Summary

Surfactants are commonly used to stabilise polymer colloids (i.e. latex) that are used in waterborne coatings and adhesives. The exudation of surfactants to surfaces and interfaces has detrimental effects on adhesion and appearance, and therefore there is a need to prevent its occurrence. A promising approach to the problem is the use of reactive or polymerisable surfactants (known as surfmers) that form chemical bonds to the polymer and are therefore not exuded. This project has used Rutherford Backscattering Spectrometry, performed at the Surrey Ion Beam Centre, to determine the concentration depth profile of surfmers in acrylic latex films in comparison to a conventional, anionic surfactant (sodium lauryl sulphate). It was found conclusively that the use of surfmers prevents surfactant exudation to the air surface. Even when latex films are heated to high temperatures, where rapid and complete particle coalescence occurs, surfmers are not exuded to the surface. The project has resulted in a publication in a leading international journal and in the transfer of knowledge to industry.

Background and Context

Driven largely by tightening legislation in Europe and the USA, there has been an increased use of waterborne (i.e. latex) coatings and adhesives in lieu of solvent-based formulations. The performance of waterborne systems, however, has generally been inferior to their solvent-based analogue. A likely reason is a more heterogeneous morphology of waterborne materials in which there are often nanosized voids and hydrophilic internal interfaces. This morphology is intimately related to the mechanisms of film formation. Surfactants and other water-soluble species, which are omnipresent in the serum of the latex used in the formation of coatings and adhesives, are often considered to be primary culprits in causing poor performance.

A highly promising way to reduce or eliminate the negative effects of surfactants is to use surfmers, which are polymerisable surfactants. In the emulsion polymerisation process, surfmers are used to emulsify the monomers and initiators, and then they bond covalently to the polymer molecules as they polymerise. Consequently, desorption from polymer particles and migration through the polymer film is impeded, because the surfmers are bound within the film.

Surfmers have attracted much attention in both the open\textsuperscript{1} and the patent\textsuperscript{2} literature, as improvements in product quality have emerged. The mechanisms of surfmers in heterophase polymerisation have been reviewed recently.\textsuperscript{3} The reactivity ratios of the monomers with respect to the surfmer should be between 0.5 and 10 to avoid premature polymerisation of the surfmer, which would bury the surfmer within particles, and to achieve a high degree of incorporation at the end of the process. Surfmeter homopolymerisation must also be avoided.

The research group of Professor José Asua at the Institute for Polymer Materials (POLYMAT) at the University of the Basque Country in San Sebastián, Spain has produced latexes with superior properties using new nonionic alkenyl-functional surfmers. The resulting films exhibit less water absorption and lower water
vapour and liquid permeability in comparison to compositions prepared with conventional surfactants. More recently, the group has prepared latexes using anionic surfmers containing Na and K counter-ions. A main aim of this project was to use Rutherford Backscattering Spectrometry (RBS) to compare the distribution of surfmers with the distribution of a conventional anionic surfactant (sodium lauryl sulphate) in latex films. The RBS technique provides an elemental depth profile up to a few µm from the surface for heavy elements in a lighter matrix.

In the original proposal, it was hypothesised that the vertical transport of surfactant would be related to the drying and film formation mechanisms. If the water concentration is non-uniform, and if the particles are highly deformable, a process model of film formation predicts that coalescence will occur at the air surface, and water and surfactant might then be trapped within the film. On the other hand, a uniform distribution of surfactant is expected when the drying is more uniform, provided the surfactants are highly soluble in water and are carried with the water front during drying.

The Peclet number, $Pe$, which is a gauge of the relative rate of the recession of water by evaporation over the rate of particle transport by Brownian diffusion, can be used as a predictor of the vertical water uniformity. In this project, the distribution of surfactants in latex films was determined for films prepared with a range of $Pe$ ($\gg 1$, $\sim 1$, and $\ll 1$), achieved by careful choice of evaporation rate, film thickness, viscosity and particle size.

**Research Achievements, Key Advances and Supporting Methodology**

We have studied the phenomenon of surfactant exudation in acrylic latexes prepared by two-step emulsion polymerization. We compared the exudation in films stabilised by a conventional surfactant, sodium lauryl sulfate (SLS), to those stabilised by a surfmer, sodium tetradecyl maleate (M14). The conversion of surfmer was high in all the latexes: 74% for a 55 nm seed and 91% for a 36 nm seed. The latexes were synthesised at POLYMAT, which is a major centre for emulsion polymerisation. A student from POLYMAT (Esteban Aramendia) visited the University of Surrey and assisted with the RBS experiments.

AFM analysis of the latex showed that an irregular layer covered the latex film made using the conventional surfactant. This layer, which could be removed from the films by immersing them in water, probably consists of SLS. When the films were annealed to a temperature of 125 °C, a surface layer obscured the particle surface, and this layer is likewise interpreted as being composed of SLS. By contrast, the latex prepared with the reactive surfactant had a surface in which the particles were not blanketed by a surface layer. After annealing, the surface was very flat, and particles were fully coalesced. This AFM analysis is only qualitative, and the interpretations need to be confirmed by an independent technique: RBS.

The RBS experiments showed that in all cases, the surface enrichment of Na and S (contained in both SLS and the surfmer) was higher for the films made using SLS. An example of this trend is shown in Figure 1. The very slight excess concentration of Na and S in the M14 films is consistent with a layer having an excess of up to only 2%.
Figure 1. Rutherford Backscattering Spectrometry (RBS) data obtained from acrylic latex films after casting at room temperature in air. The channels corresponding to scattering from various elements at the film surface (C, O, Na and S) are indicated by the vertical lines. A comparison is made between a latex stabilised with sodium lauryl sulfate (Ο) and one stabilised with the surfmer, sodium tetradecyl maleate (<). The solid lines are the best fits to the data used to determine the elemental depth profile.

The differences between the M14 and SLS films were even more evident when the films were annealed. There is very little change in the surfactant surface excess in the M14 films, but surfactant excess concentration was found to increase with annealing temperature in the SLS films. The amount of conventional surfactant exuded to the surface increased with the temperature at which the films were annealed (60, 90 and 125 °C), but the migration of the surfmer was not significantly affected. An unexpectedly large amount of SLS was exuded to the film surface after being annealed at 125 °C. (Data are shown in Figure 2). RBS analysis revealed that the thicknesses of the SLS layers increase up to about 100 nm, and the layer is continuous (not island-like) (Figure 3). This result might be explained by the structure of the latex particles. A hard shell of poly(acrylic acid) might impede particle coalescence below its glass transition temperature of ca. 106 °C. Surfactant exudation might accompany particle coalescence, and so it does not occur until higher temperatures when the polymer has greater mobility. A full discussion of the results is provided elsewhere.6

Figure 2. A comparison of the RBS spectra obtained from films that had been annealed at 125 °C for 30 min. for a latex stabilised with sodium lauryl sulfate (Ο) and one stabilised with the surfmer, sodium tetradecyl maleate (<).
Figure 3. Surfactant concentration depth profiles obtained via RBS analysis of latex films containing SLS after annealing to various temperatures as indicated in the legend.

The results show that surfactant migration to the surface of acrylic latex films is highly problematic, especially after annealing at elevated temperatures. A reactive surfactant (or surfmer), however, can be permanently attached to the polymer. In that case, a minimal surfactant surface excess is found. The use of surfmers is thus an effective means of preventing unwanted surfactant migration and surface segregation.

Additional experiments were conducted on acrylic latexes to determine the effect of water distribution during drying on the final distribution of surfactant. Films were dried under conditions leading to high, low and intermediate Peclet numbers. The evaporation rate was the primary parameter used to adjust $Pe$. In drying a film with a low $Pe$ number (0.2), a very slow evaporation rate was used, with the consequence of maintaining a uniform water distribution (as has been shown to be the case in other work\textsuperscript{7}). We had hypothesised that a low $Pe$ would lead to a more uniform surfactant distribution. RBS analysis found, however, that a greater surfactant excess occurred. With a high $Pe$ (and non-uniform drying), the surfactant distribution was more uniform. This result suggests that the time available for surfactant desorption, transport and re-distribution is an important factor. The water distribution alone does not determine the final surfactant distribution. These results have been presented in detail elsewhere.\textsuperscript{8}

Project Plan Review

The general goals of the project were achieved and the objectives were, for the most part, met. There were no major obstacles to achieving the aims of the project. There were occasional problems at the ion beam facility, such as having a low beam current, but these did not impede the overall progress of the project.

Most of the work was performed using Surrey’s van de Graaff accelerator. Towards the end of the project, this accelerator was being de-commissioned, because a new tandem accelerator (funded by EPSRC) was being installed. There was a gap during which the facility could not be used. The transition from one accelerator to another caused understandable disruption but did not interfere with the achievement of the project’s objectives. A few days of beam time on the newly-commissioned tandem accelerator were allocated to the project.
Research Impact and Benefits to Society

Prior to this work, there had been numerous experimental studies that showed that properties, such as water resistance, were improved through the substitution of polymerisable surfactants for conventional surfactants. There was no thorough study, however, to compare the distribution of reactive surfactants to those of conventional surfactants. There was no conclusive evidence to show that surfmers did not segregate at film surfaces. Furthermore, there had been no studies to correlate the drying conditions with the distribution of surfactant.

This work has shown conclusively that the distribution of polymerisable surfactants is uniform throughout the film. Even when the films are annealed at temperatures well above their glass transition temperature, the surfactant does not exude to an interface. The distribution of conventional anionic surfactant does not correlate with water distribution during drying, but it is also influenced by other factors, such as the time available for surfactant desorption and re-distribution.

Uniqema, which is a business of Unilever, a multi-national company with UK headquarters, manufacture polymerisable surfactant. Scientists at Uniqema have been encouraged by the results, which were shared with the company through presentations by the PhD student, Esteban Aramendia. The particular surfmer used in this project (M14) presents difficulties when scaling-up its synthesis to industrial quantities. Uniqema has made use of the M14 study, however, to launch a new electrostatic surfmer, which is similar to M14 but is easier to synthesise on an industrial scale. Thus, this project is already having a positive economic impact.

Explanation of Expenditure

The spending on the project stayed close to the budget. Most of the funds went directly to the Surrey Ion Beam Centre at their standard daily rate. In turn, the Liaison Officer and a post-doctoral researcher provided support in data acquisition and analysis. The visit of a student from Professor Asua’s laboratory in San Sebastian, Spain was funded through the EC’s Marie Curie Centre in the Department of Physics at the University of Surrey. There was therefore added-value in the EPSRC project.

The funds for consumables (£500) were spent on safety equipment, chemicals and substrates required for the sample preparation. The latexes were provided by collaborators at the University of the Basque Country and in industry. A small amount of funding was vired from consumables to travel expenditure, to pay for the transportation to attend the UK Polymer Colloid Forum, where results from this project were being presented.

Further Research and Dissemination Activities

The results of this research were presented to the scientific community and to industrial collaborators shortly after being obtained. An oral presentation was made at the September 2002 meeting of the UK Polymer Colloids Forum, which was attended by a mix of UK academics and industrialists. The project formally started in April 2002, and results were published in Langmuir, a leading colloids journal, about
one year later. As a means of communicating the results to others in the ion-beam community, a paper was presented at the Ion Beam Users' Meeting held at the University of Surrey. Some of the preliminary results from the project were presented at an international coatings conference (The Athens Meeting on Organic Coatings) in July of 2002, where it was well received, particularly by industrial delegates.

UCB Chemicals, who support other research on polymer colloids at Surrey, was very encouraged by the results. Because the project was so successful in showing how valuable RBS is in the study of surfactants in latex films, UCB fully support plans for a future project using the technique. They are partners in a proposal that has been submitted to the EC Framework 6 Programme. The proposed project will use RBS to examine the transport and segregation of small molecules in latex films.

This EPSRC project has also led to a new collaboration with Dr Alex Routh in the Department of Chemical Engineering at the University of Sheffield. He has developed some new numerical simulations of surfactant transport during the drying of latex. A PhD student, Ms. Wai Peng Lee, has visited the University of Surrey for some preliminary RBS studies.

In summary, a modest investment by EPSRC has resulted in important new fundamental knowledge, important insights for industry, a key publication, and plans for further collaboration.

References


