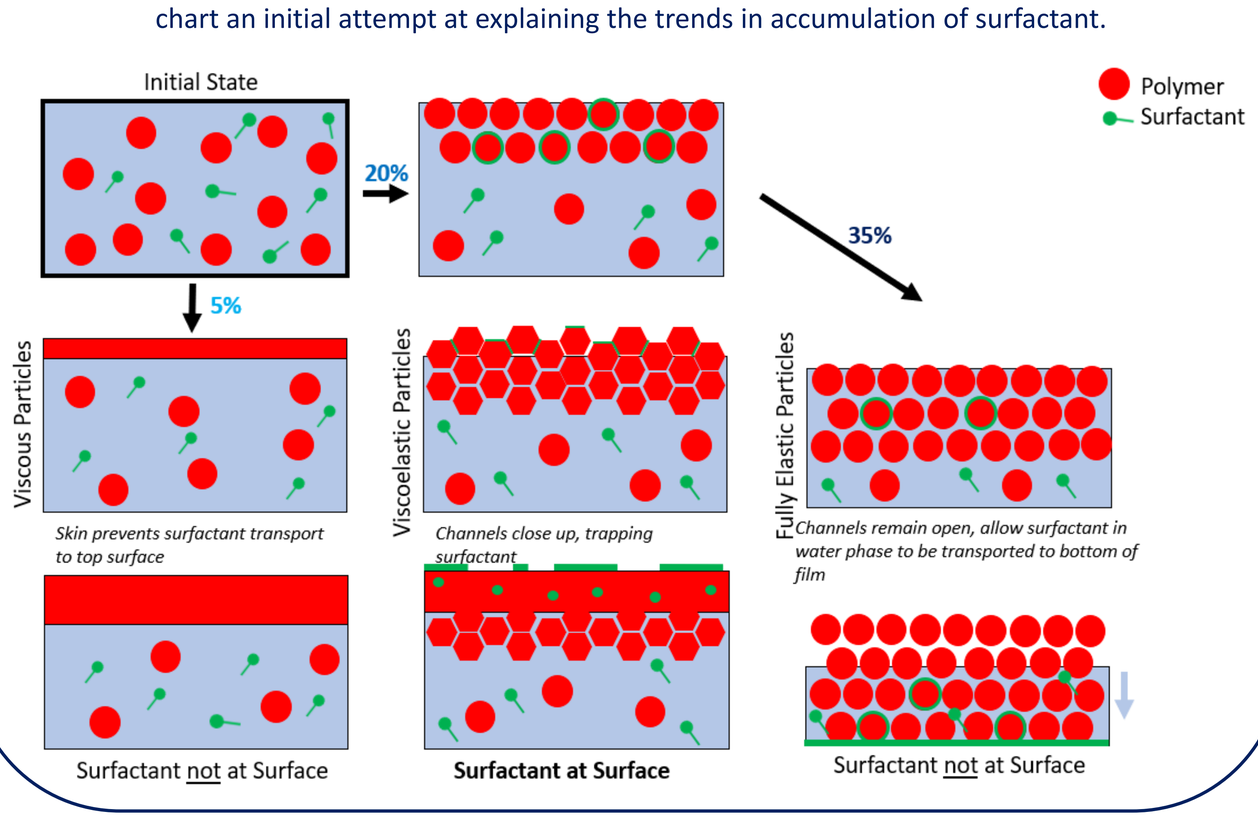
Water soluble surfactant verified by rinsing with water



- The results of the **AFM** appear to nicely confirm those from the **RBS**, agreeing that **surfactant is only seen on the surface of films with an intermediate level of polymer cross-linking**.

6. Interpretation

The result of the RBS & AFM agree well, however explaining **why surfactant only accumulates at the surface of certain films** still needs to be done. The following chart an initial attempt at explaining the trends in accumulation of surfactant.



7. Interpretation cont.

- **Low Cross-linking**: Soft particles that readily film form and act as a barrier to the surface.
- **Intermediate Cross-linking**: Surfactant is trapped between deforming particles near the surface.
- **High Cross-linking**: Channels between particles stay open, surfactant travels to the bottom of the film whilst in the water phase.

8. Summary & Conclusions

- **RBS** & **AFM** has been used to study **surfactant migration** in **cross-linked** colloidal polymer films, specifically PSAs.
- Surfactant accumulates at the surface for films with **intermediate levels of cross-linking**, however surfactant did not enrich the surfaces for low and high levels of cross-linking.
- Keeping **surfactant away from the surface** is desired for applications such as **PSAs**, therefore avoiding this intermediate cross-linking level would be suggested [1].

References

[1] Charmeau, J.Y., *et al*, Progress in Organic Coatings. **27**, p.p. 87-93 (1996), [2] H.M. van der Kooji, G.T. van de Kerkhof, J. Sprakel, *"A Mechanistic view of drying suspension droplets,"* Soft Matter, 2016, vol. 12, pp. 2858-2867

Acknowledgements

TRP would like to thank Violeta Doukova & Malin Schulz for their technical assistance in the lab. Thanks go to Hanne van der Kooij & Joris Sprakel from Wageningen for providing the pBuA dispersions. Funding for the PhD studentship from Synthomer & EPSRC is gratefully acknowledged. Access to the Surrey Ion Beam Centre was provide through EPSRC PhD student grant G560.