Substitution of Non-Biodegradable Surfactants Used in Emulsion Polymerizations - A Study of the Polymerization Process and Performance of Products Obtained

C. R. S. Buono[a], E. Bittencourt[b]

Departamento de Tecnologia de Polímeros, Faculdade de Engenharia Química, UNICAMP ,Av Albert Einstein, 500, CEP 13083970, Campinas ,SP, Brasil.
[a] Celia.Buono@cytec.com ,[b] e_bittencourt@uol.com.br

Abstract

Emulsion polymerization is considered a safe, economic, versatile, and consequently of interest as an environmentally friendly process. However , surfactants utilized need to be biodegradable , and still guarantee a good film quality , with an adequate performance according to its end use. We investigated the substitution of an alkyl phenol ethoxylated (APE) surfactant ,commonly for a sulfosuccinate surfactant , which degrades in a week in contact with soil. Replacement was conducted keeping in mind the properties obtained in the final latex, in addition to the biodegradability of the surfactant. To adequately understand the behavior resulting from the replacement , it was necessary to study the surfactant kinetic effect, as well as the effect on particle size distribution , considering that water soluble and water insoluble monomers are utilized , as needed for paint formulations . Different copolymerization and terpolymerizations were conducted , with combinations of the monomers styrene, n-butyl acrylate, acrylic acid, methacrylic acid, and acrylamide, which are of very significant industrial interest for the film performance of paint formulations. Particle sizes were measured and related to the dual mechanism of polymerization , with the contribution of the aqueous phase polymerization, and which also affects to the final emulsion viscosity.

Keywords: polymerization , emulsion, surfactants, biodegradability.

1 Introduction

Surfactants behavior in the emulsion polymerization has already been extensively studied as reported in books, articles, patents.. Emulsion polymerization is considered an economical, safe and friendly process since water is the main solvent. Although water is desirable to be used as a solvent , additives as surfactants , depending on their structure may or may not be biodegradable. Besides potential toxicity, contaminating of rivers and lakes may last for large periods, until nature degrades them.

In this study it will be discussed some latex formulation where APE and APE free surfactants were used, and latex properties compared. Afterwards, the latexes were formulated into paints, and properties of interest analyzed.

In general surfactants are responsible for: monomers drop stabilization, micelle formation, number of particle, size, and growing rate, particle size control, and

latex particle stability during and after polymerization process.

If a surfactant is going to be replaced by another one it is very important to add better properties, or at least keep existent desirable properties. In this study a series of sulfosuccinates were compared to a nonilphenol ethoxylated sulfate which nowadays the architectural paint producers are trying to replace. Also, it was studied their behavior when water soluble and insoluble monomers were combined.

2. Process Variables

Selected process variables that affect the kinetics of the polymerization and the performance of the   products   obtained   area   discussed   below -   type of monomers , particle size and its effects on the product performance, particle size distribution , and its effects on viscosity and product properties.

2.1   Monomers and Emulsion Polymerization

In emulsion polymerization water monomer solubility is very important. There are monomers classified as totally soluble, partially soluble, and insoluble in water. Insoluble monomers are generally inside the micelles and water soluble in the water phase. Insoluble monomers polymerize by micelle nucleation. Soluble monomers polymerizes in the water phase where will have a significant effect in the final stage of the process when the latex is filtered. A co- surfactant is generally used to avoid this loss effect. The equations were derived , expressing R_p (rate of polymerization), N (number of particles)), and de dependence of R_p on the soap   concentration (S),   were derived (Smith and Ewart, 1948) .

$$R_p = k_p [M] p \left\{ \frac{nM}{N_a} \right\} + k_{p,w} [M]_w [I]_w \tag{1}$$

Where k_p constant of monomers polymerization, M_p concentration of monomers present in the particle, k_w due to monomers polymerization in the water phase and I_w concentration of initiator in the water phase.
A well known expression, below, shows the, dependence between the number of particles,   on   surfactant concentration, rate of initiation . The equation below shows that the number of particles is directly related to initiator and surfactant quantities:

$$N = K \left(\frac{R_i}{\mu} \right)^{2/5} \left(\alpha [E] \right)^{3/5} \tag{2}$$

N is the particle number, K is a constant varying from 0,37 to 0,53, μ speed of particle volume growth, [E] micellar concentration of surfactant, α interfacial area occupied by surfactant molecule, and R_i speed of new radicals formation.
When combined the two equations we obtain:

$$R_p = k_1 [I]^{2/5} [E]^{3/5} [M] \tag{3}$$

Where k_1 is kinetic constant, [I] the concentration of initiator, [E] the micellar concentration of surfactant and [M] the monomer concentration in the particle.

2.2 Other effects in particle size

Water soluble monomers start polymerization in the water phase. They grow until they reach to a certain size, where they will become insoluble. This homopolymer is added to the growing chain and it becomes part of polymer. It will remain partially solubilized in the water phase. It forms "*in situ*" polymer stabilizers, containing hydrophobic and hydrophilic parts in the molecule.

Another possibility is the colloidal stabilization when a persulfate initiator is used. Radicals as SO_4^- stay in particle surface forming a large insoluble chain presenting an ionic group. Also, oligomers as $M_2(SO_4^-)_2$,are formed, where M is the monomer unity, which also act like a surfactant. These surfactants formed "*in situ*" helping to stabilize viscosity over time (Poehlein ,1986), (Blakkley, 1975) , (Odian, 1981) .

2.3 The effects of particle size in the latex and its applications.

Particle size distribution (PSD) has an effect in the latex final physical properties. PSD control is important to the latex quality and its final application. The latex viscosity and rheology can affect the final properties in the paint. Another important property affected is gloss. Flocculation is also affected by PSD. So, it is very important to predict the overall affect of particle size distribuiton on paint properties. (El Aaser,1986) , (Lovell and El Asser, 1986), (Gilbert, 1995)
PSD is controlled primarily by type and quantity of surfactant. Another factor influencing PSD is the combination of monomers utilized.

2.4 Viscosity and particle size distribution.

Mooney (Mooney,1951) studied the viscosity behavior of mixtures of mono disperse particles , particle-particle interaction and collisions between them were introduced in a model. . The smaller spheres occupy the empty space between the bigger ones affecting directly the viscosity obtained in liquid media. The relevance to emulsion polymerization and latex properties are obvious. The equation below was finally derived (Krieger ., and Dougherty, 1959

$$\eta_r = \left(1 - \frac{\theta}{\theta_m}\right)^{-2,5\,\theta_m}$$

(4)

Where $\eta_r = \eta/\eta_0$ y θ **is** the initial volume **and** θ_m is the average particle size.

The experiments showed clearly that viscosity is directly affected by particle size distribution. Smallest particles present higher viscosity effects when the system is slowly agitated, due to the high energy necessary to move smaller particles. Particle surface also has its influence in viscosity especially when surfactants are absorbed into it. Bimodal particle size distribution present better film formation properties, and also the latex has lower viscosity. So, the final application will determine the recommended particle size distribution

3. Experimental

The polymerizations were conducted by a semi-continuous process. The seed was prepared with 0.3% surfactant, 8% of insoluble monomers, 0.27% initiator, and

water Ammonium persulfate was the initiator. The temperature used was 75±2ºC. The pre emulsion was formulated with 1.4% surfactant and 92% monomer..

3.1 Surfactants.

In this study surfactants used were all anionic where three types were mono esther sodium sulfosuccinate, Aerosol EF-800 , and Aerosol A-102 biodegradable , and Aerosol A-501, a non biodegradable . nonilphenol ethoxylated sulfate with 9 moles of ethoxylation.

The polymerizations were carried out starting with the insoluble monomers, and gradually, the water soluble monomers were introduced one by one.

 Polymerizations were as follows:

First step - styrene + butyl acrylate

Second step - styrene + butyl acrylate + acrylamide

Third step - styrene + butyl acrylate + acrylic acid

Fourth step - styrene + butyl acrylate + methacrylic acid

Fifth step – styrene + butyl acrylate + acrylamide + acrylic acid

Sixth step – styrene + butyl acrylate + acrylamide + methacylic acid

3.2 Latex properties

Table 1- Average Particle Size

Surfactants	S/BA	S/BA/ AMD	S/BA /AA	S/BA/ MAA	S/BA/AMD /AA	S/BA/AMD/ MAA
	nm	nm	nm	nm	nm	nm
NPES 930	111	132	112	116	116	119
EF-800	147	173	148	179	181	153
501	277	304	191	267	240	260
A-102	140	152	138	153	137	137

Adding acrylamide helps to increase the PS explained by a type of homo polymerization in the water phase, producing a kind of surfactant "*in situ*" which then is absorbed to polymer chains, allowing a relaxation in the particle surface. As seen , above Aerosol EF-800 PSD was the most narrow and mono dispersed.

Adding combinations of water soluble monomers it was noticed an increase in the PS. Which probably also modified the particle surface. The conclusion is that water soluble monomers in fact affect particle size, modifying also the latex viscosity.
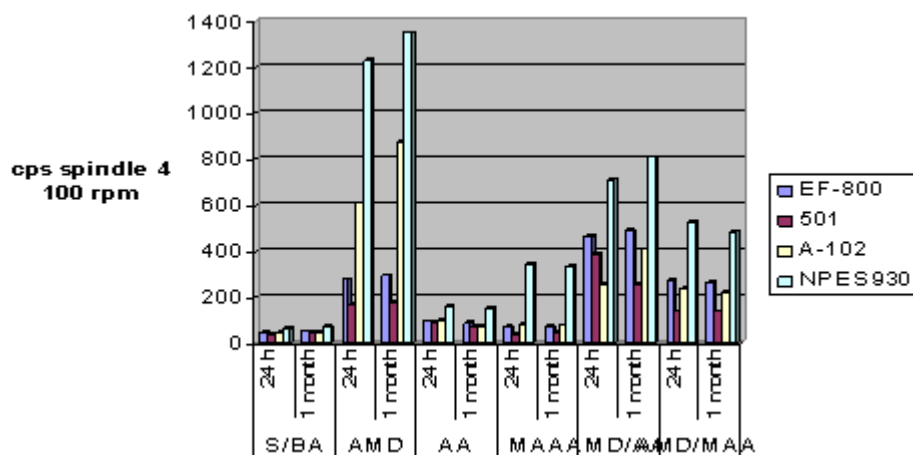

Figure 1. Latex viscosity over time

 Aerosol EF-800 viscosity was the most stable over time for all systems which combines the PSD results. Also very low insoluble were found for all systems even when the water soluble monomers were used. For all the other surfactants it can be seen a huge effect in viscosity or too low or too high and changing over time. The lowest viscosity can be explained by the polymer particles being very small.

4. Conclusion

Latexes produced with nonilphenol ethoxylated sulfate surfactants, over all these years, have proved to have excellent properties. This outstanding performance was the reason for the delay   to replace it. On the other hand, today biodegradability is a major requirement for all industries. Mono esther sodium sulfosuccinate surfactants showed in these experiments great possibilities to the future of emulsion polymerization where   biodegradability as a target. They showed that not only can replace APEs in terms of biodegradability, but also improves other important properties, like viscosity control over time; gloss due to the narrow PSD; and better   control of surface particle , when water soluble monomers were used.

In the Figures it can be noticed that particle size and particle size distribution control is much important to create and modify latex properties, quite important to a final application like in architectural paints. This can guarantee adequate shelf life of the final product is essential.

Most important than any other property ,it should be pointed   out, washability also can be improved with the criterions choice of surfactant, and the careful choice of water soluble monomer system .

When a formula is balanced using insoluble and water soluble monomers combinations, surfactants are responsible for improvement in terms of

polymerization and work in to avoid loss t of monomers in the water phase.

In this experiments mono ester sodium sulfosuccinate showed great performance for emulsion polymerization process , and also for latex final properties, which will result in properties and benefits comparable to nonilphenol ethoxylated sulfate. Also, other benefits can be found for final applications other than architectural paint.Mono esther sodium sulfosuccinate will biodegrade within one week when disposed on soil. Therefore, biodegradability is guaranteed as an ethical option and responsible care, from companies that believe that we have better choices with respect to the future of our planet

5. References

Blackley D.C., Emulsion Polymerization: Theory and Practice, Applied Science Ltd, London, 1975

El Aasser M., The Role of Surfactants in Emulsion Polymerization" en "Advances in Emulsion Polymerization and Latex Technology. Lehigh University, Bethlehem, Pennsylvania,1986

Eliseeva V.I., Ivanchev S.S., Kuchanov SI, Lebedev AV , Emulsion Polymerization and Its Applications in Industry, Journal of Polymer Science: Polymer Letters Edition, v 20, Issue 8, 1981, p. 460-461

Gilbert RG , Emulsion polymerization: a mechanistic approach , Academic Press, New York 1995 , 362 pp

 Krieger, I. M., and Dougherty, T. J.,*Trans. Soc. Rheol.* **3**, 137 (1959).

Lovell P, El-Asser MS Emulsion Polymerization and Emulsion Polymers, John Wiley, New York (1997)

M. Mooney, J. Colloid Sci. 6 (1951) 162

Odian G. , Principles of Polymerization. Wiley-Interscience, New York 1981

Poehlein G.., Emulsion Polymerization Mechanisms and Latex Technology" in Advances in Emulsion Polymerization and Latex Technology. Lehigh University, Bethlehem, Pennsylvania

Poehlein G.W., "Emulsion Polymerization" in   "Encyclopedia of Polymer Science and Engineering" HF Mark, NM Bikales, CG Overberger, G Mendes (Editors), volume 6, Interscience, New York 1986

Schork F.J. , Kinetics of Free Radical-Initiated Polymerization in "Advances in Emulsion Polymerization and Latex Technology".Lehigh University, Bethlehem, Pennsylvania,1986

Smith, W. V.; Ewart, R. H.; J. Chem. Phys. 1948, 16, 592