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Polymeric Surfactants from Styrene-co-Maleic-Anhydride Copolymers

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Abstract:

Polymeric surfactants are usually prepared via copolymerisation of suitably substituted monomers. In this study, polymer surfactants were made by modifying a highly functionalized polymer chain back bone: a copolymer of styrene and maleic anhydride, SMA (34wt.-% MA), was turned into anionic, cationic and nonionic surfactants by saponification and imidation of the MA functions. In some cases, the chains were partly hydrophobized by stearyl substituents. All surfactants were water soluble without forming hydrogels. To different degrees, they proved themselves as dispersants and thickeners. Carbon black and titanium dioxide were excellently dispersed by the ionic derivatives o SMA while latices were particularly well thickened by hydrophobized nonionic derivatives.

1 Introduction

Polymeric surfactants[1] are water soluble but sufficiently amphiphilic to be adsorbed by surfaces and interfaces, in particular by dispersed solid or liquid phases. This balance is indicated in Fig.1: the polymer chains either cling to the dispersed particles or float between them in the water.

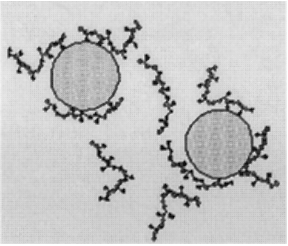

Fig.1.
Aqueous dispersion: phase domains and chains of a polymeric surfactant on them and in the water

Two important roles of polymeric surfactants are illustrated by Fig.2: *dispersant*[2] (Fig.2a) break up agglomerates of pigments, covering the single particles with a dense adsorption layer; *thickeners*[3,4] (Fig.2b) increase the viscosity of latices, forming a physical chain network in the water that bridges the particles indirectly. A third role is missing in the figure: *flocculants*[5]

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agglomerate and precipitate dispersed particles (Fig.2a reversed), by forming direct chain bridges between the particles. Dispersants and thickeners are discussed in this paper, but not flocculants which need higher molecular weights.

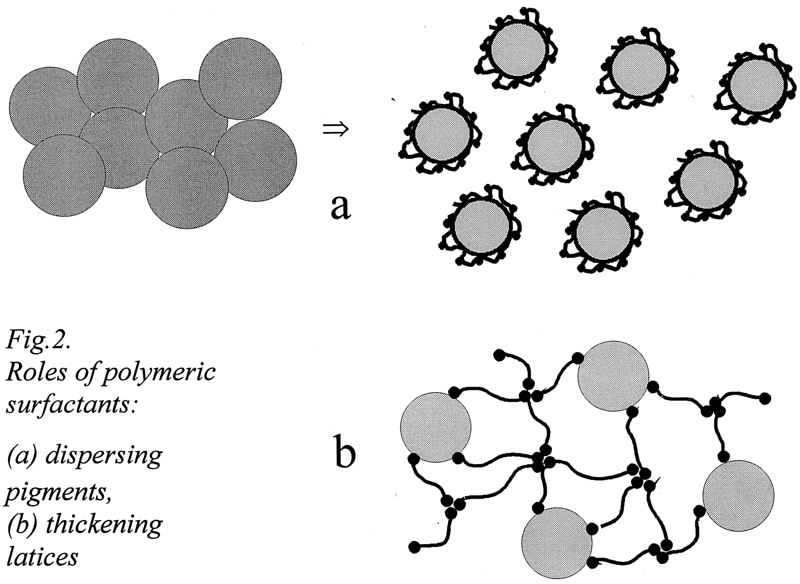

Fig.2.
Roles of polymeric surfactants:

(a) dispersing pigments,
(b) thickening latices

To acquire sufficient water solubility, the chains of polymeric surfactants must inherently be very polar or must be equipped with ionic charges or polar substituents in high concentration. Conventionally, these chains are synthesized by copolymerizing the monomers that are substituted accordingly. But in this study, polymeric surfactants were prepared by polymer analogous chemistry: a maleinated polystyrene, SMA (DSM, The Netherlands), with 34wt.-% of maleic anhydride copolymerized randomly into the styrene chains, was used as a back bone chain to which water soluble substituents were attached (Fig.3).

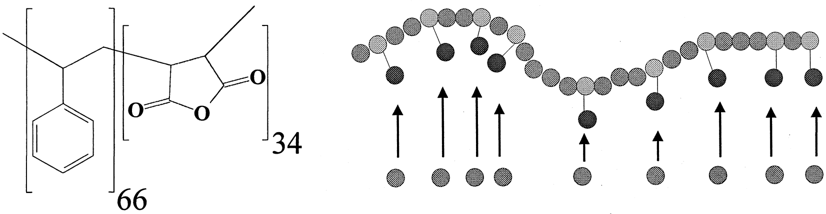

Fig.3. Maleinated polystyrene SMA; surfactant derivatives were made by adding polar substituents to the anhydride functions along the chains

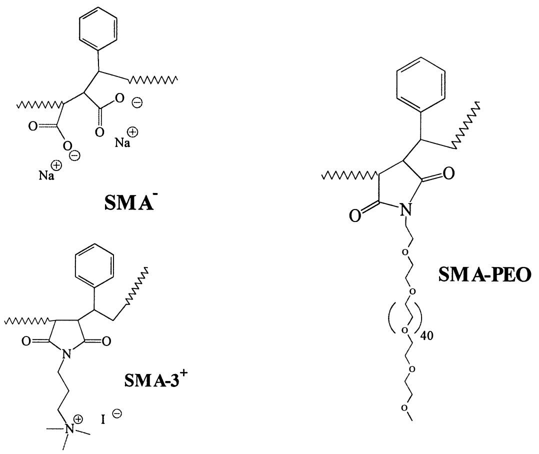

Fig.4. Derivatives of SMA: anionic SMA$^-$ with carboxylate, cationic SMA-3$^+$ with ammonium and nonionic SMA-PEO with oligoethyleneoxide groups

The polymer SMA (molecular weight $M_w = 110 \times 10^3$) is a thermoplastic that is used, often in homogeneous blends with SAN, because of its high glass transition temperature of $T_g = 178°C$. But with every third monomer unit carrying an anhydride function, SMA is evidently an attractive polyfunctional back bone for modified products as well.

2 Surfactants from a Copolymer of Styrene and Maleic Anhydride

Surfactants derived from SMA are shown in Fig.4: anionic chains (SMA$^-$) were made by saponification of the anhydride functions and cationic (SMA-3$^+$) and nonionic (SMA-PEO) chains by imidation with an ammonium salt or amino-terminated oligoethyleneoxide. These surfactants are amphiphilic because, while the special substituents (Fig.4) are definitely hydrophilic, the styrene unizs in the back bone are hydrophobic. To strengthen the hydrophobic character, SMA$^-$, SMA-3$^+$ and SMA-PEO chains were sometimes hydrophobized by incorporating, randomly, stearyl substituents that were added to the MSA chains by imidisation with stearylamin. Particularly interesting were the derivatives of SMA-PEO, i.e. SMA-PEO$_x$ (x/(1-x): molar ratio of stearyl and PEO units).

The polymeric surfactants thus prepared were soluble in water, while the hydrophobized derivatives exhibited decreasing solubility. None of these surfactants formed hydrogels in water: as shown in Fig.5, the viscosity of water is only slightly increased by SMA$^-$ or SMA-PEO.

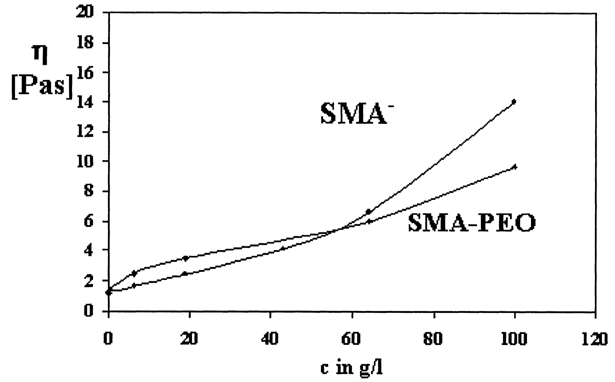

Fig.5. Viscosity of aqueous surfactant solutions as a function of the concentration c: no hydrogel effect

2.1 Dispersing of Pigments

To test the dispersive power of the surfactants, two pigments were chosen: a graphitized furnace carbon black (Printex L, Degussa, particle diameter 23nm) with a slightly negatively charged surface (charge density -3.85mmol/g) and a strongly negatively charged TiO_2 (Bayertitan R-KB-3, Bayer, particle diameter 200-250nm, charge density -12.37mmol/g).

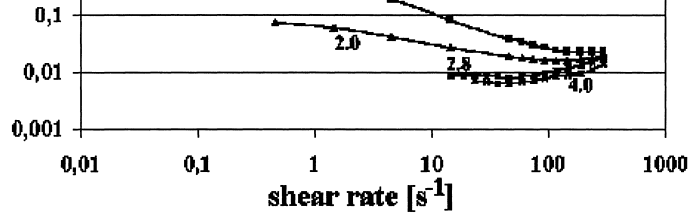

Fig.6. Viscosity of an aqueous carbon black (20wt.-%) dispersion with slightly hydrophobized SMA_1^- (1mol-% stearyl units); curve parameter: surfactant concentration in wt.-%

In practice, less carbon black is used than TiO_2, in aqueous dispersions. Dispersions with typical concentrations were investigated, i.e. 20wt.-% carbon black and 60wt.-% TiO_2.

In aqueous dispersion, the size of the primary particles of these pigments is not relevant because of extensive agglomeration. The carbon black formed in water untractable dispersions with the highly viscous consistency of shoe shine. But small amounts of SMA^- produced already very fluid dispersions, as shown in Fig.6. Slight hydrophobisation proved useful. With 4wt.-% of SMA^-_1, the viscosity was not far from that of pure water. The other surfactants, SMA-3^+ and SMA-PEO, were less efficient.

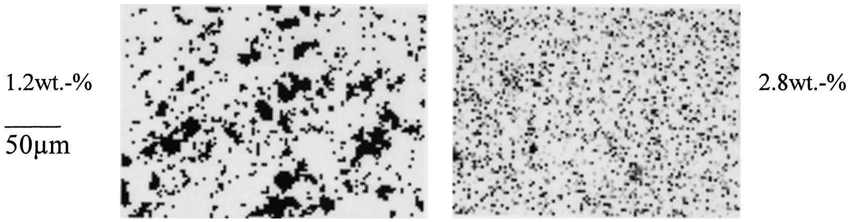

Fig. 7. Carbon black aggregates at different concentrations of SMA^- (light microscopy)

As demonstrated by Fig.7, the carbon black is well dispersed by SMA^-.

Similarly satisfactory results were obtained with TiO_2 dispersions, however, with the cationic surfactant SMA-3^+. Figure 8 proves that very small amounts of the surfactant were sufficient to bring the viscosity down to fluid, almost Newtonian behaviour. That the cationic SMA-3^+ was so efficient reflects the fact that the TiO_2 carried had a strong negative surface charge.

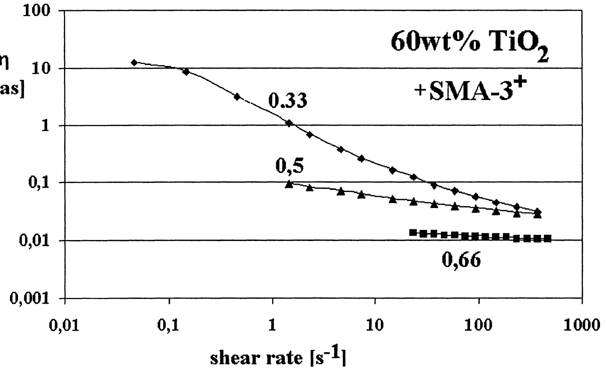

Fig.8. Viscosity of an aqueous TiO_2 (60wt.-%) dispersion with SMA-3^+; curve parameter: surfactant concentration in wt.-%

2.2 Thickening of Latices

To study latex thickening, a PMMA latex was prepared using SDS (sodium dodecylsulfat) as an emulgator so the particles (180nm diameter) were negatively charged. As shown in Fig.9, this latex (35wt.-% polymer) was very fluid, exhibiting Newtonian behaviour.

The nonionic surfactant SMA-PEO proved to be particularly efficient in thickening this latex.

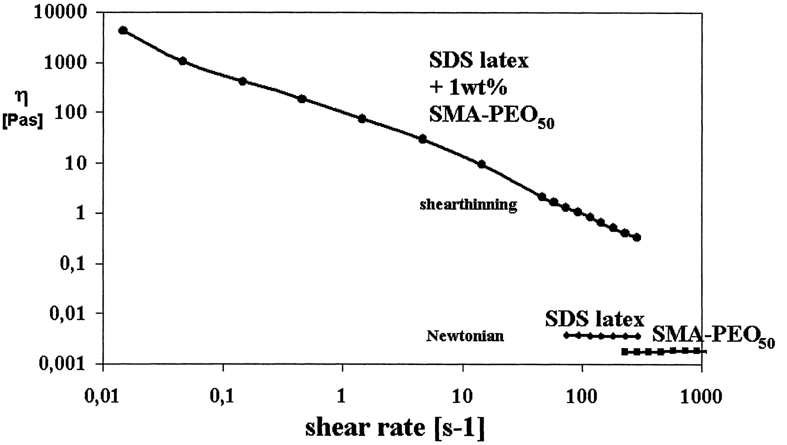

Fig.9. Viscosity of the SDS latex, a SMA-PEO$_{50}$ solution and the SDS latex plus 1wt.-% of SMA-PEO$_{50}$

In Fig.9, the effect of the strongly hydrophobized SMA-PEO$_{50}$ is demonstrated. This surfactant, despite its many stearyl groups, is still easily soluble in water. Water solutions are almost as fluid as water itself. But the latex plus little SMA-PEO$_{50}$ is extremely viscous at rest (and at low shear rates), 10^6 times the latex itself, and the factor is still 10^2 at high shear rates, although the dispersion is strongly shear thinning.

That a polymer which does not form a hydrogel in water, nonetheless, aggregates in the latex to a physical chain network, thickening it extremely, but without flocculating it, is spectacular. A mechanism of *associative thickening* that is known from other thickeners seems to apply[3,4]. As shown in Fig.10, the PEO branches of the surfactant chains are partly adsorbed on the particle surfaces and are tied together in a physical network by micelles formed by the hydrophobic parts, i.e. the backbone and the stearyl substituents.

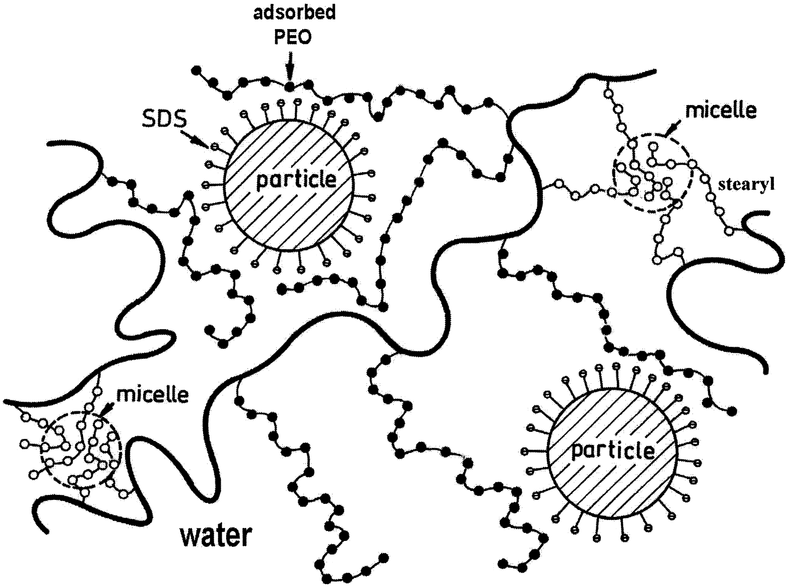

Fig. 10. Associative thickening of a latex: chain network of graft copolymer surfactants as SMA-PEO$_x$, PEO branches partly adsorbed at the particle surface, physical network through hydrophobic micelles of the stearyl substituents

3 Conclusions

The thermoplastic SMA, majorly consisting of styrene units but strongly functionalized with maleic anhydride units, proved to be a very useful source of polymeric surfactants. Anionic, cationic and nonionic surfactants could be prepared. These derivatives proved competitive as dispersants and thickeners. They cannot be used as flocculants, the molecular weight being too small.

SMA is a thermoplastic that can be processed in the melt by all methods of thermoplastic processing. Therefore, syntheses of the surfactants in the melt are presently being developed. While this is difficult in case of the ionic derivatives, it seems successful with the nonionic derivatives and the hydrophobisation.

Acknowledgement

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