

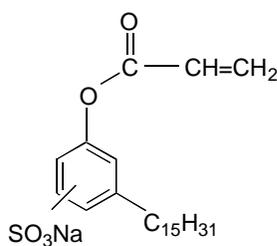
1. FINAL PUBLISHABLE SUMMARY REPORT

Investigations on the effect of reactive surfactants on latex film microstructure and properties via tracer diffusion

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The formation of polymer films from aqueous dispersions of latex particles has become the major industrial process for a variety of applications like coatings, paints, adhesives etc. as it minimizes the emission of volatile organic compounds (VOCs) in comparison to film formation from polymer solutions. In this process surfactants play an ambiguous role. They are required to impart colloidal stability which is a prerequisite for processing dispersions. At the same time surfactants introduce performance problems in the final coating as they have a tendency to form surfactant clusters in drying latex films which migrate to the polymer-air and polymer-substrate interfaces, causing water resistance and adhesion problems. A strategy to improve upon this situation is the use of reactive surfactants (or “surfmers”) which become chemically attached to the latex particles during synthesis. Thus, surfactant migration is avoided while the stabilization property is still active. In addition, by a judicious choice of surfmers of suitable structure and reactivity, a homogenous distribution of the surfmer in the polymer film should be achievable, opening up the option of introducing some additional functionality (e.g. imparting increased mechanical stability) into coatings via the reactive surfmer. In the past years several reactive surfactants have been developed and some have been tested with respect to coating production and performance. However, the available studies essentially focus on the macroscopic behaviour of latex films. Studies which monitor the influence of surfmers on film formation and film performance on a molecular level are, however, rare. For this reason this project aimed at correlating the role of surfmers on the macroscopic performance of the coating (e.g. mechanical stability, water resistance) with their influence on the drying behaviour at molecular level as observed by a tracer diffusion technique. From the changes of the tracer mobility conclusions should be drawn on the physical mechanism underlying the macroscopically observed surfmer effects.

For this purpose a surfmer Na-APDBS (cf. Scheme I) was specifically synthesized and characterized which is structurally analogous to the surfactant sodium dodecyl sulphate (SDS) which is commonly used in industrial latex formulations.



Na-APDBS

Scheme I

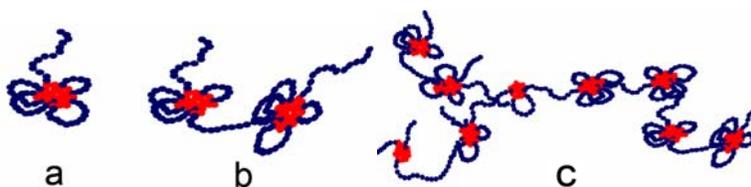


Fig.1 Microstructure of PS-surfmer copolymers in a nonpolar solvent (toluene). Red: charged head groups of the surfmer. Blue: hydrophobic regions (PS segments and surfmer tails). From a) to c) the polymer concentration increases at constant surfmer content indicating increasing equilibrium association of copolymer clusters (a).

The performance of this surfmer in latex synthesis via emulsion polymerization was found to be comparable to SDS with respect to particle size, polydispersity and stability of the dispersions. Polystyrene (PS) latexes were prepared with surfmer and the microstructure of the obtained PS-surfmer copolymers was then studied with static light scattering in the nonpolar solvent toluene. PS was used as this polymer is very well studied and results could be easily compared with literature. Toluene was chosen as it can be expected that structure formation in this nonpolar solvent will provide insights in structures present in the final latex films after drying. We found a supramolecular structure formation which originates from a combination of aggregation to inverse micelles with a concentration dependent association of these aggregates to long filamentous microstructures as shown in Fig.1.

In latex films the surfmer influence has two origins – the ion-pairs of the charged head groups and the hydrophobic tails of the surfmer. The hydrophobic tails acts in wet and dry films as an internal plasticizer, similar to the well known plasticizing effect of short chain alkyl groups in common polymers. In wet films the dissociated ion pairs of the head groups have a synergistic effect – additionally softening the particle surfaces via hydroplasticization: the charged groups induce an accumulation of water molecules at the particle surfaces, which then lead to an increase of polymer segment mobility. The combined plasticization effect can be seen macroscopically by the significant reduction of the minimum film formation temperature (MFFT) of poly(*n*-butyl methacrylate) (PBMA) films by about 10 degrees on addition of only slight amounts (0.3 mol%) of surfmer as depicted in Fig.2. The MFFT is an indicator for the ease with which a coating is formed.

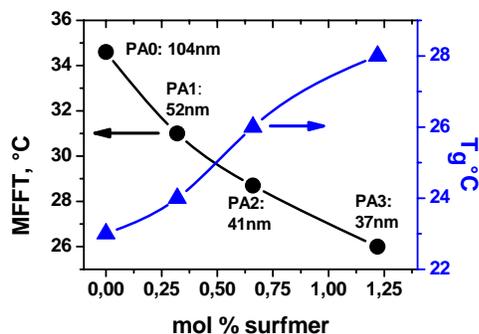


Fig.2 Variation of the minimum film formation temperature (MFFT; ●) and the glass transition temperature ("dry" T_g ; ▲) with surfmer content. Sample codes and particle radii are indicated in the figure.

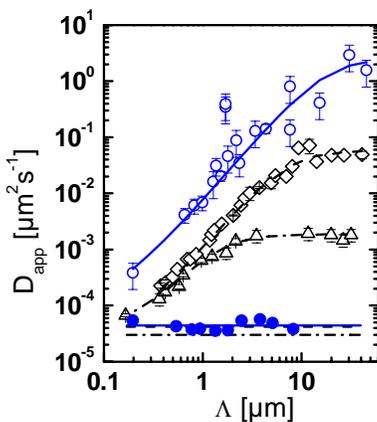


Fig.3 Dependence of the apparent diffusion coefficient $D_{app}(\Lambda)$ of wet (5 wt.% water; open symbols) and dry (solid symbols) PBMA latex films on the length scale Λ . The results for sample PA1 (●, ○; 0.3 mol% surfmer;) are compared to PBMA films prepared with SDS (△, ◇).

Particle surface coverages with surfactant: 24% (○), 40% (△) and 100% (◇). Lines are guides to the eye. For clarity only average D_{app} are indicated (---; - - -) for dry PBMA/SDS.

On a molecular scale this softening is seen in the dramatic enhancement of dye diffusion in the interfacial domains formed by partially fused particles ($D_{app}(\Lambda \rightarrow \infty)$) over that in the particle cores ($D_{app}(\Lambda \rightarrow 0)$). This effect is amplified in PBMA with only 0.3 mol% surfmer (○) by a factor of 1000 over the one in a typical industrial dispersion (△) and even stronger than in a dispersion with particle surfaces saturated with SDS (◇). In case of dry films the ionomer effect and the internal plasticization effect counteract each other: the former leads to a strengthening of the polymer by a supramolecular structure formation similar to the one found in solution (cf. Fig.1c) whereas the latter softens the material. For a surfmer concentration of 0.3 mol% the internal plasticization appears to win as one observes an enhanced dye diffusion by a factor of two as compared to a conventional PBMA/SDS film while for with 0.6 mol% the ionomer effect dominates leading to a slightly small dye diffusion coefficient than in PBMA/SDS (not shown). On a macroscopic scale a continuous strengthening of the film on increasing addition of surfmer is observed as visible in the increase of the glass transition temperature shown in Fig.2.

In summary: Our study indicates that the use of surfmers like Na-APDBS could be advantageous for improvement of latex formulations for coatings in several respects. The significant enhancement of particle deformation due to the substantially increased hydroplasticization of the particle interfaces could allow reducing (or even totally avoiding) the amount of filming aids (VOC's) that are usually added to plasticize the latex particle to promote film formation. These filming aids are usually small aromatic compounds the use of which is becoming increasingly criticised as a source of volatile organic compounds (VOC's) emitted into the atmosphere on drying of coatings and as potential health hazard in consumer products (plasticizer emission). In addition, by a judicious choice of type and amount of surfmer, the final film may be even mechanically toughened by the supramolecular structure formation induced by the surfmer. If surfactant migration is eliminated by the use of chemically attached surfmers, surfactant exudation and surfactant cluster formation can be avoided which can enhance resistance against water reabsorption on wetting by avoiding remnant hydrophilic channels in the film. As an additional boon, the particular surfmer used in this study can be synthesized from renewable resources (cashew nut shells).