

**WATER-BORNE COATINGS AND
PRESSURE-SENSITIVE ADHESIVES
PRODUCED WITH POLYMERIZABLE
SURFACTANTS**

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Donostia-San Sebastián
(2016)**

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Chapter 1. Introduction

1.1. Introduction

Water-borne dispersed polymers are used in a wide range of applications including paints, adhesives, paper coatings, additives for construction materials, textile and leather industry, biomedicine, etc.¹⁻⁴. The most important production process for water-borne dispersed polymers is emulsion polymerization.

Emulsion polymerization is a heterogeneous free-radical polymerization process in which colloidal polymer particles are produced in a continuous medium, most often water. This technique has several distinct advantages over bulk and solution polymerization:

- High molecular weight polymers can be produced at high polymerization rates.
- The heat generated during the reaction is easily dissipated and the control of temperature is more effective due to the presence of water as a continuous phase (which has a high heat capacity and low viscosity).
- The polymer microstructure and particle morphology can be controlled.
- The product obtained from emulsion polymerization is often directly applied, without further purification.

- The final product can be formulated into many different products to meet market needs.
- The use of water as a continuous medium instead of solvents makes this process environmentally friendly.

Surfactants play a crucial role in the processes and products of emulsion polymerization since they are very important for the nucleation of polymer particles as well as for the stabilization of polymer particles during the polymerization and shelf life of the product^{5,6}. The dual function provided by the conventional surfactants is due to their adsorption at the particle-water interface. Surfactants are mainly adsorbed at the polymer particles by means of hydrophobic interactions.

Beside their crucial role in the preparation and stabilization of latexes, the use of conventional surfactants can have negative effects on product properties and, that is why conventional surfactants are usually referred as necessary evils in emulsion polymerization. These negative effects are caused by the fact that the physically adsorbed surfactant can be desorbed from the latex particle surface due to the weak hydrophobic interaction between the surfactant and the polymer particles. This can caused a reduction in latex stability^{7,8}, especially under high shear, freezing and high ionic strength conditions. Furthermore, when the latex is applied as a film the adsorbed surfactant can migrate toward the film-air or the film-substrate interface⁹⁻¹⁸. During film formation, surfactants that are strongly adsorbed can also be trapped at particle/particle boundaries creating hydrophilic pathways in the film^{19,20} and in some cases, the surfactant is pushed away from the particle/particle boundaries creating small pockets or aggregates throughout the film^{14,17,21}. The heterogeneous distribution of the surfactant within

the film readily affects the performance of the film formed. For instance, it has been reported that adhesion strength²², shear strength²³, peel strength^{24,25}, water resistance²⁵⁻³¹ and, gloss and film appearance^{32,33} can be adversely affected by the surfactant migration.

A promising approach that has been considered during last years to overcome the negative effects caused by conventional surfactants is to use reactive surfactants, where the surfactant is chemically incorporated into the polymer particles during the course of the polymerization so that desorption of the surfactant from the polymer particles or migration in the resulting polymer film is impeded or limited. Some interesting reviews in the area of reactive surfactants can be found in the open literature³³⁻³⁸.

A reactive surfactant can participate in the polymerization process as an initiating moiety (inisurf)³⁹⁻⁴², a moiety capable of chain transfer (transurf)⁴³⁻⁴⁶ or a group capable of copolymerization during free-radical polymerization (surfmer or polymerizable surfactant)^{40,47-51}. In principle any kind of reactive surfactant can be used to reduce the amount of free surfactant. However, when inisurfs and transurfs are used the stability of the system could not be adjusted independently by varying the amount of reactive surfactant without strongly affecting the polymerization rate (mainly inisurfs) and the molecular weight distribution (mainly transurfs)³³. Therefore, in the present work the use of polymerizable surfactants is going to be considered.

1.2. Background of polymerizable surfactants

Polymerizable surfactants maintain the essential amphiphilic structure of conventional surfactants, so they can adsorb onto the polymer particles. The main difference between both is that polymerizable surfactants bear a C=C double bond in their structure and therefore, they can copolymerize with the monomers during the course of the polymerization. As a consequence, the polymerized surfactant remains covalently bonded to the polymer material preventing desorption or migration during storage of the latex or film formation process.

Polymerizable surfactants were first described in 1956 by Bistline et al.⁴⁷. In that work, sodium allyl α -sulfopalmitate and sodium allyl α -sulfostearate anionic polymerizable surfactants were synthesized by esterification of the corresponding α -sulfo fatty acids with allyl alcohol. However, from our best knowledge, the use of polymerizable surfactants in emulsion polymerization was not reported until 1970 by Greene et al.^{7,8,48}. They reported the use of sodium 9-(and 10)-acrylamido stearate (NaAAS) in the styrene/butadiene emulsion polymerization and they found that the mechanical stability⁷ and electrolyte stability⁸ of the latexes stabilized by in situ polymerized NaAAS was higher than that of the latexes stabilized with monomeric NaAAS. Tsaur et al.⁵⁰ reported the synthesis of sodium sulfodecylstyryl ether (SSDSE) anionic polymerizable surfactant and its use in the styrene emulsion polymerization. Since these early works, a huge number of polymerizable surfactants have been synthesized and employed in the (mini)emulsion (co)polymerization of a high variety of monomers including styrene⁵²⁻⁶⁵, acrylates^{52,55,56,58,62,63,66-79} and vinyl acetate^{52,80,81} in order to improve the performance of the final products. The most commonly used polymerizable surfactants are those containing allyl^{67,80}, alkenyl^{71,72}, (meth)acrylate^{52,53,55,56,64,65,75}, styrenic^{54,68,73,78},

maleate^{57-61,65,77,82-84}, fumarate⁸⁵, crotonate^{55,56}, allyloxy^{62,69,70,76,77} and acrylamide^{63,74} functional groups.

1.2.1. Reported product improvements

Since the works reported by Greene et al.^{7,8,48}, many improvements on product properties have been described by the use of polymerizable surfactants. One important area in where substantial improvements have been obtained by using polymerizable surfactants is in latex stability, especially under freezing and high ionic strength conditions^{53-55,58,63,66,77,86,87}. The water resistance is another important aspect where many improvements have been obtained due to the covalent binding of polymerizable surfactants into the polymer backbone^{15,31,55,63,69,75-77,86,88,89}. Some reports can be also found in where the adhesion properties are improved by the use of polymerizable surfactants⁸⁹⁻⁹¹.

Ottewill et al.⁵³ found that polystyrene latex particles stabilized by the nonionic methoxy-polyethyleneglycol methacrylate (MeOPEGMA) polymerizable surfactant (also considered as a macromonomer) presented better colloidal stability to the addition of high concentrations of electrolyte and to freeze-thaw conditions compared to polystyrene latex particles synthesized in the absence of MeOPEGMA. The best performance was observed when MeOPEGMA was added at the beginning of the reaction.

Filet et al.⁵⁴ reported that the use of nonionic styrenic polymerizable surfactants in the emulsion polymerization of styrene as well as in the copolymerization of styrene with (meth)acrylates led to latexes with excellent stability against the addition of electrolytes, and

also against freeze-thaw cycles in most of the cases, although the majority of the polymerizable surfactant was found in the serum due to its high reactivity (they were consumed more rapidly than the monomers). They observed that the copolymer containing 50% of methyl methacrylate (MMA) was the one with the lowest yield of surfactant incorporation (88% of the surfactant was in the serum) and in this case, the latex flocculated under freezing-thaw conditions.

Chern et al.⁶⁶ investigated the batch emulsion copolymerization of methyl methacrylate (MMA) and butyl acrylate (BA) stabilized by a commercially available nonionic polymerizable surfactant (NE-40, Asahi Denka Kogyo) and by its non-reactive analogue (NP-40, Union Carbide). The chemical structure of NE-40 is shown in Figure 1.1. They observed that the polymerization system stabilized by the conventional surfactant NP-40 generally resulted in a smaller particle size in comparison to the NE-40 stabilized system, which was attributed to the different distribution patterns of surfactant molecules in the particles. The probability of finding NE-40 units buried inside the particles was high whereas the small and mobile NP-40 species was expected to remain on the particle surface being more effective in nucleating and stabilizing the primary particles during early stage of polymerization. Despite the differences found in the particle nucleation, latexes stabilized by NE-40 showed excellent stability toward added sodium salt.

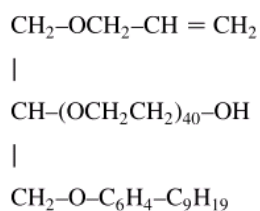


Figure 1.1. The chemical structure of NE-40 surfactant⁶⁶.

Unzue et al.⁵⁵ studied the semicontinuous emulsion terpolymerization of styrene (S), butyl acrylate (BA) and acrylic acid (AA) employing several anionic polymerizable surfactants with different copolymerization reactivity. The polymerizable surfactants employed in their work were the following ones: an ester of methacrylic acid (sodium 11-methacryloyl undecan-1-yl sulfate, MET), an ester of crotonic acid (sodium 11-crotonoyl undecan-1-yl sulfate, CRO) and a diester of maleic acid (sodium 3-sulfopropyl tetradecyl maleate, M14). They observed that in non-seeded semicontinuous polymerizations, the very reactive methacrylic surfactant gave unstable latexes with large amount of coagulum, irrespective whether they were added continuously or at the end of a reaction carried out with another polymerizable surfactant, probably due to the formation of water-soluble polyelectrolytes (depreving the latex particle surface from stabilizing groups). Therefore, the methacrylate surfactant was not suitable for the S/BA/AA system. Polymerizable surfactants with intermediate reactivity, such as maleates, gave latexes with stabilities comparable with, or even better than, similar latexes stabilized by the conventional surfactant sodium dodecyl sulfate (SDS). The use of the less reactive crotonate surfactant resulted in relatively stable latexes. They observed that the latex stabilized by the maleate polymerizable surfactant had a better stability against electrolyte addition. Furthermore, the crotonate and maleate derivative surfactants did not affect the kinetics of the seeded semicontinuous polymerizations and latexes stabilized by the maleate surfactant presented the best stability against electrolytes. Also, the film cast from the latex stabilized by the maleate had a water sensitivity slightly better than the film containing the conventional surfactant SDS, whereas the film containing the crotonate polymerizable surfactant was the one absorbing more water because its poor incorporation into the polymer backbone⁵⁶.

Polymerizable styrenic surfactants and non-reactive analogs were applied in emulsion copolymerization of acrylic monomers in a seeded semi-batch process by Soula et al.⁸⁶. They found that using polymerizable surfactants migration toward the surface of the film was limited and hence, films cast from latexes stabilized by polymerizable surfactants were more hydrophobic showing higher contact angle values. The water uptake of the films containing polymerizable surfactants was much lower. After dipping these films in water, their weight gain was reduced to less than 60 % instead of 90 % for the conventional surfactants.

Sindt et al.⁵⁸ studied the influence of anionic and nonionic maleate polymerizable surfactants on the latex stability. They showed that the incorporation degree of polymerizable surfactants depended on the polymerization conditions and, when good conditions were used the incorporation degree was as high as 80%. The colloidal stability (against freeze-thawing cycles or in the presence of concentrated divalent electrolyte solutions) was largely improved when a great incorporation of the polymerizable surfactant was obtained.

Tang et al.⁶⁹ studied the use of 3-allyloxy-2-hydroxyl-propanesulfonic salt (AHPS) as a kind of polymerizable stabilizer in the emulsion copolymerization of methyl methacrylate (MMA) and n-butyl acrylate (BA). They showed that latexes stabilized with AHPS exhibit a elastic stress-strain behavior similar to that of the latexes stabilized by a conventional surfactant. However, the tensile strength of latexes stabilized by the conventional surfactant was much lower because the free surfactant within the film led to weakening of the interaction between molecular chains and resulted in lowering of the tensile strength. The water resistance was also improved by using AHPS as stabilizer, although increasing the amount of AHPS the water

uptake increased due to higher concentration of hydrophilic groups in the film. Therefore, it was concluded that the improvement of latex stability accompanied a sacrifice of water resistance.

Amalvy et al.¹⁵ investigated the effect of covalent binding of the surfactant to the polymer backbone on the colloidal properties, film-water absorption, and surfactant exudation by comparing the performance of a maleate ionic polymerizable surfactant with a conventional ionic surfactant. In this study well defined S/BA/AA latex was synthesized using a strategy for the addition of the polymerizable surfactant M14 to maximize the amount of surfactant bound to the particle surface, and to avoid being buried in the particle interior. FTIR-ATR spectroscopy was used to examine the surfactant migration to the film interfaces and they found that when M14 polymerizable surfactant was used migration was impeded due to efficient incorporation into the polymer backbone. As a consequence, mechanical stability of the latex and water resistance of the film were improved.

Aramendia et al.³¹ compared the performance of acrylic latexes prepared using two alkenyl functional nonionic polymerizable surfactants differing in the number of poly(ethylene oxide) (PEO) groups (Maxemul 5011 and Maxemul 5010, Uniquema) to that of the latexes stabilized with conventional surfactants (a nonionic ethoxylated surfactant, NP30, and the anionic SDS). Latexes stabilized by nonionic surfactants presented better tolerance to salt stability than latexes stabilized by the anionic surfactant SLS. However, among the nonionic stabilized latexes no improvement of using polymerizable surfactant was observed. The nonionic polymerizable surfactant Maxemul 5010 presented worst stability against electrolytes than Maxemul 5011 due to the lower steric stabilization (shorter PEO chain in the structure) and the conventional NP30 performed similarly to Maxemul 5011. Regarding the water uptake

of the films, the films containing Maxemul polymerizable surfactants exhibited intermediate performance between the films containing NP30 and SLS. The fact that the film containing the conventional NP30 had the smaller water uptake was attributed to the desorption of migrated surfactant to the water, which increased the hydrophobicity of the film. The use of polymerizable surfactants only improved the water permeability and water vapor permeability, suggesting that the defects created in the film by surfactant migration promote the permeation of water by capillarity.

Huang et al.⁷⁶ investigated the emulsion copolymerization of methyl methacrylate and octyl acrylate using an anionic polymerizable surfactant (ammonium sulfate allyloxy nonylphenoxy poly(ethyleneoxy) ether, DNS-86) and the conventional surfactant sodium dodecylbenzene sulfonate (DBS). The incorporation of DNS-86 was proved by ¹H-NMR and Atomic Force Microscopy (AFM) was used to prove that the polymerizable surfactant DNS-86 migrated to the film surface to a less extent than the conventional surfactant did. The stability of the latex stabilized by the polymerizable surfactant was better and the water absorption of latex films prepared by the polymerizable surfactant DNS-86 was lower than the one prepared by the conventional surfactant.

More recently, stable and high solids content (about 50 wt%) styrene/butyl acrylate latexes were synthesized with the addition of small amount of 2-acrylamido-2-methylpropane sulfonic acid stabilizer (AMPS) and it was observed that films cast from these latexes presented better water resistance and solvent resistance than the films containing conventional surfactant⁶³. Similar results were reported by Deping et al.⁷⁷. They showed that the use of a nonionic polymerizable emulsifier allyloxy nonylphenoxy poly(ethyleneoxy) (10) ether

(ANPEO₁₀) in the emulsion copolymerization of methyl methacrylate and octyl acrylate led to improvements on water resistance and solvent resistance.

He et al.⁸⁹ investigated the application of ammonium α -allyl alkyl phenol polyoxyethylene ether sulfonate (Aqualon HS-10) polymerizable surfactant in the synthesis of acrylic emulsion pressure-sensitive adhesives. They observed that the adhesive containing Aqualon HS-10 presented higher tack, peel strength and holding power than adhesives containing conventional surfactants due to the incorporation of the polymerizable surfactant that did not weaken the interface of the adhesive layer when it was applied to an adherent. Improvements on tack, peel and shear performance of pressure-sensitive adhesives were also reported by Zhang et al.⁹⁰ when a polymerizable sulphated nonylphenol ethoxylated surfactant (Hitenol BC-1025) was used.

Lim et al.⁹¹ synthesized a sorbital based nonionic polymerizable surfactant in order to investigate the possibility of substituting a traditional nonylphenol ethoxylate surfactant NPE40 in the synthesis of pressure-sensitive adhesives. The synthesized environmental friendly polymerizable surfactant was satisfactorily used in the emulsion copolymerization of 2-ethylhexyl acrylate, n-butyl acrylate and acrylic acid. These pressure-sensitive adhesives showed better adhesive properties in peel strength and holding power than those synthesized using NPE40.

It is worth to mention that in some cases no improvement was obtained when polymerizable surfactants were used. For example, Ferguson et al.⁵² used different acrylated alkyl ethoxylate polymerizable surfactants in the emulsion polymerization of styrene, methyl

methacrylate and vinyl acetate. The acrylated polymerizable surfactants performed well in styrene polymerization but in the case of methyl methacrylate and vinyl acetate systems, the polymerizable surfactants yield much less stable latexes than their non-polymerizable analogues. The fact that these acrylated polymerizable surfactants performed better in the styrene emulsion polymerization was attributed to the greater hydrophobicity of polystyrene, which offered more effective interaction with the hydrophobe of the surfactant. However, stable polystyrene latexes stabilized by non-polymerizable surfactants performed better against electrolyte addition and freeze-thaw conditions. This was explained by means of surfactant structure and locus of polymerization. On the one hand, the polymerizable acrylated group was located at the hydrophilic end of the amphiphile that did not favour the incorporation of the surfactant into the polymer backbone and on the other hand, part of the surfactant was lost due to copolymerization in the aqueous phase.

Montoya-Goñi et al.⁸⁷ investigated the emulsion polymerization of styrene with maleate and succinate-containing cationic polymerizable surfactants. They found that latexes stabilized with maleate surfactants were generally less stable to the addition of salts than those stabilized using the non-polymerizable succinate surfactants. To explain this behavior the following two reasons were given. On the one hand, as the maleate polymerizable surfactant reacted early in the process would be buried inside the particles decreasing the surface charge and leading to less stable latexes. On the other hand, even if the surfactant was present in the surface of the particles, the fact that it was chemically attached to the particles would produce a change in the whole thermodynamics of the system because the equilibrium between adsorbed surfactant and surfactant in the aqueous phase would no longer be possible.

Uzulina et al.⁵⁹ reported the synthesis of maleic surfactants and its successful use in emulsion copolymerization of styrene and butyl acrylate. However disappointing results were obtained regarding the stability of the latexes. Although the polymerizable surfactants were incorporated to the polymer backbone with a high yield, the latexes flocculated, as well upon freezing as upon addition of electrolyte.

1.2.2. Optimal behavior of polymerizable surfactants

An effective performance of polymerizable surfactants is of vital importance because the price of polymerizable surfactants is higher than that of conventional ones due to the more complicated synthesis pathway and the lower tonnage. One of the most important aspect to consider when using polymerizable surfactants is their incorporation at the surface of the particles without jeopardizing the polymerization process and final properties of the latex that should remain unaltered or even improved as compared to conventional surfactants.

However, there is not an ideal polymerizable surfactant that can work efficiently in any monomer system because their performance depends on monomer system as well as on the polymerization process³³. Schoonbrood and Asua⁹² defined the optimal surfmer behavior as: maintaining low conversion of the polymerizable surfactant at the beginning of the process in order to avoid surfactant burial in the interior of the particles that do not contribute in particle stabilization and achieving high conversion of the polymerizable surfactant towards the end of the process in order to avoid having too much unbound surfactant that could act as a conventional surfactant. This definition was based on a comprehensive study involving the use of polymerizable surfactants with different surface active characteristics and reactivity ratios in

the emulsion polymerization of several monomers^{12,55-57,92}. It is worth mentioning that those original papers were published as a result of an extensive study undertaken within a network, "Reactive Surfactants in Heterophase Polymerization" sponsored by the European Union (Human Capital and Mobility Programme). Within this network, different polymerizable surfactants were synthesized, analyzed, and used in emulsion polymerization, and the resulting polymer lattices characterized^{12,15,55-58,82,83,87,88,92-94}.

In the report presented by Schoonbrood and Asua⁹² it was concluded that a suitable combination of comonomers and polymerizable surfactants in terms of reactivity ratios were those with $0.5 < r_{\text{comonomer}} < 10$ and $r_{\text{polymerizable surfactant}} \rightarrow 0$. They also proposed how to deal with polymerizable surfactants that are not very reactive in order to improve their performance. The strategies proposed by Schoonbrood and Asua⁹² were the following ones:

- Change in monomer reactivity. This can be done towards the end of the reaction modifying the composition of the monomers. For example, adding a monomer that is very reactive with the polymerizable surfactant towards the end of the reaction. The conversion of an anionic maleate based polymerizable surfactant (M14) increased from 52 to 80% when a small amount of Veova 10 and vinyl acetate was introduced in the emulsion polymerization of S/BA/AA⁹². However, Aramendia showed that this delayed addition is not effective when non very reactive surfactants, such as alkenyl-based nonionic polymerizable surfactants (Maxemul 5011), are used because the delay in monomer addition only contributed to a modest increase in the conversion of the polymerizable surfactant⁹⁵.

- Change in the reactivity of the polymerizable surfactant. This can be induced by modifying some operational variables such as temperature or pH during the polymerization. These involve not so much an increase in the reactivity of the surfactant but ways to avoid too much burying of surfactant groups.
- Surfactant addition profile to control its incorporation. In order to calculate the optimal addition policies, a mathematical model for the process is needed^{95,96}.
- Suppression of the particle growth. The surfactant burial can be avoided if the particle size is not allowed to increase significantly during the polymerization. This can be done by miniemulsion polymerization where the existing monomer droplets are polymerized.

Although the reactivity of the polymerizable surfactants with the main monomers is a factor that should be borne in mind, the definition of the optimal behavior of polymerizable surfactants should be expanded with another important aspects which are related with the particle nucleation and the formation of water-soluble oligomers³³. Polymerizable surfactants are expected to behave as conventional surfactants and hence, they have to effectively stabilize the polymer particles during the polymerization process and they have to provide smooth and reproducible nucleation stages. Furthermore, they should allow certain degree of emulsification of the monomer mixture in order to minimize the diffusional limitations that have been observed when non-preemulsified, scarcely water-soluble monomers and chain transfer agents are fed into the reactor⁹⁷. The critical micelle concentration (CMC) of polymerizable surfactants should be low so as to limit aqueous phase polymerization of the surfactant, so that the production of

water-soluble polysoaps will be reduced. The latter helps to improve latex stability because the formation of such polysoaps can lead to bridging flocculation^{55,98}.

1.2.3. Synthesis of high solids content latexes using polymerizable surfactants

High solids content (HSC) latexes are of growing interest since increasing the polymer content of a latex maximizes the reactor production, minimizes transportation, and storage costs, gives more flexibility in product formulation, improves surface coverage when applied and reduces drying time, which can increase the marginal value of the product^{99,100}. Therefore, most industrial processes involve high solids content (>50 wt% solids) emulsion polymerizations. However, although during the last years much work has been done with the use of polymerizable surfactants in emulsion polymerization not too many works dealing with the synthesis of high solids content latexes using polymerizable surfactants can be found in the open literature^{55,56,63,69–72,75–77,90,92,101,102}. Some examples of these works are reviewed here.

Tauer et al.¹⁰¹ prepared high solids content (50 wt%) polymer dispersions by semi-batch emulsion copolymerizations of butyl acrylate with styrene and methyl methacrylate, respectively, using partly sulfonated polyolefins as stabilizer and VA-086 (2,2'-Azobis[2-methyl-N-(2-hydroxyethyl)propionamide]) as initiator. In this case, during the semi-batch process the organic and the aqueous phase were fed separately because the surface activity of these polymerizable surfactants was much lower than that of conventional surfactants (as for instance SDS) and therefore, it was not possible to prepare stable monomer emulsions.

Aramendia et al.⁷¹ synthesized stable 50 wt% solids content acrylic latexes using a nonionic alkenyl-based polymerizable surfactant (Maxemul 5011) by seeded semi-batch emulsion polymerization. The studies were centered on latexes with small particle sizes in which the stabilization conditions are more demanding. They observed that it was possible to obtain stable high solids content latexes with final particle sizes in the range of 150-180 nm using 3wt% of polymerizable surfactant⁷¹. As the employed polymerizable surfactant was nonionic, the inorganic KPS/SBS (potassium persulfate/sodium metabisulfite) initiator system was more convenient than the organic TBHP/AsA (tert-butyl hydroperoxide/ascorbic acid) due to the contribution of the anionic end groups that provide stability to the latex. Furthermore, they observed that the addition of some acidic monomers (such as methacrylic or acrylic acid) towards the end of the reaction improved the stability of the latexes. They also observed that increasing the feeding time the higher was the surfactant incorporation, but the lower was the stability of the latex. Decreasing the feeding time led to a lower incorporation of the surfactant but more stable latexes, because less surfactant was buried inside the growing polymer particles.

Morizur et al.⁷⁵ reported the synthesis of different alkyl α -methylacrylate-based nonionic polymerizable surfactants (mainly differing in the hydrophobic part) and their incorporation into high solids content (50 wt%) acrylic latexes. MMA/BA/AA copolymer latexes were synthesized by seeded semi-batch emulsion copolymerization using 4.2 wbm% (weight based on monomer %) of polymerizable surfactant and latexes with final particle sizes in the range of 150-190 nm were obtained. In most of the cases, except in the polymerization carried out with the most hydrophilic polymerizable surfactant, stable latexes with low amount of coagulum were

obtained. Unzué et al.⁵⁵ reported that in a similar reaction at 50 wt% solids content with the same amount (equivalent in moles) of nonionic methacrylate-based polymerizable surfactant a large amount of coagulum was obtained. They suggested that this behavior was a consequence of the homopolymerization of the methacrylate polymerizable surfactant in the aqueous phase, leading to a formation of water-soluble polysoaps capable of causing bridging flocculation. In the work carried out by Morizur et al.⁷⁵ although homopolymerization of the surfactants was certainly possible, the fact that stable high solids content latexes were obtained indicated that homopolymerization of surfactant occurred in a less extent and that polymerizable surfactants were able to copolymerize efficiently during the polymerization process. Therefore, it was concluded that the molecular design of the home-made polymerizable surfactants (optimizing the balance between the reactivity of the double bond and the bulkiness of the molecules) had successfully influenced the balance between homopolymerization in the aqueous phase and copolymerization with the main monomers leading to obtain stable 50 wt% acrylic latexes.

Dai et al.⁶³ reported the synthesis of 50 wt% styrene/butyl acrylate (S/BA) latexes using 2-acrylamido-2-methylpropane sulfonic acid (AMPS) as stabilizer. The latexes were synthesized by semicontinuous emulsion polymerization with different S/BA ratios and different amount of stabilizer (varied from 1 to 3 wbm%). It was observed that for the same monomer composition (55/45 wt% of S/BA) and same amount of surfactant (1wbm%) the polydispersity index of the latex stabilized by AMPS was lower compared to the latex synthesized by the conventional surfactant SDS (sodium dodecyl sulfate) and that the average diameter of AMPS stabilized latex was larger than that stabilized by SDS. This was attributed to the difference in

latex particle nucleation mechanism. Whereas micellar nucleation occurred when SDS was used, homogeneous nucleation occurred when AMPS was used leading to a latex with very large particle size (around 500 nm). When the amount of AMPS was increased in the formulation, the particle size of the latex was considerably reduced because more oligomeric free-radicals and then, more primary particles were produced.

55 wt% solids content acrylic copolymer latexes were synthesized by semicontinuous emulsion polymerization varying the amount (from 1.5 to 3.5 wbm%) of the anionic DNS-86 (ammonium sulfate allyloxy nonylphenoxy poly(ethyleneoxy) ether) polymerizable surfactant⁷⁶. In this study, it was observed that only when 1.5 wbm% of DNS-86 was used coagulum was obtained and that increasing the surfactant amount the particle size decreased. When the conventional surfactant sodium dodecylbenzene sulfonate (DBS) was used the increase in surfactant concentration led to a reduction in monomer conversion whereas not significant differences were observed in monomer conversion with increasing the amount of DNS-86. However this result was not explained.

Deping et al.⁷⁷ presented the synthesis of high solids content (55 wt%) acrylic latexes by semicontinuous emulsion polymerization using a nonionic polymerizable emulsifier allyloxy nonylphenoxy poly(ethyleneoxy) (10) ether (ANPEO₁₀). It was seen that increasing the amount of the polymerizable surfactant from 1 to 3.5 wbm% the particle size decreased from 783 to 562 nm, but they were larger in comparison to the analogue latexes synthesized with the conventional surfactant OP-10 (polyoxyethylene octylphenol ether). The latter was only attributed to the fact that the polymerizable surfactant bears a C=C double bond and could be incorporated into the latex particles.

Zhang et al.⁹⁰ synthesized high solids content water-borne pressure-sensitive adhesives using the polymerizable nonylphenoethoxylate surfactant Hitenol BD-1025 and the conventional nonylphenoethoxylate surfactant Aerosol NPES-458 by seeded semi-batch emulsion polymerization. They were able to synthesize latexes with 56-59 wt% of solids content and with particle sizes in between 270 and 390 nm. They showed that increasing the amount of polymerizable or conventional surfactant from 2 to 6 wbm%, the particle size increased while when 8wbm% was used, the particle size decreased. Furthermore, latexes synthesized with the polymerizable surfactant presented larger particle sizes. As this work was only focused in analyzing the adhesive properties of the final pressure-sensitive adhesives, the results regarding the polymerization process and latex characteristics were not reported.

From our best knowledge, the synthesis of latexes with solids content of 60 wt% was only reported by Tang et al.⁶⁹ and Guo et al.⁷⁰. In both works, 3-allyloxy-2-hydroxyl-propanesulfonic salt (AHPS) was used as a kind of polymerizable stabilizer. In the work carried out by Tang et al.⁶⁹ methyl methacrylate/butyl acrylate copolymers were synthesized by semicontinuous emulsion polymerization varying the monomer ratio but keeping constant the amount of surfactant used (1.2 wbm%). The particle sizes of the latexes synthesized using AHPS were 450-500 nm, which were larger than the latexes synthesized using the conventional surfactant SDS. This was attributed to the different particle nucleation mechanism; whereas micellar nucleation occurred using SDS, homogeneous nucleation occurred when AHPS was used. When the reactions were carried out varying the amount of AHPS from 1.2 to 4 wbm% (keeping the monomer ratio constant) they observed that increasing the surfactant amount the final particle size of the latex decreased from 460 to 340 nm. In the

work carried out by Guo et al.⁷⁰, different poly(methyl methacrylate/n-butyl acrylate)/poly(n-butyl acrylate/methyl methacrylate) and poly(n-butyl acrylate/methyl methacrylate)/polystyrene high solids content core-shell latexes were synthesized by semicontinuous emulsion polymerization using 1.2 wbm% of AHPS. The obtained latexes presented particle sizes in the range of 220 and 260nm. They proposed that the well structured core-shell particles were formed due to the semicontinuous feeding method used in which the core and shell monomers were fed slowly in the reactor in succession. They assumed that the particles were chiefly formed by the homogeneous nucleation proposed by Fitch¹⁰³.

1.3. Motivation and main objective of the thesis

Nowadays, solvent-borne coatings and pressure-sensitive adhesives (PSAs) are still widely used in the industry. However, environmental regulations favor the elimination of solvents, and as a consequence, acrylic water-borne coatings and PSAs have become more attractive due to their intrinsic advantages: environmental safety, ease of handling, and economical reasons. However, water-borne latexes often have poorer properties when they are applied as film forming polymers due to the migration of the surfactant. In most of the industrial processes high solids content latexes are involved, therefore, over the last years high solids content water-borne latexes have been also of growing interest. However, high solids content latexes are very exigent from the colloidal stability point of view and they may require a substantial amount of surfactant, which is not beneficial for the final application. Therefore, there is an interest to synthesize high solids content water-borne latexes with the least possible amount of free surfactants.

The main goal of this work was to synthesize high solids content water-borne acrylic latexes using polymerizable surfactants in order to overcome the negative effects caused by the migration of conventional surfactants and hence, to improve the performance of the final products.

1.4. Outline of the thesis

The content of this thesis is divided in eight chapters. The first one describes the introduction and the motivation of this work.

In **Chapter 2**, the main characteristics of the polymerizable surfactants and polymerizable stabilizer used throughout this work are analyzed, namely, their structure, surface properties and homopolymerization and copolymerization behavior.

In **Chapter 3**, the performance of the polymerizable surfactants and polymerizable stabilizer (presented in Chapter 2) in batch emulsion copolymerization of low solids content (20 wt%) acrylic latexes is assessed. The effect of the surfactant type and surfactant amount on the polymerization mechanism and, properties of the final latexes is studied.

Chapter 4 shows the feasibility of using polymerizable surfactants in the synthesis of 60 wt% solids content poly(methyl methacrylate-co-butyl acrylate-co-methacrylic acid) latexes. The effect of surfactant type and surfactant amount on the polymerization process is studied. The effect of the pH is also investigated.

In order to see if the employed polymerizable surfactants and polymerizable stabilizer improved the performance of the finished products, in **Chapter 5** the performance of high solids content latexes stabilized by polymerizable surfactants is compared to latexes stabilized with conventional surfactants. The colloidal stability of the latexes, and the water resistance and mechanical properties of the films are investigated. The study is completed with the topographic inspection of the films using Atomic Force Microscopy (AFM).

Chapter 6 and **Chapter 7** are devoted to the study of pressure-sensitive adhesives produced with polymerizable surfactants. Whereas in Chapter 6 the synthesis of pressure-sensitive adhesives is discussed, in Chapter 7 the water whitening resistance and adhesive properties of the final films are discussed.

Finally, in **Chapter 8** the most relevant conclusions of this thesis are summarized.

A detailed description of the latex characterization techniques and film properties are given in **Appendix I** and **II**, respectively. In **Appendix III** some aspects to consider for the successful synthesis of high solids content latexes are discussed.

1.5. References

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Chapter 2. Characterization of polymerizable surfactants

2.1. Introduction

Although polymerizable surfactants have been extensively used in emulsion polymerization, it is not possible to find an ideal polymerizable surfactant that works efficiently for any system because their performance depend on the monomer system as well as on the polymerization process^{1,2}. For a given emulsion polymerization system, the best option would be to synthesize a polymerizable surfactant with an optimal structure; however this task is tedious and time-consuming. Nowadays, a wide variety of polymerizable surfactants can be found in the market.

Several factors should be taken into account to choose an appropriate polymerizable surfactant for a given emulsion polymerization system. One important aspect is the nature of the double bond because the reactivity and polymerizability of the polymerizable surfactant would depend on that¹⁻³. For example, Unzué et al.³ used different anionic polymerizable surfactants (mainly differing in the nature of the double bond) in the emulsion copolymerization of styrene, butyl acrylate and acrylic acid. They found that when not very reactive polymerizable surfactants were used, such as crotonate and allylic surfactants, relatively stable

high solids content latexes were obtained. More reactive surfactants, such as maleates, gave latexes with stabilities comparable with, or even better than, similar latexes synthesized using the conventional surfactant sodium dodecyl sulfate (SDS). However, the use of very reactive methacrylic surfactants led to unstable latexes with high amount of coagulum, which was attributed to the formation of polyelectrolytes soluble in the aqueous phase (depriving the latex particle surface from a stabilizing group).

Another important aspect to take into consideration is the position of the double bond in the structure of the polymerizable surfactant^{2,4-7}. On the one hand, the location of the double bond within the hydrophobic tail could have an effect on the surface properties of the polymerizable surfactants; tail-type (the double bond located at the end of the hydrophobic tail, Figure 2.1a) and head-type (the double bond located near the hydrophilic head, Figure 2.1b) analogue polymerizable surfactants have been reported to show different critical micelle concentrations (CMCs)⁴. Montoya-Gofñi et al.⁶ showed that in a cationic pyridinium bromide polymerizable surfactant the more the double bond was moved toward the end of the hydrophobic chain, the higher was the critical micelle concentration (CMC). On the other hand, the position of the double bond may affect the incorporation of the polymerizable surfactant into the polymer backbone. Normally, the double bond is located in the hydrophobic part of the surfactant which is beneficial because most of the polymerization process takes part in the polymer particles, on which the hydrophobic tail of the surfactant is adsorbed². It has been shown that the incorporation of the polymerizable surfactant was more successful as the double bond was closer to the hydrophobic part⁷.

a) Tail-type**b) Head-type**

Figure 2.1. An illustrative example of tail-type and head-type polymerizable surfactants.

Asua and Shoonbrood^{1,2} gave some general criteria for choosing a specific polymerizable surfactant and to use it in an appropriate way. According to them, the requirements for a good polymerizable surfactant are the following ones:

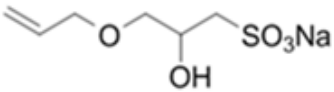
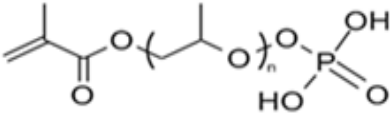
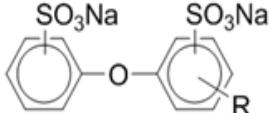
- The polymerizable surfactant must be a good surfactant, i.e., it has to efficiently stabilize the polymer particles.
- The polymerizable surfactant should allow a certain degree of emulsification of the monomer mixture in order to reduce diffusional limitations that have been observed for the monomers⁸.
- The CMC of the polymerizable surfactant should be low. In this way the polymerization of the surfactant in the aqueous phase and the amount of surfactant lost by formation of water-soluble polymer will be reduced.
- The polymerizable surfactant has to provide smooth and reproducible nucleation stages.

- The polymerizable surfactant should not homopolymerize in the aqueous phase and it needs to have moderate reactivity. The surfactant should not react early in the polymerization process, in order to avoid being buried inside the growing polymer particles, but it should be incorporated into the polymer backbone at the end of the reaction. If it remains unreacted it will behave as a conventional surfactant.
- The use of polymerizable surfactants should improve the performance of the final latexes.

Due to the wide variety of commercially available polymerizable surfactants, in this work, those with different double bond reactivity and different head group type were chosen to be used in the emulsion polymerization of acrylic latexes. On the one hand the anionic polymerizable surfactant Sipomer[®]Pam-200 (Trademark of Solvay) with a methacrylate double bond and the anionic polymerizable surfactant Latemul[®]PD-104 (Trademark of Kao Corporation) with a less reactive vinyl double bond and sulfate anionic group, and on the other hand, the polymerizable anionic stabilizer (or hydrophilic monomer) Sipomer[®]Cops-1 (Trademark of Solvay).

Table 2.1 presents the structure and molecular weight of the polymerizable surfactants employed in this work. As it can be observed all of them are anionic and tail-type surfactants, but they are widely different with respect to their chemical structure and molecular weight.

Table 2.1. Chemical structure and molecular weight of the surfactants.

Surfactant	Structure	Molecular weight (g/mol)
Sipomer [®] Cops-1 ^{a)}		218
Sipomer [®] Pam-200		~500
Latemu [®] PD-104 ^{b)}	$\text{H}_2\text{C}=\underset{\text{CH}_3}{\text{C}}-\text{CH}_2\text{CH}_2\text{O}-(\text{CH}_2\text{CH}_2\text{O})_n(\text{CH}_2\underset{\text{CH}_3}{\text{CHO}})_m\text{O}-\text{S}(=\text{O})_2\text{O}^-$	1674 ^{c)}
Dowfax [®] 2A1		575

^{a)}Sipomer[®]Cops-1 is a polymerizable stabilizer rather than a surfactant. ^{b)}Tentative structure determined by ¹H-NMR and ¹³C-NMR. ^{c)} Number-average molecular weight measured by GPC.

The polymerizable stabilizer Sipomer[®]Cops-1 is a 40% aqueous solution of sodium 1-allyloxy-2-hydroxypropyl sulfonate and as it can be observed in Table 2.1 its molecular weight is the lowest one.

Sipomer[®]Pam-200 is a penta(propylene glycol) methacrylate phosphate. This anionic polymerizable surfactant is built by three structural elements: a methacrylic function that presents excellent reactivity with all common monomers, an extender which contains

polypropylene oxide (PPO) and a phosphate group, that in addition to provide electrostatic stability could improve adhesion and corrosion resistance.

Latemul[®]PD-104 is a 20% aqueous solution of ammonium polyoxyalkylene alkenyl ether sulfate. In this case, the supplier did not provide the chemical structure; therefore the one presented in Table 2.1 is the tentative chemical structure which was determined by Nuclear Magnetic Resonance spectroscopy (NMR) (Section 2.3.1). This polymerizable surfactant has the highest molecular weight (determined by Gel Permeation Chromatography).

The structure of the conventional surfactant Dowfax[®]2A1 (45 % aqueous solution of alkyldiphenyloxide disulfonate, Trademark of The Dow Chemical company) has also been included in Table 2.1.

In this chapter the main characteristics of the polymerizable surfactants used throughout this thesis are investigated, namely, their structure, surface properties and homopolymerization and copolymerization behavior, in order to understand the performance of these surfactants in emulsion polymerization.

2.2. Experimental

2.2.1. Chemical structure

As it was mentioned before, in the case of the polymerizable surfactant Latemul[®]PD-104 the supplier did not provide any information about the structure and molecular weight of the surfactant. Therefore, in this work the chemical structure and molecular weight of Latemul[®]PD-104 were determined.

The chemical structure of Latemul[®]PD-104 was determined by Nuclear Magnetic Resonance (NMR). NMR measurements were carried out in a Bruker AVANCE 500 apparatus. The surfactant was first dried in the oven at 60°C and then dissolved in deuterated chloroform (CDCl₃, Sigma-Aldrich).

The molecular weight of Latemul[®]PD-104 was determined by Gel Permeation Chromatography (GPC). Latemul[®]PD-104 was dried and dissolved in THF. The solution was filtered (polyamide Ø= 0.45µm) before injection into the GPC instrument, which consisted of a pump (Shimadzu LC-20AD), three columns (Styragel HR2, HR4 and HR6) and a refractive index detector (Waters 2410). The analysis was carried at 35°C using THF as eluent at a flow rate of 1mL/min and the obtained molecular weight was related to polystyrene standards.

2.2.2. Surface properties

When a surfactant is dissolved in water, the properties of the solution (e.g. osmotic pressure, interfacial tension, conductivity in case of ionic surfactants) change monotonically to

the point in which water becomes saturated in surfactant. At concentrations higher than that of the saturation, surfactant molecules aggregate into micelles. The concentration at which micelles are formed is called critical micelle concentration (CMC). Around the CMC the properties of the solution change dramatically. Therefore, changes in osmotic pressure, surface tension or conductivity can be used to determine the CMC. Among these techniques, tensiometry is likely the most often used.

Above the CMC, surfactant molecules are distributed among micelles, aqueous phase and water-air interface according to the thermodynamic equilibrium. If polymer particles are present in the system, this equilibrium is modified and a number of molecules of surfactant will cover the particle-water interface. Therefore, a higher amount of surfactant is needed to completely saturate the aqueous phase, i.e., to reach its CMC, as it can be observed in Figure 2.2. Moreover, the amount of surfactant needed to completely saturate the aqueous phase will depend on the hydrophobicity of the polymer particle surface. As it can be observed in Figure 2.2, the more hydrophobic the polymer particles (PMMA/BA at weight composition of 10/90 wt%) the higher the surfactant amount needed to saturate the aqueous phase, meaning that a higher number of surfactant molecules are needed to completely cover the particle-water interface.

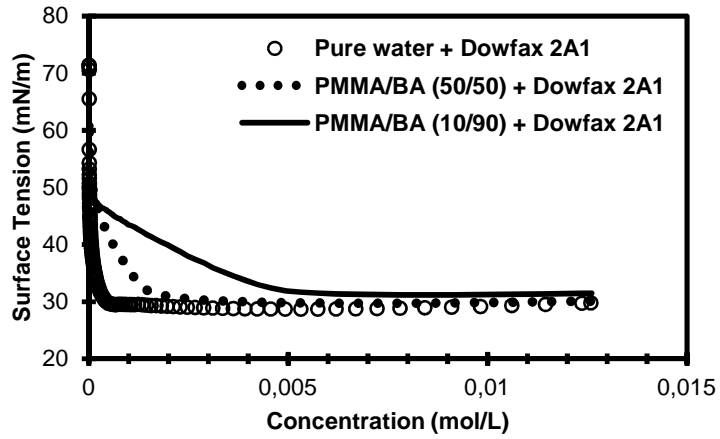


Figure 2.2. Surface tension evolution with surfactant concentration in presence and absence of polymer particles.

The particle area occupied by one molecule of surfactant under saturation conditions is called the parking area (a_s) and can be calculated through the following equation⁹:

$$a_s = \frac{10^{16} M_w}{N_A \Gamma_1} \quad (\text{\AA}^2/\text{molecule}) \quad (2.1)$$

where M_w (g/mol) is the molecular weight of the surfactant, N_A is the Avogadro's number and Γ_1 (g/cm²) is the surface concentration of surfactant under saturation conditions. In turn, Γ_1 is given by

$$\Gamma_1 = \frac{\Delta C \times V}{A_p \times m} \quad (\text{g/cm}^2) \quad (2.2)$$

where V (L) is the volume of the liquid phase, A_p (cm^2/g) the specific surface area of the polymer particles, m (g) is the mass of the latex and $\Delta C = \text{CMC}_p - \text{CMC}$ (g/L), where CMC_p (g/L) is the concentration of surfactant at the point in which micelles appeared in the diluted latex, and CMC (g/L) the critical micelle concentration⁹.

In this work to determine the critical micelle concentration, surface tension measurements were carried out using a tensiometer (KSV Sigma 70, KSV Instruments Ltd.). The CMC was measured following the change in the surface tension of the aqueous solution with the concentration of added surfactant. For that, the addition of surfactant was carried out using an aqueous solution of the surfactant by means of controlled addition pump (Dosimat 665, Metromh). The CMC was determined at the intersection point of the two lines obtained by linear regression of the experimental data.

The same equipment was used to estimate the parking area (the particle area occupied by one molecule of surfactant) of the surfactant on polymer latexes by titrating a diluted latex (at solids content of 10 wt %) with a solution of surfactant until micelles appeared in the system. Previously to titration of diluted latexes with a solution of surfactant, the latexes were cleaned by means of dialysis tubes (Spectra/Por[®], MWCO: 12000-14000).

2.2.3. Homopolymerization

In order to assess the possibility of homopolymerization of polymerizable surfactants, the following procedure was followed. An aqueous solution of surfactant and potassium persulfate (KPS, Fluka) was prepared in NMR tubes. The temperature was increased to 75°C

and homopolymerization was monitored for 4 hours. The occurrence of homopolymerization was determined by means of monitoring the NMR intensity of the double bond signals. The spectra were recorded using the sequence Watergate to suppress the signal of water.

2.2.4. Copolymerization

To assess the reactivity of the polymerizable surfactants with the comonomers to be used in this work (mainly methyl methacrylate and butyl acrylate), the following polymerizations were carried out in NMR tubes using dimethyl sulfoxide- d_6 (DMSO- d_6 , Sigma-Aldrich) as solvent: polymerizable surfactant, monomer and AIBN (2,2¹-Azobis(2-methylpropionitrile), Sigma-Aldrich) were added and the temperature was increased until 75°C and the reaction monitored for 4 hours. The monomer/surfactant ratio was 50/50 mol%. The occurrence of copolymerization was determined by means of monitoring the NMR intensity of the double bond signals.

2.3. Results and discussion

2.3.1. Chemical structure of Latemul[®]PD-104

The chemical structure of Latemul[®]PD-104 was inferred from NMR analysis. ¹H-NMR and ¹³C-NMR spectra of Latemul[®]PD-104 are displayed in Figure 2.3 and Figure 2.4, respectively and as it can be observed the proposed chemical structure fitted well with the obtained NMR spectra.

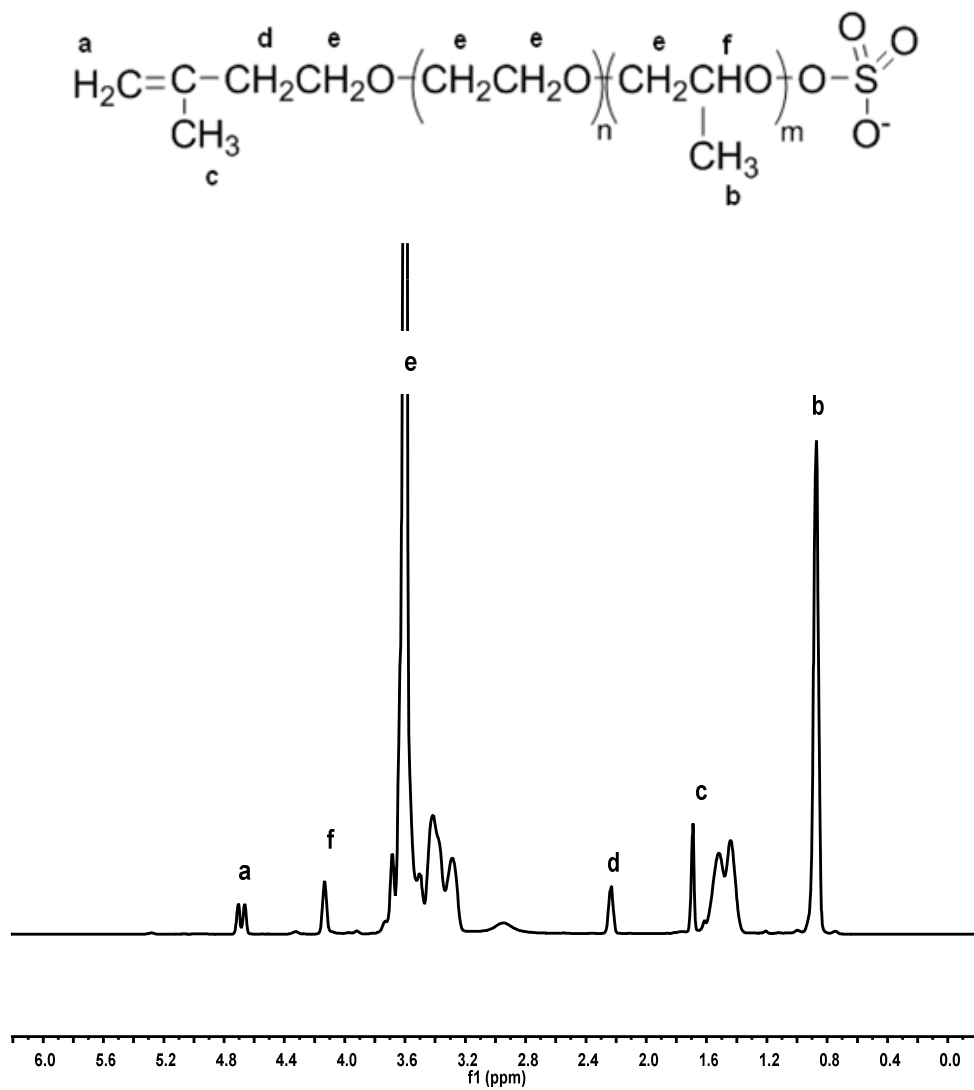


Figure 2.3. ¹H-NMR spectrum of Latemul[®]PD-104 in CDCl₃.

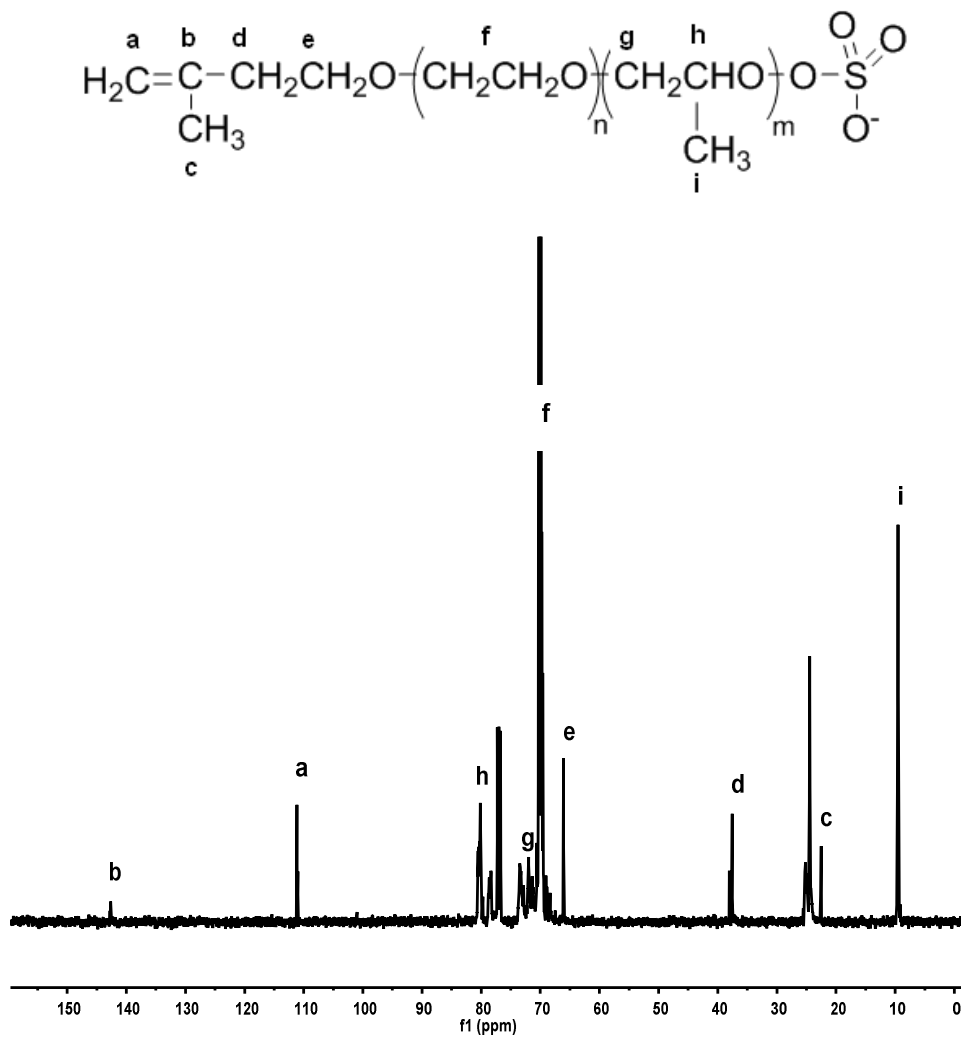


Figure 2.4. ¹³C-NMR spectrum of Latemul[®]PD-104 in CDCl₃.

Figure 2.5 presents the molecular weight distribution of Latemul[®]PD-104 obtained by gel permeation chromatography. The number-average molecular weight (M_n) of Latemul[®]PD-104 was found to be 1674 g/mol ($\mathcal{D} = 1.51$).

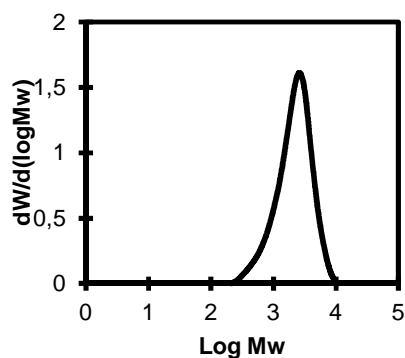


Figure 2.5. Molecular weight distribution (MWD) of Latemul[®]PD-104.

2.3.2. Surface properties

2.3.2.1. Determination of the critical micelle concentration (CMC)

In order to determine the critical micelle concentration (CMC) aqueous solution of surfactants were first prepared. The pH of the aqueous solutions of Dowfax[®]2A1, Latemul[®]PD-104 and Sipomer[®]Cops-1 was between 7 and 7.5. However, the pH of the aqueous solution of Sipomer[®]Pam-200 was around 1.8 and the solution was milky. It is worth mentioning that Sipomer[®]Pam-200 is the only one having a phosphate group in the structure. The phosphate head group can exist in three protonation states, depending on the pH¹⁰. At low pH the phosphate head group is fully protonated, but increasing the pH results in a gradual

deprotonation of the head group (Figure 2.6). When the aqueous solution of Sipomer®Pam-200 was neutralized the solution quickly turned from milky to transparent at pH around 2.5 – 3. To ensure that Sipomer®Pam-200 was deprotonated and also for comparison purposes, the pH of the aqueous solution of Sipomer®Pam-200 was set to 7.5.



Figure 2.6. Successive protonation states of the phosphate head group¹⁰.

Figure 2.7 presents the evolution of the surface tension as the concentration of the polymerizable surfactants/stabilizer increased. Result of the conventional surfactant Dowfax®2A1 has been also included for the sake of comparison.

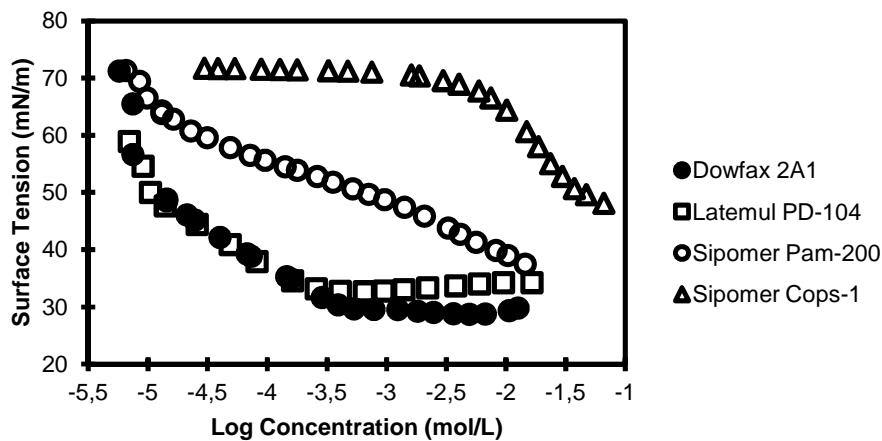


Figure 2.7. Surface tension evolution with surfactant/stabilizer concentration.

In the case of the conventional surfactant Dowfax[®]2A1 as well as in the case of Latemul[®]PD-104, a monotonous decrease in surface tension with increasing surfactant concentration was observed. For concentrations higher than the CMC, a constant value of the surface tension was observed in both cases. As it can be observed in Table 2.2 the CMC of Latemul[®]PD-104 is lower than that of the conventional surfactant Dowfax[®]2A1, meaning that Latemul[®]PD-104 is less water-soluble, most likely due to the longer hydrophobic group present in its structure. It is worth to mention that polymerizable surfactants need to have low CMC, because having low CMC aqueous phase polymerization of the surfactant will be limited and hence the amount of surfactant lost by water-soluble polysoaps will be reduced².

Table 2.2. Critical micelle concentration of different surfactants.

Surfactant	CMC (mol/L)
Dowfax[®]2A1	4.5×10^{-4}
Latemul[®]PD-104	2.38×10^{-4}
Sipomer[®]Pam-200	---
Sipomer[®]Cops-1	---

In the case of Sipomer[®]Pam-200 surface tension dropped slower than in the case of Dowfax[®]2A1 and Latemul[®]PD-104 and a constant value of the surface tension was not obtained even at high surfactant concentration. Therefore, it was not possible to determine the CMC value for this polymerizable surfactant using this method. Conductometric measurements were also carried out to measure the CMC of Sipomer[®]Pam-200, but the conductivity

continuously increased with increasing surfactant concentration and no change in the slope was observed below and above the CMC. Similar trend was observed by Hu et al.¹¹ for the biobased polymerizable surfactant ω -maleate tetradecanoic acid (MA-2). This behaviour was attributed to the bola-type structure of the polymerizable surfactant due to the presence of two carboxylic ionic groups located at each end of the MA-2 chain that can form various shaped self-assembled structures or agglomerates rather than obvious micellar structures. It has been seen that the aggregation properties of mono-n-alkyl phosphates in water not only depend on the concentration, temperature, or the presence of additional salt but also on the degree of protonation of the head group^{12,13}. Walde et al.¹³ found that at pH below 3, when about half of the phosphate head groups were completely protonated and half of the molecules were in the monoanionic form, n-dodecylphosphoric acid formed vesicles in water due to attractive intermolecular head group interactions (hydrogen-bonding network). When the pH was between 3 and 9 crystallization of n-dodecylphosphoric acid was observed. At pH higher than 9, when the phosphate was bearing two negative charges and the solubility of the molecule was higher, intermolecular repulsions destabilize the bilayer of the vesicles and micellar structures were formed. Therefore, taking into account the pH used in the surface tension measurements (pH = 7.5) it could be expected that Sipomer[®]Pam-200 was not forming micelles in water. Hence, other experiments were carried out at higher pH values. Figure 2.8 presents the evolution of the surface tension as a function of Sipomer[®]Pam-200 concentration at three different pHs. Note that in this graph instead of representing the surface tension vs. the logarithm of surfactant concentration as in Figure 2.7, the surface tension vs. surfactant concentration is represented. As it can be observed, increasing the pH the surface tension dropped faster probably due to the higher amphiphilic character of the surfactant with

increasing the pH, but even at the highest pH a constant value of the surface tension was not observed. According to the Gibbs adsorption equation¹⁴, the continuous decrease of the surface tension (γ) indicates that the concentration of amphiphilic species at the air-liquid interface continuously increased. In the case of Sipomer[®]Pam-200, the continuous decrease of the surface tension with increasing surfactant concentration could be due to different mechanisms. On the one hand, even at the highest pH (pH=10), not all the phosphate head groups would be fully deprotonated (bearing two negative charge) and hence there is a possibility of having hydrogen-bonding networks between molecules which would continuously modify the adsorption of molecules at the air-liquid interface due to the formation of bilayer structures reducing the surface tension with increasing surfactant concentration. On the other hand, due to the presence of molecules with different protonation states (most of them fully deprotonated and some in the monoionic form), molecules with different amphiphilic character and hence with different adsorption equilibrium could be expected. At low concentrations of Sipomer[®]Pam-200, all the species adsorb at the air-liquid interface according to the individual adsorption equilibrium. The species with higher adsorption constants become depleted in the aqueous phase. As they are not present in a high amount, they leave space for the adsorption of the other species. As the total concentration of Sipomer[®]Pam-200 increases, the interface air-liquid becomes more crowded and the species with lower adsorptions constants are replaced by those with higher constants. This results in a continuous increase of the concentration of amphiphilic compounds at the interface air-liquid, and hence in a decrease of the surface tension.

It is worth to mention that Joumaa et al.¹⁵ reported that the CMC for Sipomer[®]Pam-200 was 0.01 mol/L; however they did not mention which was the technique used or the experimental conditions employed (e.g. pH of the aqueous solution of Sipomer[®]Pam-200). This result seems to be far from the apparent CMC obtained in this work ($CMC_{\text{apparent}} \approx 0.001$ mol/L) which could be attributed to the heterogeneity of the system.

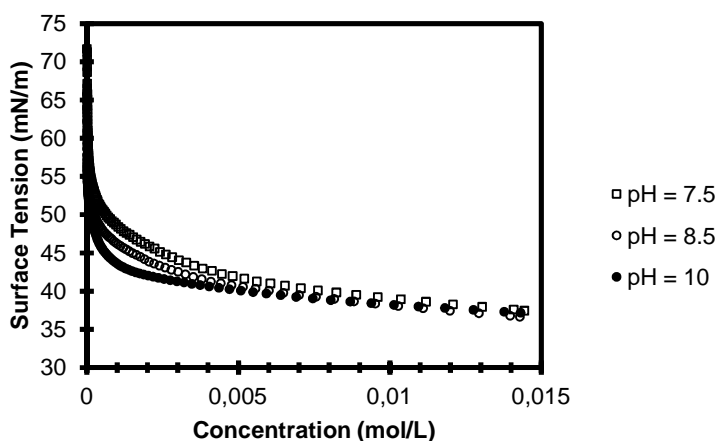


Figure 2.8. Surface tension evolution with Sipomer[®]Pam-200 concentration at different pH values.

Finally, as it can be observed in Figure 2.7 in the case of Sipomer[®]Cops-1, as it is a stabilizer rather than a surfactant, the surface tension dropped very slowly, until 0.006 mol/L of Sipomer[®]Cops-1 the surface tension remained almost constant at 70 mN/m, which is similar to the value of the pure water. This means that the surface activity of Sipomer[®]Cops-1 is very low and therefore, does not present emulsifying properties. The fact that the surface tension did not

reach a constant value with increasing the stabilizer concentration (Figure 2.7) confirmed that Sipomer[®]Cops-1 is not hydrophobic enough to form micelles.

2.3.2.2. Determination of the parking area (a_s)

The parking area (a_s) of the surfactant depends on the hydrophilicity of the polymer particles. In this work different methyl methacrylate/butyl acrylate emulsion copolymers will be synthesized; on the one hand BA-rich copolymers (MMA/BA at weight composition of 10/90 %) which are extensively used as adhesives and on the other hand MMA/BA copolymers at weight composition of 50/50 % to be used as coatings. Therefore the parking area of each surfactant was determined using latexes with different hydrophilic character.

Figure 2.9 presents the evolution of the surface tension as the concentration of Latemul[®]PD-104 increased in the presence and absence of polymer particles. As it can be observed, in the presence of latex particles higher surfactant concentration was needed to completely saturate the aqueous phase and hence to form micelles. Furthermore, when the surface of the polymer particles was more hydrophobic (PMMA/BA at weight composition of 10/90%) higher surfactant amount was needed to reach the CMC, meaning that a higher number of surfactant molecules were needed to completely cover the particle-water interface. The same behaviour was observed when the conventional surfactant Dowfax[®]2A1 was used (Figure 2.2).

Table 2.3 presents the parking area of different surfactants. Note that it was not possible to determine the parking area for Sipomer[®]Pam-200 and Sipomer[®]Cops-1 because the CMC could not be determined as discussed previously.

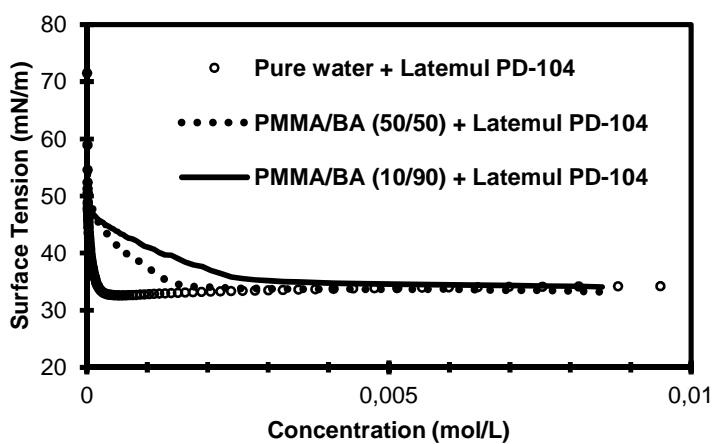


Figure 2.9. Surface tension evolution with surfactant concentration in presence and absence of polymer particles.

Table 2.3. Parking area (a_s) of the surfactants.

Surfactant	a_s ($\text{\AA}^2/\text{molecule}$)	
	PMMA/BA	PMMA/BA
	(50/50 wt%)	(10/90 wt%)
Dowfax [®] 2A1	170	89
Latemul [®] PD-104	220	149
Sipomer [®] Pam-200	---	---
Sipomer [®] Cops-1	---	---

2.3.3. Homopolymerization

The possibility of homopolymerization of Latemul[®]PD-104 was checked by ¹³C-NMR monitoring the area of the unsaturated carbon (around 110 ppm) with respect to that of the CH₃ of the PPO group (around 10 ppm). The ¹³C-NMR spectra of samples at the beginning and at the end of the reaction are displayed in Figure 2.10 and Figure 2.11, respectively. In both spectra, the areas were normalized to the signal of the carbon corresponding to the CH₃ of the PPO group. It could not be observed any change in the area; therefore it was concluded that Latemul[®]PD-104 does not homopolymerize. This conclusion is in agreement with the results reported by Kresge et al.¹⁶, who concluded that 1,2 disubstituted ethylenes do not homopolymerize.

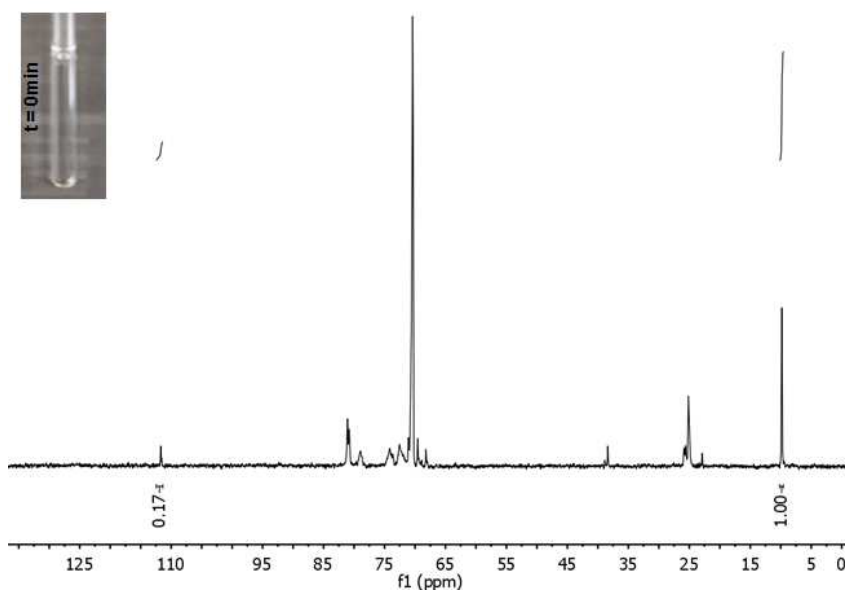


Figure 2.10. ¹³C-NMR spectra of Latemul[®]PD-104 at the beginning of the reaction (t=0 min).

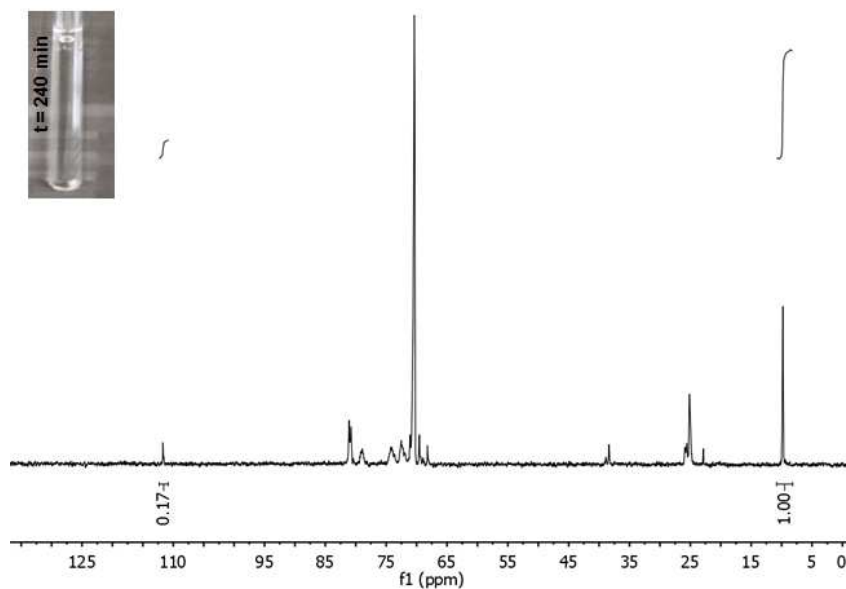


Figure 2.11. ^{13}C -NMR spectra of Latemul[®]PD-104 at the end of the reaction (t=240 min).

In the case of Sipomer[®]Pam-200 at first glance it could be observed that homopolymerizes because after four hours of reaction the solution become milky. Furthermore, the technical data sheet warns that Sipomer[®]Pam-200 could rapidly homopolymerize when it is mixed with an initiator solution even without heating. Figure 2.12 and Figure 2.13 show the ^{13}C -NMR spectra of Sipomer[®]Pam-200 aqueous solution before and after homopolymerization, respectively. It could be clearly observed that the signal corresponding to the unsaturated carbon (the ones appearing at around 125 and 135 ppm) completely disappeared.

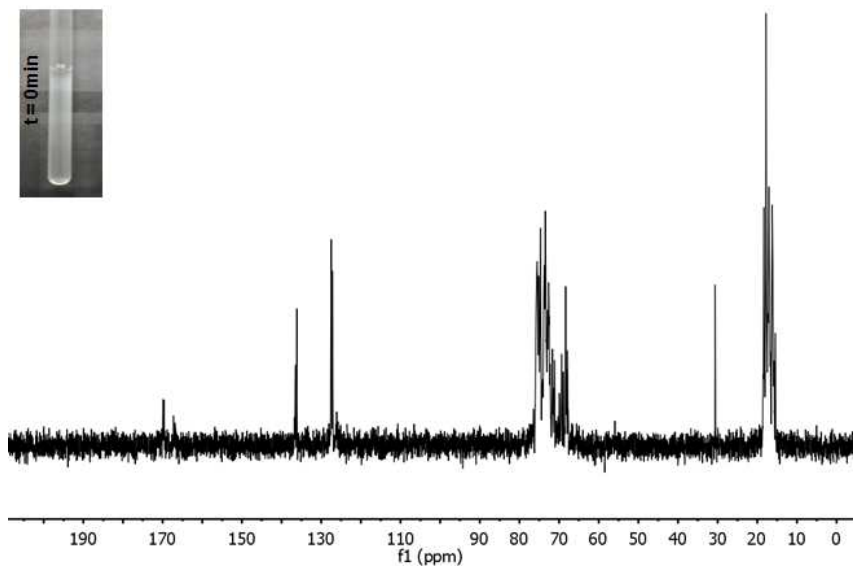


Figure 2.12. ¹³C-NMR spectra of Sipomer®Pam-200 at the beginning of the reaction (t=0 min).

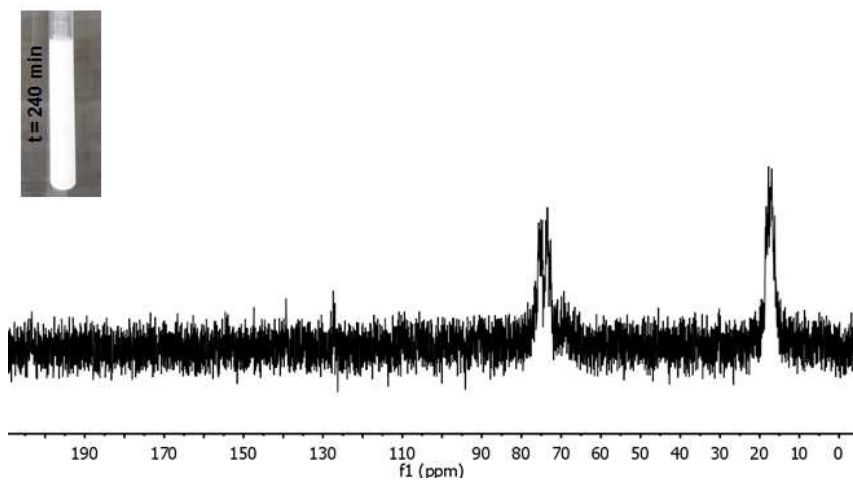


Figure 2.13. ¹³C-NMR spectra of Sipomer®Pam-200 at the end of the reaction (t=240 min).

In the case of the polymerizable stabilizer Sipomer[®]Cops-1 no reactions were carried out in order to check the possibility of homopolymerization. In this case, from the reactivity ratio data given by the supplier (Table 2.4) it can be assumed that homopolymerization of this stabilizer in monomer/stabilizer system is unlikely because r_1 values for Sipomer[®]Cops-1 are close to 0¹.

Table 2.4. Reactivity ratio data for Sipomer[®]Cops-1 (M_1) given by the supplier.

M_2	r_1	r_2
Styrene	0.0001	29.49
Methyl Methacrylate	0.0483	19.62
Butyl Acrylate	0.0411	15.00
Vinyl Acetate	0.001	1.52
Veova 10	0.002	3.17

2.3.4. Copolymerization

The occurrence of copolymerization between Latemul[®]PD-104 and methyl methacrylate (MMA) was determined by means of ¹H-NMR monitoring the intensity of the double bond signals. The protons of the unsaturated carbons of MMA appear between 5.5 and 6 ppm and the protons of the unsaturated carbons of Latemul[®]PD-104 appear between 4.5 and 5 ppm. The ¹H-NMR spectra of the samples at the beginning and at the end of the reaction are displayed in Figure 2.14 and Figure 2.15, respectively. Normalizing the areas of the protons of the unsaturated carbons with respect to the solvent signal in both spectra, allows calculation of

partial conversions. In this particular case it was found that the partial conversion for MMA was 98% and 4% for Latemul[®]PD-104. Therefore it was concluded that Latemul[®]PD-104 does not copolymerize well with MMA.

The same procedure was followed with other monomers such as butyl acrylate (BA) and 2-ethylhexyl acrylate (2-EHA). Table 2.5 shows the partial conversions of Latemul[®]PD-104 and monomers obtained by ¹H-NMR. As it can be observed Latemul[®]PD-104 reacts better with acrylates (BA and 2-EHA) than with methacrylates (MMA). However, the reactivity of Latemul[®]PD-104 should be low in comparison to that of the monomers.

Table 2.5. Partial conversions of Latemul[®]PD-104 and monomers obtained by ¹H-NMR.

Reaction	Latemul[®]PD-104	Monomer
Latemul/MMA	4%	98%
Latemul/BA	26%	89%
Latemul/2-EHA	27%	99%

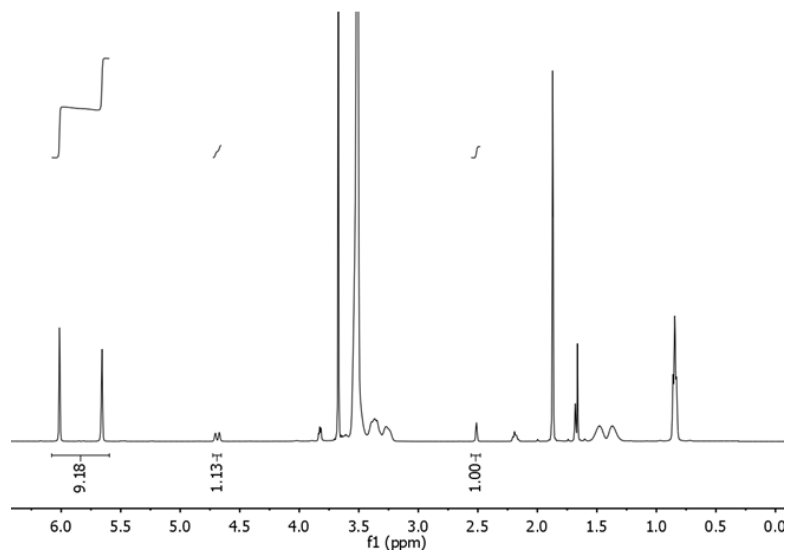


Figure 2.14. ¹H-NMR spectra at the beginning (t=0 min) of the reaction of Latemul[®]PD-104 and MMA in DMSO-d₆.

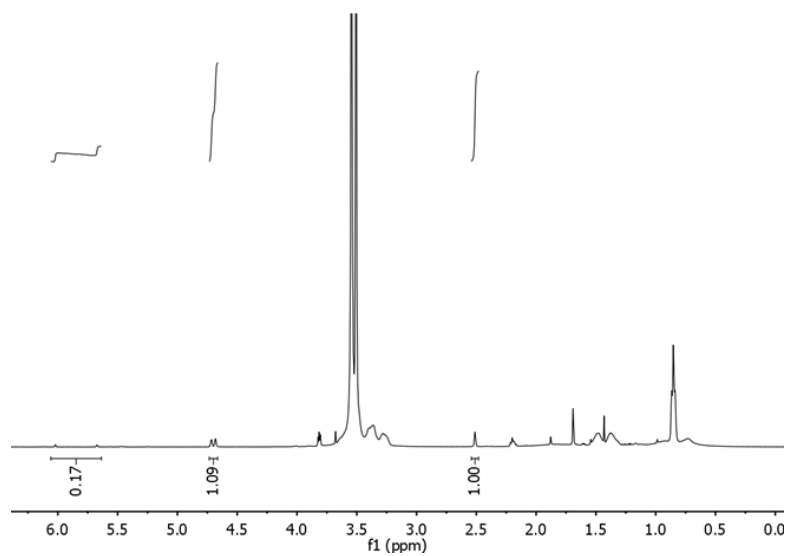


Figure 2.15. ¹H-NMR spectra at the end of the reaction (t=240 min) of Latemul[®]PD-104 and MMA in DMSO-d₆.

Sipomer[®]Pam-200 has a methacrylic function in its structure. Therefore its reactivity ratio should be similar to that of methyl methacrylate. The occurrence of copolymerization between Sipomer[®]Pam-200 and MMA was also determined by ¹H-NMR and the spectra of the samples at the beginning and at the end of the reaction are displayed in Figure 2.16 and Figure 2.17, respectively. In this case the signal of the protons of the unsaturated carbons of Sipomer[®]Pam-200 and MMA appear in the same position (between 5.5 and 6 ppm) therefore, the partial conversion of Sipomer[®]Pam-200 could not be obtained and the total conversion was determined. Normalizing the areas of the unsaturated carbons with respect to the solvent signal it was found that the total conversion was 84 %. Since the initial formulation was 50/50 % in moles and assuming that all MMA reacted, it can be concluded that at least 70 % of Sipomer[®]Pam-200 reacted.

For Sipomer[®]Cops-1 the most favourable reactivity ratios (Table 2.4) were found with vinyl acetate and Veova 10. However, Sipomer[®]Cops-1 can also work efficiently in acrylic systems. Aramendia et al.¹⁷ showed that the incorporation of an alkenyl-based nonionic surfactant into acrylic latexes was around 40-60% depending on the polymerization process they used.

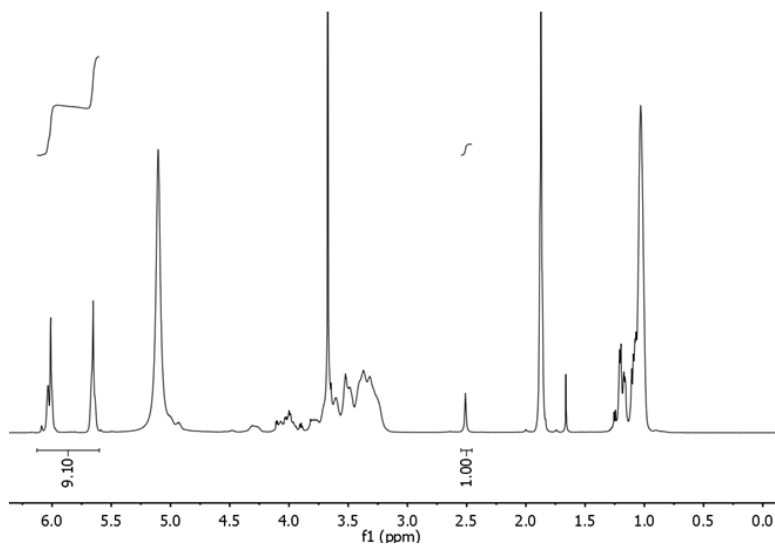


Figure 2.16. $^1\text{H-NMR}$ spectra at the beginning ($t=0$ min) of the reaction of Sipomer[®]Pam-200 and MMA in DMSO-d_6 .

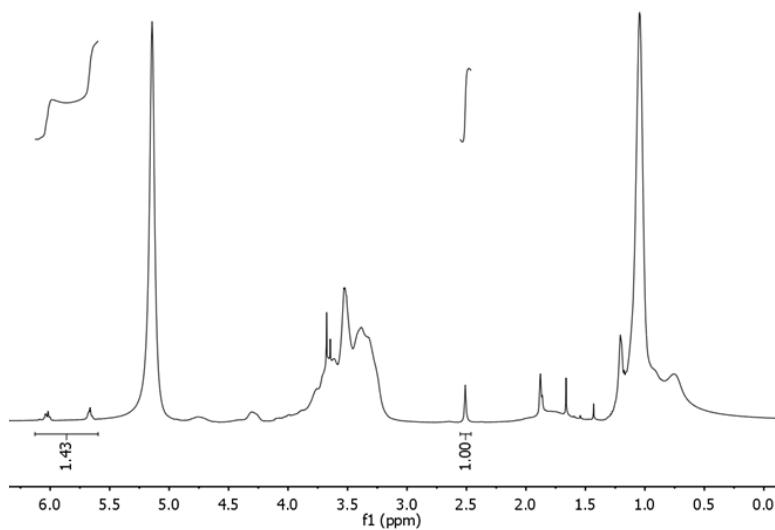


Figure 2.17. $^1\text{H-NMR}$ spectra at the end ($t=240$ min) of the reaction of Sipomer[®]Pam-200 and MMA in DMSO-d_6 .

2.4. Conclusions

The objective of this chapter was to investigate the main characteristics of the polymerizable surfactants that will be used through the rest of this thesis.

Regarding the behavior of the polymerizable surfactants in aqueous solution it was found that Latemul[®]PD-104 behaved similar to the conventional surfactant Dowfax[®]2A1. Latemul[®]PD-104 presented low CMC value which is good to prevent polymerization of the surfactant in the aqueous phase. It was also found that the area occupied by one molecule of Latemul[®]PD-104 was higher than that of Dowfax[®]2A1 molecules, meaning that less amount of Latemul[®]PD-104 was needed to completely cover the surface of the polymer particles. In the case of Sipomer[®]Pam-200 no value of the CMC was obtained. It was demonstrated that Sipomer[®]Cops-1 is very hydrophilic to form micelles because it is a polymerizable stabilizer rather than a surfactant.

With respect to the nature of the double bond of the surfactants/stabilizer it could be said that Latemul[®]PD-104 and Sipomer[®]Cops-1 are less reactive than Sipomer[®]Pam-200, but Sipomer[®]Pam-200 is able to homopolymerize which is not a good feature to be a good polymerizable surfactant.

2.5. References

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Chapter 3. Assessing the performance of polymerizable surfactants in emulsion polymerization

3.1. Introduction

In the processes and products of emulsion polymerization, surfactants play a crucial role. They are very important for the nucleation of the latex particles, emulsification of monomer droplets and/or preformed polymer, and the stabilization of the polymer particles during the polymerization and the shelf life of the products. The type and concentration of surfactant used can significantly alter the polymerization rate, final particle size, particle size distribution, the molecular weight of the resulting polymer and the final properties of the latex¹⁻⁹. In addition to this, in many cases it is important to control the process of particle nucleation because the final particle size and final particle size distribution of the latex are of paramount importance to achieve optimum final properties of the dispersion¹⁰⁻¹⁴.

The two main mechanisms by which nucleation can occur in emulsion polymerization are heterogeneous nucleation (micellar nucleation)¹⁵⁻¹⁸ and homogeneous nucleation¹⁹⁻²¹. In a common emulsion polymerization process the surfactant concentration in the aqueous phase is

above the critical micelle concentration (CMC); in the initial stages of the reaction, oligoradicals formed in the aqueous phase nucleate these micelles and therefore, heterogeneous nucleation is the dominant mechanism for particle formation. Assuming no termination of radicals in the aqueous phase and that during nucleation the average number of radicals per particle is $\bar{n} = 0.5$, the well known Smith-Ewart theory¹⁶ (case II) predicts that the number of polymer particles formed per unit volume of water (N_p) is proportional to the surfactant concentration ($[S]$) and initiator concentration ($[I]$) to the 0.6 and 0.4 power, respectively. In parallel to heterogeneous nucleation, new polymer particles can be formed by homogeneous nucleation when the growing oligoradicals precipitate in the aqueous phase forming new polymer particles. The surfactant molecules needed to stabilize this polymer particles come from those dissolved in water, from those adsorbed on the monomer droplet surface or from the existing polymer particles.

As it was mentioned in Chapter 1, polymerizable surfactants are expected to behave as conventional surfactants, namely, they have to effectively stabilize the polymer particles and they have to provide smooth and reproducible nucleation stages²². Several publications containing information on particle nucleation in systems using polymerizable surfactants can be found in the open literature.

Guillaume et al.²³ used the surface active monomer sodium acrylamido undecanoate (AUNa) in the emulsion copolymerization of styrene and butyl acrylate. The polymerizations were carried out in a batch reactor at low solids content (6.7 wt %). When the concentration of [AUNa] was lower than $6 \cdot 10^{-3}$ M, N_p was proportional to [AUNa], but above this concentration N_p did not further increase and at higher concentration decreased. The decrease in N_p was

attributed to the formation of large amounts of hydrosoluble chains, which caused bridging flocculation.

Urquiola et al.^{24,25} studied the emulsion polymerization of vinyl acetate using TREM LF-40 (sodium dodecyl alkyl sulfosuccinate) as polymerizable surfactant and the hydrogenated derivative of TREM LF-40 as the conventional surfactant. They found that in both cases an increase in the surfactant concentration led to a smaller particle size. The dependence of N_p upon TREM LF-40 concentration varied from a 0.4 power at high initiator concentration to a 0.62 power at low initiator concentration.

Stähler²⁶ used several polymerizable surfactants (sodium sulfopropyldodecyl maleate, sodium sulfopropyltetradecyl maleate, sodium sulfopropyloctadecyl maleate and sodium sulfopropyldodecyl fumarate) in the emulsion polymerization of styrene. It was found that using maleate polymerizable surfactants particle nucleation was similar to that observed when the conventional surfactant SDS was used. However, as the fumaric polymerizable surfactant polymerized with the styrene during the nucleation period polyelectrolites were formed that contributed to the colloidal stability of the particles yielding higher number of particles than that obtained with the maleate surfactants.

Chern and Chen²⁷ studied the emulsion polymerization of butyl acrylate using sodium dodecyl alkyl sulfosuccinate as polymerizable surfactant in a semi-batch reactor. They found that when the surfactant concentration was above the CMC, the number of polymer particles formed was proportional to the concentration of the surfactant in the initial charge to the 0.72-0.80 power. Similar results were observed when the conventional surfactant SDS was used.

Chern et al.²⁸ compared the performance of the commercial nonionic polymerizable surfactant NE-40 with that of the conventional surfactant NP-40. They found that increasing the concentration of the polymerizable surfactant the particle size decreased. The polymerizable surfactant gave higher particle sizes but less coagulum than the conventional surfactant.

Amalvy et al.² studied the particle nucleation process in the batch emulsion polymerization of three monomers of widely different water solubility and reactivity ratios (styrene, methyl methacrylate and vinyl acetate) stabilized with the anionic polymerizable surfactant sodium dodecyl sulfopropyl maleate (M12). The conventional anionic surfactant SDS was used as a reference. From the shape of the $\log N_p$ vs. $\log [\text{surfactant}]$ curves they concluded that in the case of styrene the polymer particles were formed by micellar nucleation whereas in the case of methyl methacrylate and vinyl acetate particles were formed by homogeneous nucleation. They concluded that the nucleation mechanism was not affected by the surfactant type (conventional vs. polymerizable). In the emulsion polymerization of styrene the dependence of N_p on surfactant concentration was equal to that predicted by Smith-Ewart theory¹⁶. Although M12 was rather reactive with styrene ($r_s = 8-10$, $r_{\text{maleate}} = 0^{2,29}$) it was found that nucleation was ended before significant amounts of M12 had been consumed. Therefore, the polymerizable surfactant behaved as the conventional surfactant SDS during nucleation. In the polymerizations of MMA ($r_{\text{MMA}} = 354 \pm 57$, $r_{\text{diethyl maleate}} = 0^{2,29}$) and VAc ($r_{\text{VAc}} = 0.043$, $r_{\text{diethyl maleate}} = 0.17^{2,29}$) a lower dependence of N_p upon [M12] than upon [SDS] was observed due to the loss of part of the polymerizable surfactant by formation of water-soluble oligomers that did not effectively participate in the stabilization of the particles.

Lai et al.³⁰ studied the kinetics of emulsion polymerization of styrene using the polymerizable surfactant Hitenol BC20 and results were compared with those obtained using SDS as surfactant. Although the dependence of N_p on surfactant concentration was found to be lower than the Smith-Ewart value the polymerizable surfactant Hitenol BC20 behaved as the conventional surfactant SDS during most of the emulsion polymerization process.

As the number of polymer particles formed during the process is sensitive to the surfactant concentration used in the polymerization, in order to develop a successful emulsion polymerization process and product, it is important to choose an appropriate surfactant as well as to understand how the surfactant type and concentration affect the nucleation mechanism.

Therefore, the main objective of this chapter was to assess the performance of previously characterized polymerizable surfactants and polymerizable stabilizer in the emulsion copolymerization of acrylic latexes. To this end, screening experiments were done in order to study their behaviour in batch emulsion polymerization process and to gain knowledge on how the surfactant type and amount could affect the nucleation mechanism.

3.2. Experimental

3.2.1. Materials

Methyl methacrylate (MMA, Quimidroga) and n-butyl acrylate (BA, Quimidroga) were used as supplied. Methacrylic acid (MAA, Quimidroga) was used as functional monomer. Potassium persulfate (KPS, Fluka) was used as thermal initiator. Polymerizable surfactants Latemul[®]PD-104 (Kao Group) and Sipomer[®]Pam-200 (Solvay) and polymerizable stabilizer

Sipomer[®]Cops-1 (Solvay) were used as received. The conventional surfactant Dowfax[®]2A1 (The Dow Chemical Company) was used for comparison purposes. Deionized water was used in all reactions. To increase the pH of the latexes a 25% solution of ammonia (Fluka) was used.

3.2.2. Emulsion polymerization

20 wt% solids content polymethyl methacrylate-co-butyl acrylate-co-acrylic acid (MMA/BA/MAA at weight composition of 49.5/49.5/1) latexes were synthesized by batch emulsion polymerization. All the reactions were carried out in glass bottles (100 mL) rotated end-over-end at a speed of 47rpm at 70°C after purging with nitrogen for 10 minutes. Polymerizations were allowed to proceed for 240 minutes. The general formulation used in the polymerizations is given in Table 3.1. For each surfactant type the studied process variable was the surfactant concentration which was varied from 0.136 to 10.038 mM.

3.2.3. Characterization

Conversion was gravimetrically determined and the coagulum amount was determined by filtering the latex through a 85µm nylon mesh. The average particle size was measured by Dynamic Light Scattering (DLS). The number of polymer particles (N_p) was calculated from the intensity average diameter of particles obtained from DLS. The pH of the final latexes was also measured. The microstructure of the final latex was determined by measuring the gel fraction in tetrahydrofuran (THF) by Soxhlet extraction and the molecular weight of the soluble part was analyzed by Gel Permeation chromatography (GPC). The details of the characterization procedures and methods are given in Appendix I.

Table 3.1. General formulation used in batch emulsion polymerization experiments.

Compound	Charge (g)
MMA	4.95
BA	4.95
MAA	0.1
Ammonia ^{a)}	0.1
KPS	0.05
Water ^{b)}	39.3 – 39.8
Surfactant	variable

^{a)} 25 % aqueous solution. ^{b)} The total amount of water used was varied in order to adjust the formulation to 20 wt% of final solids content. The amount of water corresponds to the total amount of water added (added water + water coming from surfactant solutions).

3.3. Results and discussion

20 wt% solids content polymethyl methacrylate-co-butyl acrylate-co-acrylic acid (MMA/BA/MAA at weight composition of 49.5/49.5/1) latexes were synthesized by batch emulsion polymerization. The main characteristics of the final latexes are shown in Table 3.2. In Table 3.2 and throughout this chapter, latexes synthesized using the conventional surfactant Dowfax[®]2A1 were designated as D20. Those synthesized with the polymerizable surfactants Latemul[®]PD-104 and Sipomer[®]Pam-200, L20 and S20, respectively, and latexes synthesized using the polymerizable stabilizer Sipomer[®]Cops-1 as C20. For each surfactant type, eight reactions were carried out varying the surfactant concentration, which were designated with a different number (1-8).

Table 3.2. Main characteristics of the final latexes synthesized by batch emulsion polymerization.

Latex	Surfactant	Surfactant Concentration ^{a)} (mM)	Conversion (%)	Coagulum (%)	dp (nm)
D20-1	Dowfax [®] 2A1	0.136	98.01	0.8	565
D20-2		0.332	98.98	0.6	396
D20-3		0.718	99.4	0.7	184
D20-4		1.258	100	0.3	150
D20-5		1.857	100	0.1	132
D20-6		2.542	100	0.1	111
D20-7		4.305	100	0.1	92
D20-8		8.628	100	0.1	70
L20-1	Latemul [®] PD-104	0.209	99.2	0.8	257
L20-2		0.358	99.4	0.8	212
L20-3		0.657	99.6	0.8	170
L20-4		1.186	99.7	0.7	136
L20-5		1.763	99.7	0.6	120
L20-6		2.117	99.6	0.3	111
L20-7		4.867	100	0.2	81
L20-8		7.867	100	0.2	72
S20-1	Sipomer [®] Pam-200	0.150	97.1	1.0	517
S20-2		0.350	97.7	0.4	55
S20-3		0.595	98.8	0.3	421
S20-4		1.201	99.4	0.1	356
S20-5		1.704	99.9	0.2	335
S20-6		2.973	100	0.2	215
S20-7		6.014	99.9	0.1	144
S20-8		10.038	100	0.1	110
C20-1	Sipomer [®] Cops-1	0.140	98.4	0.4	565
C20-2		0.420	98.9	0.2	531
C20-3		0.701	98.5	0.1	545
C20-4		1.027	98.7	0.1	535
C20-5		1.869	98.8	0.2	532
C20-6		2.384	99.1	0.1	546
C20-7		4.864	98.7	0.2	548
C20-8		8.809	99.1	0.1	475

^{a)} Per L of water (mmol/L).

In all polymerizations stable latexes with low amounts of coagulum (< 1 wt%) were obtained. Noticeable was that when the conventional surfactant Dowfax[®]2A1 and

polymerizable surfactants Latemul[®]PD-104 and Sipomer[®]Pam-200 were used, the increase in surfactant concentration led to lower amounts of coagulum at the end of the polymerization, likely due to a higher electrostatic repulsion coming from the ionic groups on the surface of the particles provided by the anionic surfactants.

In all polymerizations almost full conversion of the monomers was achieved after 240 minutes of reaction. In the reactions carried out using Dowfax[®]21A (D20-1 – D20-8), Latemul[®]PD-104 (L20-1 – L20-8) and Sipomer[®]Pam-200 (S20-1 – S20-8) increasing surfactant concentration the final monomer conversion increased until reaching full conversion. However when the polymerizable stabilizer Sipomer[®]Cops-1 was used (C20-1 –C20-8) a clear trend in the final monomer conversion could not be observed with increasing the stabilizer concentration and in these reactions slightly lower monomer conversions were obtained in comparison to the reactions in where conventional or polymerizable surfactants were used. The fact that the final conversion increased with increasing surfactant concentration could be explained by the difference found in the final particle size of the latexes. As it can be observed in Table 3.2 in all the cases, except in the latexes synthesized using the polymerizable stabilizer Sipomer[®]Cops-1, increasing the surfactant concentration the final particle size decreased meaning that higher number of polymer particles were generated during the polymerization process (Figure 3.1). In reactions were Sipomer[®]Cops-1 was used the increase in the stabilizer concentration led to latexes with similar final particle size and therefore, to a similar number of polymer particles (Figure 3.1).

In emulsion polymerization the polymerization rate increases by increasing the number of polymer particles as it can be seen in equation 3.1, where the rate of polymerization per unit volume of water is defined as

$$R_p = k_p [M]_p \frac{\bar{n}}{N_A} N_p \quad (\text{mol L}_{\text{water}}^{-1} \text{s}^{-1}) \quad (3.1)$$

where k_p is the propagation rate coefficient of the monomer ($\text{L mol}^{-1} \text{s}^{-1}$), $[M]_p$ is the monomer concentration in the polymer particle (mol L^{-1}), \bar{n} the average number of radicals per particle, N_A the Avogadro's number and N_p the number of polymer particles per unit volume of water.

Therefore, in reactions where Dowfax[®]2A1 (D20-1 – D20-8), Latemul[®]PD-104 (L20-1 – L20-8) and Sipomer[®]Pam-200 (S20-1 – S20-8) were used the increase in surfactant concentration led to a higher number of polymer particles and hence a higher polymerization rate that allow reaching faster to 100% monomer conversion (Table 3.2). When Sipomer[®]Cops-1 (C20-1 – C20-8) was used, as the increase in stabilizer concentration led to similar number of polymer particles, similar polymerization rate was expected in all reactions. As the number of polymer particles generated in these reactions (C20-1 – C20-8) was much lower in comparison to the other ones, lower polymerization rates were obtained and hence more time would be needed to achieve 100 % final monomer conversion (assuming that termination in the aqueous phase was not negligible).

Figure 3.1 presents the effect of surfactant concentration on the final number of polymer particles for each surfactant type.

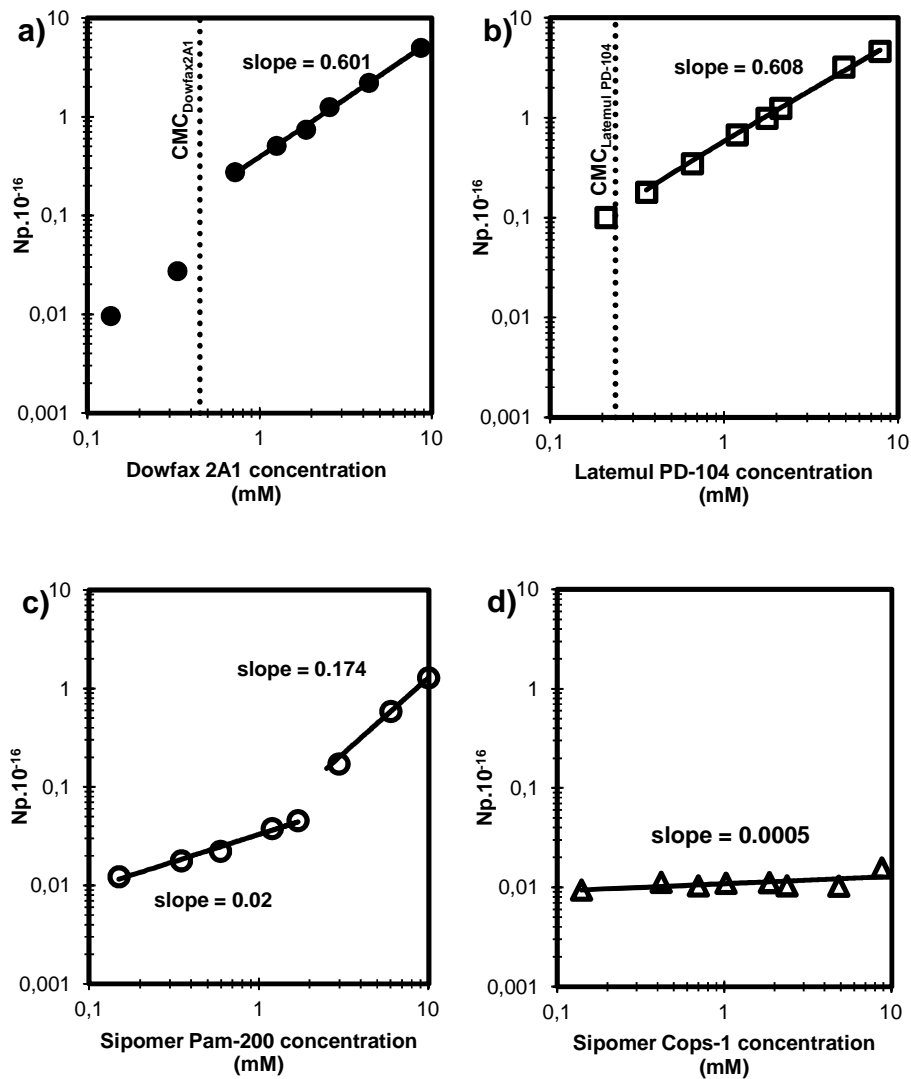


Figure 3.1. Effect of the surfactant concentration on the final number of polymer particles for each surfactant type: a) Dowfax[®]2A1, b) Latemul[®]PD-104, c) Sipomer[®]Pam-200 and d) Sipomer[®]Cops-1.

From the shape of the $\log N_p$ vs. \log surfactant concentration an idea about the nucleation mechanism can be obtained². When the conventional surfactant Dowfax[®]2A1 was used, as it can be seen in Figure 3.1a, straight lines with a discontinuity around the critical micelle concentration were observed, probably due to a change of the nucleation mechanism around the critical micelle concentration ($CMC_{Dowfax\ 2A1} = 0.45$ mmol/L previously determined in Chapter 2) of the surfactant, namely, homogeneous nucleation below the CMC and micellar nucleation above². It is interesting to point out that above the CMC, the slope of the curve (0.601) was the same value as the one predicted by the Smith-Ewart theory assuming no termination of radicals in the aqueous phase and that during nucleation $\bar{n} = 0.5$ (case II). The same behaviour was observed when the polymerizable surfactant Latemul[®]PD-104 was used (Figure 3.1b), where the dependence of N_p upon Latemul[®]PD-104 concentration was equal to that predicted by Smith-Ewart theory, suggesting that at concentrations higher than the CMC micellar nucleation occurred. This fact indicates that Latemul[®]PD-104 did not change the nucleation mechanism and that its behavior was similar to that of the conventional surfactant Dowfax[®]2A1.

When the polymerizable surfactant Sipomer[®]Pam-200 was used, straight lines with a discontinuity around 1.704-2.973 mM of Sipomer[®]Pam-200 was also observed in the $\log N_p$ vs. \log surfactant concentration plot (Figure 3.1c). However, in this case it cannot be concluded that the nucleation mechanism changed about the CMC because it was not possible to determine the CMC value for this polymerizable surfactant (see Chapter 2 for details). As it can be observed in Figure 3.1c the slope of the curve above the discontinuity was much lower than the values obtained when Dowfax[®]2A1 and Latemul[®]PD-104 were used, suggesting a lower

dependence of N_p upon Sipomer[®]Pam-200 concentration. Furthermore, in comparison to the reactions carried out with Dowfax[®]2A1 and Latemul[®]PD-104, when this polymerizable surfactant was used less polymer particles were formed and hence latexes with larger particle sizes were obtained (Table 3.2). Sipomer[®]Pam-200 has a methacrylic function in its structure and therefore it is expected to copolymerize well during the polymerization process. This could affect in the stabilization of the polymer particles because if the surfactant copolymerizes fast in the process it can be buried inside the polymer particles^{22,31}. Furthermore, as it was shown in Chapter 2, Sipomer[®]Pam-200 is able to homopolymerize in the aqueous phase forming water-soluble oligomers that do not contribute in particle stabilization^{22,31}. The mentioned events may decrease the colloidal stability of the particles yielding lower number of particles than that obtained with Dowfax[®]2A1 and Latemul[®]PD-104. The lower dependence of N_p upon Sipomer[®]Pam-200 concentration could be due to the loss of part of the polymerizable surfactant by fast burial or by formation of water-soluble oligomers that did not effectively participate in the stabilization of the particles².

In Chapter 2 it was demonstrated that Sipomer[®]Cops-1 is very hydrophilic to form micelles. Therefore, as expected, when Sipomer[®]Cops-1 was used in batch reactions, no dependence of N_p upon stabilizer concentration was observed (Figure 3.1d), meaning that the number of polymer particles formed was independent of the stabilizer concentration. This suggests that for all concentrations of Sipomer[®]Cops-1 polymer particles were formed by homogeneous nucleation followed by coagulation of the precursor particles to yield mature stable particles; namely, the so called coagulative nucleation^{32,33}. As the Sipomer[®]Cops-1 is very hydrophilic it must react with growing oligoradicals in the aqueous phase in order to

produce amphiphilic species that can act as surfactant molecules during the polymerization process. However as the reactivity of this polymerizable stabilizer is low in comparison to that of the monomers used (reactivity ratios given by the supplier: $r_{\text{Sipomer}^{\text{®}}\text{Cops-1}}=0.048$, $r_{\text{MMA}}=19.62$; $r_{\text{Sipomer}^{\text{®}}\text{Cops-1}}=0.041$, $r_{\text{BA}}=15$), Sipomer[®]Cops-1 was not able to form fast enough amphiphilic species to form micelles and hence, polymer particles were formed by homogeneous nucleation. As the polymer particles were only stabilized by the charges coming from the initiator (KPS) and MAA, the precursor polymer particles formed by homogeneous nucleation suffered coagulation due to the lack of surfactant molecules available to stabilize the polymer particles. Once the amphiphilic species were formed during the polymerization process, they were adsorbed in the polymer particles already formed. It is worth to mention that in the reactions where Sipomer[®]Cops-1 was used the Smith-Ewart Case II should not be considered due to the large particle sizes obtained (particle sizes greater than 475nm, see Table 3.2). In these reactions, the concentration of radicals in the polymer particles would approach that of bulk polymerization ($\bar{n} \gg 0.5$, Smith-Ewart Case III).

Polymer microstructure of the final latexes was also analyzed in terms of gel content (or THF insoluble part) and molecular weight of the sol part. The weight-average molecular weight (M_w) and molecular weight dispersity (\mathcal{D}) of the latexes as a function of surfactant concentration are presented in Figure 3.2 and Figure 3.3, respectively, and the measured gel content of the final latexes in Figure 3.4.

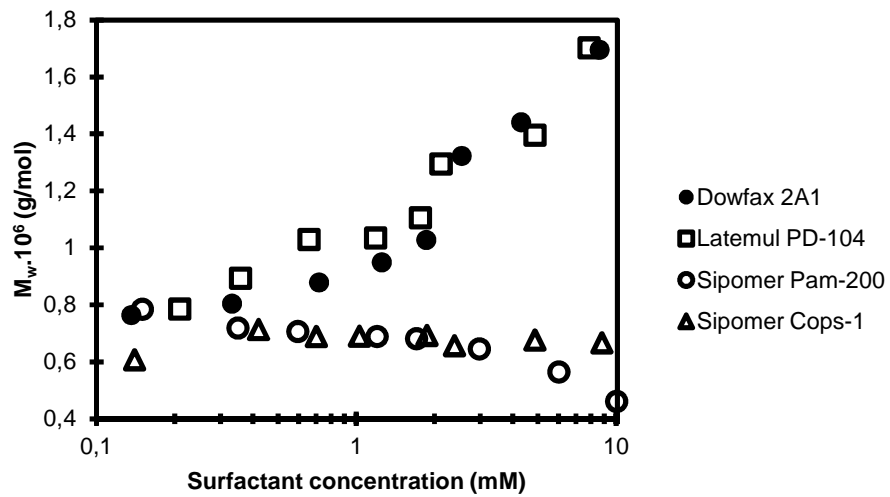


Figure 3.2. Weight-average molecular weight of latexes synthesized using different surfactant type.

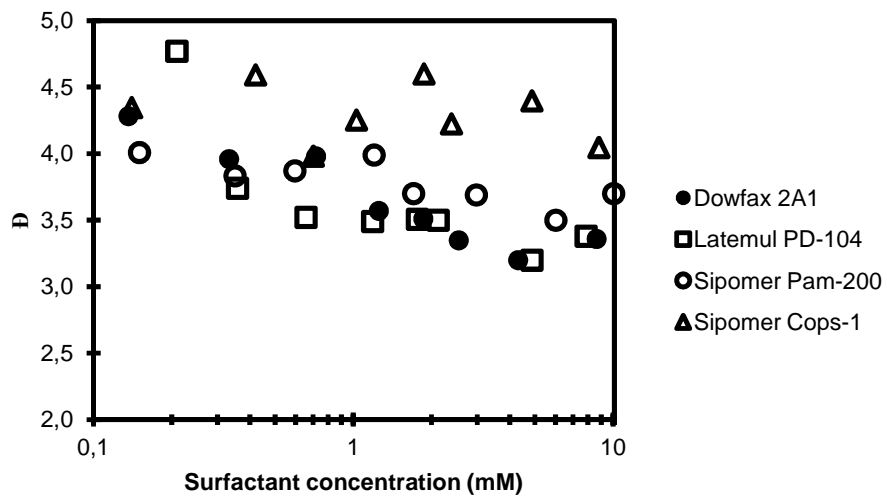


Figure 3.3. Molecular weight dispersity (\bar{D}) of latexes synthesized using different surfactant type.

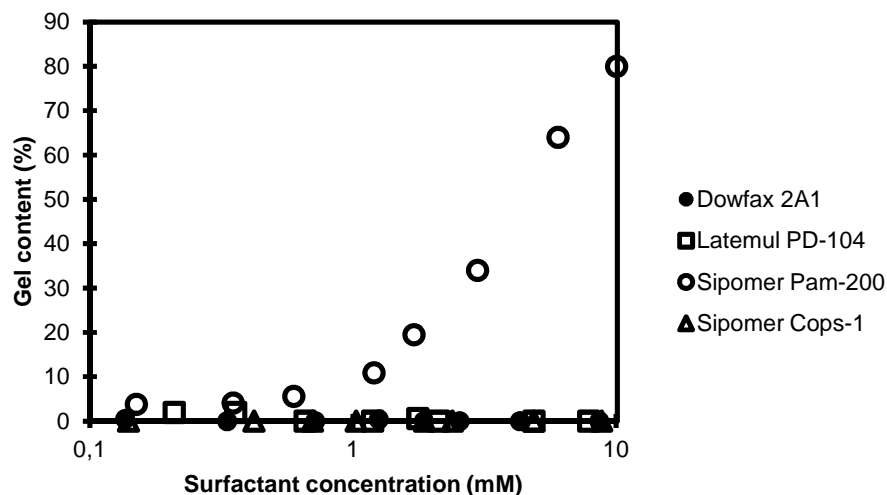


Figure 3.4. Measured gel content of the latexes synthesized using different surfactant type.

As it can be observed in Figure 3.2 and Figure 3.3, when the conventional surfactant Dowfax[®]2A1 and the polymerizable surfactant Latemul[®]PD-104 were used, in both cases the molecular weight of the final latex increased with increasing surfactant concentration. This is what one normally expects from a conventional emulsion polymerization process considering the Smith-Ewart Case II ($\bar{n} = 0.5$). Assuming that $k_a[P_{tot}]_w \gg k_{tr}^{mon}[M]_p$ (radical absorption is greater than transfer to monomer) the following approximation could be made

$$\bar{M}_n^{inst} \approx \frac{k_p[M]_p}{k_a[P_{tot}]_w} W_m \quad (3.2)$$

where \bar{M}_n^{inst} is the instantaneous number-average molecular weight, k_p the rate coefficient for propagation, $[M]_p$ the concentration of monomer in the polymer particles, k_a the rate coefficient for radical entry into polymer particles, $[P_{tot}]_w$ the concentration of radicals in the aqueous phase, w_m the molecular weight of the repeated unit in the polymer chain and k_{tr}^{mon} is the rate coefficient for chain transfer to monomer.

If radical termination in the aqueous phase is negligible,

$$\bar{M}_n^{inst} \approx \frac{k_p [M]_p}{2fk_t [I]_w N_A} \frac{N_p w_m}{V_w} \quad (3.3)$$

where N_p is the number of polymer particles in the reactor, V_w the volume of the aqueous phase in the reactor, f the initiator efficiency, k_t the rate coefficient for thermal initiator decomposition, $[I]_w$ the concentration of the initiator in the aqueous phase and N_A the Avogadro's number.

As it can be observed in Equation 3.3 the molecular weight is proportional to the number of polymer particles for the Smith-Ewart Case II. Therefore, the increase in Dowfax[®]2A1 and Latemul[®]PD-104 concentration led to latexes with higher molecular weight (Figure 3.2 and Figure 3.3) due to the higher number of polymer particles formed with increasing surfactant concentration.

When the polymerizable surfactant Sipomer[®]Pam-200 was used unexpected results were obtained because, although increasing surfactant concentration higher number of

polymer particles was formed, the molecular weight decreased (Figure 3.2 and Figure 3.3). This unexpected behavior should be related with the measured gel content. As it can be observed in Figure 3.4, increasing the concentration of Sipomer[®]Pam-200 the gel content increased and hence, the sol molecular weight decreased. Note that only in latexes containing Sipomer[®]Pam-200 gel was obtained. Therefore, the formation of gel (or THF insoluble part) should be related with the presence of Sipomer[®]Pam-200 in the formulation, because in the emulsion polymerization of MMA and BA at weight composition of 50/50 wt% negligible or little gel is usually obtained³⁴. In the emulsion polymerization of acrylates gel is formed by intermolecular chain transfer to polymer followed by termination by combination³⁴⁻³⁷. As intermolecular chain transfer to polymer needs labile H in the backbone, the presence of MMA decreases the gel content of the final latex because the more reactive MMA units incorporated to the growing chains are less reactive toward H abstraction and hence, intermolecular chain transfer to polymer is reduced³⁴.

Sipomer[®]Pam-200 is a methacrylic based phosphate ester which can be incorporated into the polymer chain via methacrylic bond. Taking into account that the final pH of the latexes was around 7-8 (polymerizations were carried out under basic conditions, see Table 3.1) the incorporation of phosphoric acid groups provides the capability of establishing intermolecular head group interactions³⁸, probably through a hydrogen-bonding because the phosphate head groups are not fully deprotonated at pH=7-8 (Chapter 2), yielding a certain physical gel or making the polymer insoluble in THF. Therefore, the higher the amount of phosphated surfactant used in the formulation the higher the fraction that was not soluble in THF and hence, the higher was the measured gel content. It could be expected that the hydrogen-

bonding would be stronger when the phosphate head groups are fully protonated, leading to latexes with higher gel content. In order to verify if the measured gel content was pH dependent, S20-6 – S20-8 reactions were repeated but without using ammonia in the formulation (at acidic pH) and the gel content of these new latexes was measured. Figure 3.5 presents the gel content of the latexes containing Sipomer[®]Pam-200 synthesized at basic and at acidic conditions and as it can be observed, for the same surfactant concentration the amount of gel was higher when the reactions were carried out under acidic conditions. Therefore, the fact that the measured gel content was a physical gel rather than a crosslinking seems to be plausible. Figure 3.6 presents the schematic representation of the possible intermolecular hydrogen-bonding between phosphate groups which would make the polymer insoluble in THF.

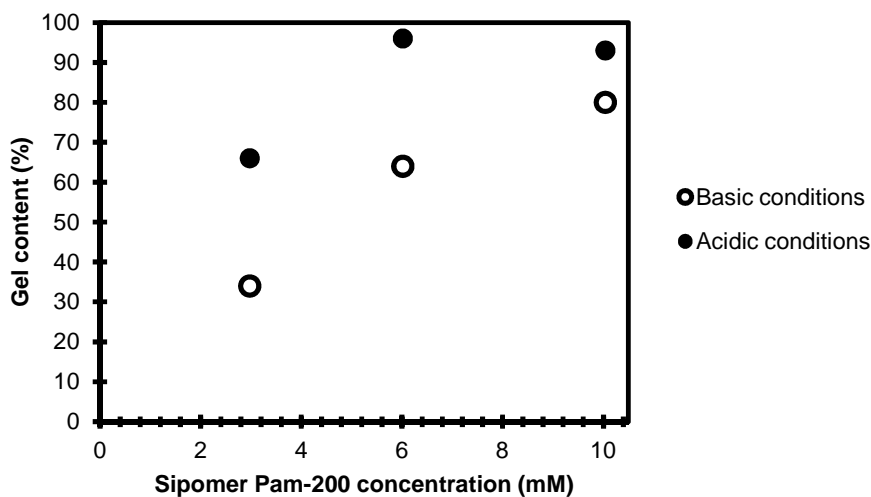


Figure 3.5. Measured gel content of the latexes containing Sipomer[®]Pam-200 synthesized at different pHs.

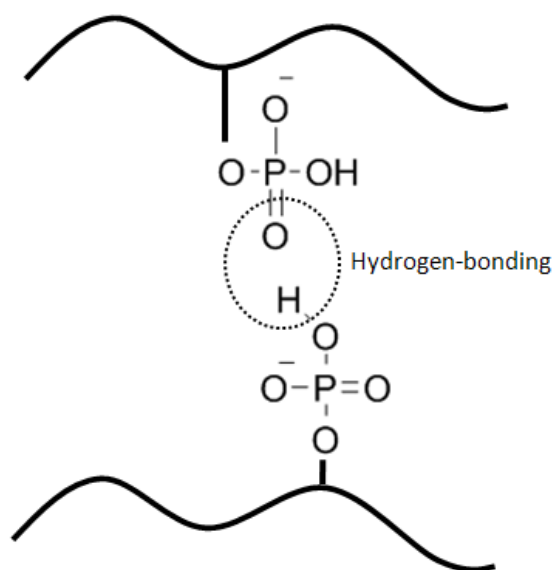


Figure 3.6. Schematic representation of the possible intermolecular hydrogen-bonding between phosphate head groups.

It is worth to point out that Gonzalez et al.³⁹ observed a similar trend when the phosphated monomer Sipomer[®]Pam-100 was used as functional monomer in the seeded semi-batch emulsion polymerization of MMA/BA/MAA/AAEME (methyl methacrylate/butyl acrylate/methacrylic acid/acetoacetoxy ethyl methacrylate) using Abex[®]2005 as surfactant. They observed that increasing the concentration of Sipomer[®]Pam-100 from 0 to 5 wt% the gel also increased from 20 to 50%. However, they reported that the increase in the gel content was

most likely due to the presence of impurities (divinyl ester phosphates) produced during the synthesis of Sipomer[®]Pam-100 that acted as cross-linker. Taking this hypothesis into consideration and knowing that the gel produced using Sipomer[®]Pam-200 was pH dependent (Figure 3.5), it could be expected that the gel produced in batch polymerization using Sipomer[®]Pam-200 as surfactant was due to two interacting effects: presence of impurities that could act as cross-linker and hydrogen-bonding which made the polymer insoluble in THF.

Regarding the molecular weight of the latexes synthesized using Sipomer[®]Cops-1, latexes with similar molecular weights were obtained and substantially smaller in comparison to the latexes obtained using conventional and polymerizable surfactants (Figure 3.2). As the number of polymer particles formed in reactions C20-1 –C20-8 were considerably lower, larger particle sizes were obtained using Sipomer[®]Cops-1 and hence, the average radicals per particle should be comparable to that of pseudo-bulk conditions ($\bar{n} \gg 0.5$, Smith-Ewart Case III), leading to lower molecular weights. It is worth to point out that under these conditions the molecular weights are independent of the number of polymer particles.

3.4. Conclusions

In this chapter, an approach to investigate the feasibility of using commercially available anionic polymerizable surfactants and polymerizable stabilizer in the emulsion polymerization of acrylic latexes was presented. As a first attempt 20 wt% solids content polymethyl methacrylate-co-butyl acrylate-co-acrylic acid (MMA/BA/MAA at weight composition of 49.5/49.5/1) latexes were synthesized by batch emulsion polymerization by using Latemul[®]PD-

104, Sipomer[®]Pam-200 and Sipomer[®]Cops-1 as sole stabilizer. The conventional anionic surfactant Dowfax[®]2A1 was used as a reference.

It was found that the polymerizable surfactant Latemul[®]PD-104 behaved as the conventional surfactant Dowfax[®]2A1. For both surfactants, the shape of the log N_p vs. log surfactant concentration curves suggested that the polymer particles were formed by homogeneous nucleation below the CMC and by micellar nucleation above the CMC. Furthermore, the dependence of N_p on surfactant concentration was equal for both surfactants and equal to that predicted by Smith-Ewart theory (Case II). Moreover, for both surfactants, increasing the surfactant concentration in the formulation led to latexes with higher molecular weight due to the generation of higher number of polymer particles during the polymerization.

When the polymerizable surfactant Sipomer[®]Pam-200 was used, although straight lines with a discontinuity were also observed in the log N_p vs. log surfactant concentration plot, the dependence of N_p upon surfactant concentration was lower than that predicted by Smith-Ewart theory. This was likely due to the loss of part of the polymerizable surfactant by fast surfactant burial or by formation of water-soluble oligomers that did not participate in the stabilization of the polymer particles. It was found that the presence of Sipomer[®]Pam-200 in the formulation had an effect on the polymer microstructure, increasing the surfactant concentration higher gel content was obtained leading to latexes with lower sol molecular weight. The fact that only gel was measured in latexes containing Sipomer[®]Pam-200 could be due to two interacting effects. On the one hand the capability of phosphate groups to form hydrogen bonds which make the polymer insoluble in THF (pH dependent) and on the other hand the presence of divinyl ester

phosphate impurities acting as cross-linkers; likely the first mechanism is dominant since decreasing the pH of the reaction led to higher gel contents.

It was demonstrated that the polymerizable stabilizer Sipomer[®]Cops-1 was not able to nucleate. Therefore in the reactions carried out using this polymerizable stabilizer the polymer particles were formed by coagulative nucleation, leading to large particle sizes. Consequently, pseudo bulk kinetics was observed and molecular weights were independent of the number of particles.

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Chapter 4. Synthesis of high solids content latexes using polymerizable surfactants

4.1. Introduction

High solids content latexes (usually referred to latexes made by emulsion polymerization with a total polymer content greater than 60 %) have been of growing interest over the past years since increasing the polymer content of a latex maximizes the reactor production, minimizes transportation, and storage costs, gives more flexibility in product formulation, improves surface coverage when applied and reduces drying time, which can increase the marginal value of the product¹⁻⁷. From the application point of view (film formation and film properties), high solids content latexes with small particle sizes are preferred because they provide skin-free latexes whose particles deformed easier leading to a more homogeneous film⁸⁻¹⁰. However the production of high solids content latexes with small particle size typically requires the use of large quantities of surfactant which is not desired for the final product application. As mentioned in Chapter 1, the presence of free surfactant molecules within the final film has a detrimental effect on the product properties. Therefore, there is an interest to produce high solids content latexes with small particle sizes with the least possible amount of free surfactant.

As reviewed in Chapter 1, during the last years much work has been done with the use of polymerizable surfactants in emulsion polymerization. However from our best knowledge, the open literature dealing with the use of polymerizable surfactants in the synthesis of high solids content latexes (up to 60 wt%) is scarce^{11,12}. Tang et al.¹¹ synthesized 60 wt% solids content latexes using 3-allyloxy-hydroxyl-propane sulfonic salt (AHPS) as a polymerizable stabilizer. Although the obtained latexes presented improved tensile strength and water resistance, in the cases where a reasonable amount of AHPS was used, 1.2 wbm % (weight based on monomer %), large particle size (450-500nm) latexes were obtained and in order to obtain smaller particle sizes (340-380 nm) 3-4 wbm% of AHPS was used. Guo et al.¹² reported the synthesis of 60 wt% solids content core-shell latexes using AHPS as stabilizer. Although latexes with small particle sizes (220-260 nm) were obtained using 1.2 wbm% of AHPS, they did not present any improvement on product properties.

During the past years a large number of works devoted to the development of strategies to produce high solids content latexes using conventional surfactants have been presented. In most of the cases the production of bimodal particle size distribution (PSD) latexes by (mini)emulsion polymerization is considered in order to accomplish the goals of high solids content and low viscosity latexes^{2,3,5,13-19}. However, producing a latex with a target multimodal PSD using polymerizable surfactants is challenging because the control of PSD with these non-conventional surfactants can be delicate complicating the stability of the latex and making difficult to obtain the desired PSD. Therefore, in this work the synthesis of unimodal latexes at the highest solids content is considered because from the practical point of view unimodal latexes are still widely used in the industry due to the facile route of synthesis.

One of the most efficient routes to obtain high solids content latexes with unimodal PSD is to enlarge the particle size during the polymerization process by using different methods such as seeded emulsion polymerization processes or agglomerating technologies⁶. However, agglomerating technologies only become an effective technique to prepare latexes with large particle size and from the application point of view this is not desired.

It is worth to point out that for unimodal PSD latexes the maximum achievable solids content is governed by the particle size. By geometrical considerations for rigid spheres, randomly packed particles with identical size will have a maximum packing fraction (referred to the maximum volume fraction of the polymer in the aqueous phase) of 0.64^{3,4,20,21}, meaning that for unimodal PSD latexes the maximum achievable solids content is 64 wt%. However, the smaller the particle diameter, the lower the solids content that can be reached before the double or adsorption layer of neighboring particles interact leading to an excessive increase on the viscosity of the dispersion and increasing the risk of flocculation and/or coagulation^{22,23}. Figure 4.1 shows the maximum achievable solids content (SC_{max}) as a function of particle diameter considering a thickness of stabilization layer of 3 nm and as it can be observed, for particle sizes above 150-200 nm the achievable solids content is above 55 wt% and further increase in particle size do not allow large increases on solids content²³.

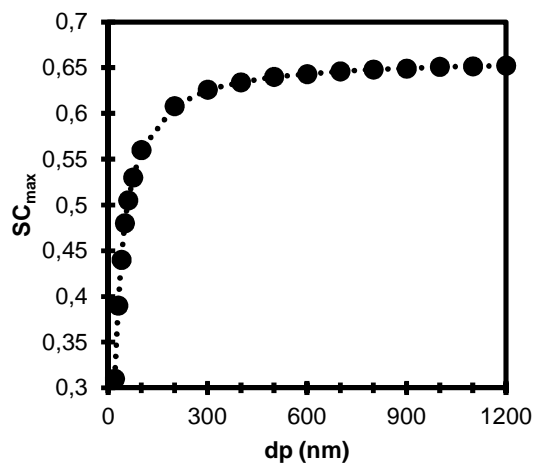


Figure 4.1. Maximum achievable solids content as a function of particle diameter considering a thickness of stabilization of 3 nm²³.

Recently, Mariz et al.²¹ synthesized stable unimodal latexes with 61 wt% of solids content and with particles smaller than 350 nm by seeded semi-batch emulsion polymerization using conventional surfactants. They investigated which were the best conditions, in terms of process variables (such as surfactant amount, functional monomer and pH of the reaction), that allow unimodal stable latexes with solids content in the range of 60-62 wt% with particles smaller than 350 nm, and with the lowest possible surfactant concentration. They found that when functional monomers were added to the formulation and the reactions were carried out under basic pH it was possible to obtain stable unimodal latexes with solids content up to 61 wt% using small amount of conventional surfactant (0.4 wbm%) and with relatively low viscosities (below 500 mPa.s at a shear rate of 100 s⁻¹).

The aim of this work was to extend the approach of Mariz et al.²¹ using polymerizable surfactants instead of conventional ones and reducing, if possible, the concentration of surfactant used during the synthesis. Therefore, in this chapter the feasibility of using the lowest possible amount of polymerizable surfactants to produce stable 60 wt % solids content acrylic latexes with small particle size is studied. To this end, poly(methyl methacrylate-co-butyl acrylate-co-methacrylic acid) model latexes were synthesized by seeded semi-batch emulsion polymerization. Although Mariz et al.²¹ found that in the synthesis of high solids content latexes the amount of surfactant needed could be substantially reduced without jeopardizing the stability of the latexes if functional monomers such as methacrylic acid are used and the polymerization is carried out at basic pH, it is known that under this polymerization conditions water-soluble oligomers are produced²⁴⁻²⁷ having an effect on the polymerization process as well as on the final product properties^{28,29}. Therefore, apart from studying the effect of the surfactant type, the effect that the pH had on the polymerization process was also investigated.

According to Figure 4.1 for narrow unimodal PSD, in order to obtain 60 wt% of solids content the particle size of the latex should be greater than 200 nm. Therefore, in this work a target particle size of around 300 nm was adopted to avoid stability and high viscosity issues. It is worth mentioning, that in order to obtain high solids content latexes with low viscosity a strict control over the PSD is required^{16,20,30}. This means that if in the synthesis of unimodal PSD latexes the evolution of the particle size during the polymerization is not controlled and hence the target particle size is not obtained, the viscosity of the latex would be considerably affected. During this work, it was found challenging the accurate control of the evolution of the particle size during the synthesis of high solids content latexes. This was related to some aspects of

the seed latexes employed rather than to the use of polymerizable surfactants. Therefore, this topic is discussed in detail Appendix III.

4.2. Experimental

4.2.1. Materials

Methyl methacrylate (MMA, Quimidroga) and n-butyl acrylate (BA, Quimidroga) were used as supplied. Methacrylic acid (MAA, Quimidroga) was used as functional monomer. Potassium persulfate (KPS, Fluka) was used as thermal initiator. Polymerizable surfactants Latemul[®]PD-104 (Kao Group) and Sipomer[®]Pam-200 (Solvay) and polymerizable stabilizer Sipomer[®]Cops-1 (Solvay) were used as received. For comparison purposes conventional surfactants Dowfax[®]2A1 (The Dow Chemical Company) and sodium lauryl sulfate (SLS, Aldrich) were used. Deionized water was used in all reactions. To increase the pH of the latexes a 25% solution of ammonia (Fluka) was used.

4.2.2. Emulsion polymerization

High solids content latexes were synthesized by seeded semi-batch emulsion polymerization. Polymerizations were carried out in a 1L jacketed reactor fitted with a reflux condenser, a sampling device, a nitrogen inlet, feeding inlet, a Pt-100 probe and a stainless steel anchor type stirrer. Reaction temperature and inlet flow rate of the feed were controlled by an automatic control system, Camile TG (CRW Automation Solutions).

15 wt% solids content polymethyl methacrylate-co-butyl acrylate-co-methacrylic acid (MMA/BA/MAA at weight composition of 49.5/49.5/1) seed latex was synthesized by semi-batch emulsion copolymerization at 75°C and 220 rpm. The formulation used to prepare the seed latex is given in Table 4.1.

Table 4.1. Formulation used to synthesize the seed latex.

Compound	Initial Charge (g)	Stream (g)
MMA	---	44.55
BA	---	44.55
MAA	---	0.9
Water ^{a)}	507.61	---
KPS	0.45	---
NaHCO ₃	0.14	---
Ammonia ^{b)}	0.9	---
Dowfax [®] 2A1 ^{c)}	0.9	---

^{a)} Added water + water coming from surfactant solution.

^{b)} 25 % aqueous solution.

^{c)} Active matter.

An initial charge of water, surfactant, buffer (NaHCO₃) and ammonia were added to the reactor. The initial charge was purged with nitrogen during 30 minutes. After reaching the desired temperature (75°C) a shot of thermal initiator (KPS) was added and then, the monomers were fed during 3 hours. After that, the latex was let to react batchwise during 1

hour. A seed latex with 14.8 wt% of solids content and 75 nm of particle diameter (measured by Dynamic Light Scattering) was obtained.

Several polymethyl methacrylate-co-butyl acrylate-co-methacrylic acid (MMA/BA/MAA at weight composition of 49.5/49.5/1) latexes were synthesized with a target solids content of 60 wt% and target particle size of 320 nm by seeded semi-batch emulsion polymerization. This polymerization technique was chosen because it allows good control of the reaction temperature, particle nucleation, final particle size, and particle size distribution.

The amount of seed required in the polymerizations to produce a latex with a certain solids content and with a certain average particle size can be estimated provided that the number of polymer particles remains constant during the polymerization by means of the following equation²³

$$m_{seed} = \frac{m_{latex} SC_{target} \bar{d}_{p,seed}^3}{SC_{seed} \bar{d}_{p,target}^3} \quad (4.1)$$

where m_{seed} (g) is the amount of the seed latex, SC_{seed} (wt%) is the polymer content of the seed, m_{latex} (g) is the amount of the latex desired at the end of the polymerization process, SC_{target} (wt%) is the target polymer content, $\bar{d}_{p,seed}$ (nm) is the diameter of the seed particles and $\bar{d}_{p,target}$ (nm) is the target particle diameter.

As it is discussed in Appendix III, the particle size of the seed latex is a key factor to control the evolution of the particle size and hence to obtain a target particle size during the polymerization of high solids content latexes. It was observed that when the shot of KPS was

added to the initial charge the particle size of the seed latexes changed due to the increase of the ionic strength of the medium. As the real particle size of the seed latex at the beginning of the reaction differed from that used to make the calculations, the target particle size was not obtained. Therefore, in the following set of reactions in order to estimate the amount of the seed required to achieve latexes with 60 wt% solids content and target particle size of around 320 nm the particle size of the seed latex (D15 seed latex) measured at the beginning of the reaction was considered (see Appendix III for further details and explanations).

In this work several reactions were carried out in order to study the effect of the surfactant type as well as the effect of the pH during the synthesis of 60 wt% solids content MMA/BA/MAA (at weight composition of 49.5/49.5/1) latexes.

On the one hand, as it was previously mentioned, in order to extend the work done by Mariz et al.²¹ five latexes were synthesized under basic pH using different surfactants. Table 4.2 presents the general formulation used to synthesize those latexes. Note that in all polymerizations the amount of surfactant used was equivalent in moles and that the amount of water used was slightly varied in order to adjust the solids content because the amount of surfactant was considered as a solid.

On the other hand, several reactions were carried out under acidic conditions in order to avoid the formation of water-soluble oligomers during the polymerization. In this set of reactions the effect of the surfactant type and amount on the synthesis of high solids content latexes was studied. Table 4.3 presents the general formulation used to synthesize high solids content latexes under acidic conditions. In these reactions the amount of water used was also

slightly varied in order to adjust the solids content because the amount of surfactant was considered as a solid.

All the polymerizations were carried out at 75°C and 220rpm in the setup described above. An initial charge containing the seed latex, water and a small amount of monomers were added to the reactor. The initial charge was purged with nitrogen during 30 minutes. After reaching 75°C a shot of thermal initiator (KPS) was added. Then, the preemulsion was fed during 4 hours and after that, the latex was let to react batchwise during 1 hour.

Throughout this work, latexes made with conventional surfactants Dowfax[®]2A1 and SLS were designated as D60 and SLS60, respectively. Those made with polymerizable surfactants Latemul[®]PD-104 and Sipomer[®]Pam-200, L60 and S60, respectively, and latexes synthesized using the polymerizable stabilizer Sipomer[®]Cops-1 as C60. Latexes synthesized under basic conditions were designated with the letter B and those synthesized under acidic conditions with the letter A. For each surfactant type different reactions were carried out varying the surfactant amount, which were designated with a different number (1-7). Reactions with the same number were synthesized using the same number of moles of surfactant (Table 4.4). It is worth to mention that in the polymerizations carried out under acidic conditions the conventional surfactant SLS was not used.

Table 4.2. Formulation used to synthesize high solids content latexes under basic pH.

Compound	Initial Charge (g)	Stream (g)
D15 seed	19.83	---
MMA	1	175.74
BA	1	175.74
MAA	---	3.57
Ammonia ^{a)}	---	3.57
Water	210.61-217.51	---
KPS	1.79	---
Surfactant ^{b)}	---	0.85 mmol

^{a)} 25 % aqueous solution.

^{b)} Active matter.

Table 4.3. Formulation used to synthesize high solids content latexes under acidic pH.

Compound	Initial Charge (g)	Stream (g)
D15 seed	19.83	---
MMA	1	175.74
BA	1	175.74
MAA	---	3.57
Water	135.504	78.68-85.64 ^{a)}
KPS	1.79	---
Surfactant ^{b)}	---	0.85-12.39 mmol

^{a)} Added water+water coming from surfactant solutions.

^{b)} Active matter.

Table 4.4. Amount of surfactant used during the synthesis of high solids content latexes.

Run	Surfactant amount (mmol)
1	0.85
2	1.27
3	2.13
4	4.95
5	6.2
6	9.3
7	12.39

4.2.3. Characterization

Monomer conversion and solids content were gravimetrically determined and the coagulum amount was obtained by filtering the latex through a 85 μm nylon mesh. The average particle size was measured by Dynamic Light Scattering (DLS) and the particle size distribution (PSD) of the latexes was analyzed by Capillary Hydrodynamic Fractionation chromatography (CHDF). The microstructure of the final latexes was determined by measuring the gel fraction in tetrahydrofuran (THF) by Soxhlet extraction and molecular weight of the soluble part was analyzed by Gel Permeation chromatography (GPC). The details of the characterization procedures and methods are given in Appendix I.

4.3. Results and discussion

4.3.1. Synthesis of high solids content latexes using polymerizable surfactants

4.3.1.1. Latexes synthesized under basic conditions

Polymethyl methacrylate-co-butyl acrylate-co-methacrylic acid (MMA/BA/MAA at weight composition of 49.5/49.5/1) latexes with 60 wt% of solids content (SC) and target particle size of 320 nm were synthesized by seeded semi-batch emulsion polymerization under basic conditions using conventional and polymerizable surfactants/stabilizer. The final characteristics of these latexes are presented in Table 4.5.

Table 4.5. Main characteristics of high solids content latexes synthesized by seeded semi-batch emulsion polymerization under basic conditions.

Latex	Surfactant	Surfactant amount		SC (wt%)	dp (nm)
		(mmol)	(wbm%)		
D60-1B	Dowfax [®] 2A1	0.85	0.14	60.95	323
SLS60-1B	Sodium Lauryl Sulfate	0.85	0.07	60.94	328
L60-1B	Latemul [®] PD-104	0.85	0.4	61.11	324
S60-1B	Sipomer [®] Pam-200	0.85	0.12	61.06	318
C60-1B	Sipomer [®] Cops-1	0.85	0.05	60.88	319

In all polymerizations stable latexes without coagulum were obtained using relatively low surfactant concentrations. As ammonia was added to the preemulsion, during the

polymerization process the pH was almost maintained constant (Figure 4.2) and the final pH of all the latexes was between 7.0 and 7.5.

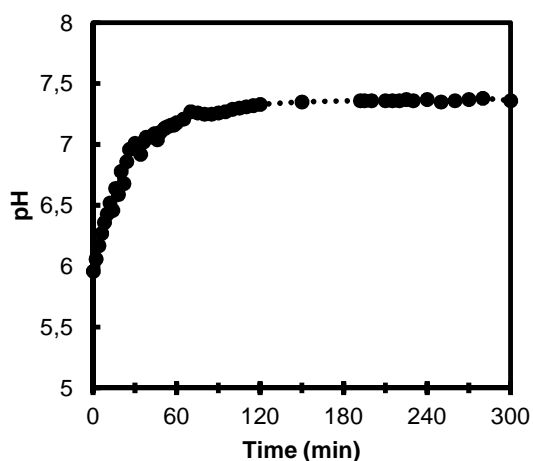


Figure 4.2. Evolution of the pH during the synthesis of D60-1B latex.

Due to starved monomer feeding conditions employed during the polymerization, in all reactions high instantaneous conversion was achieved during the polymerization time and after a batch period of 60 minutes full conversion was achieved in all cases. For the sake of clarity, Figure 4.3 only shows the evolution of the instantaneous conversion during the synthesis of D60-1B latex. Similar trends were observed for the rest of experiments.

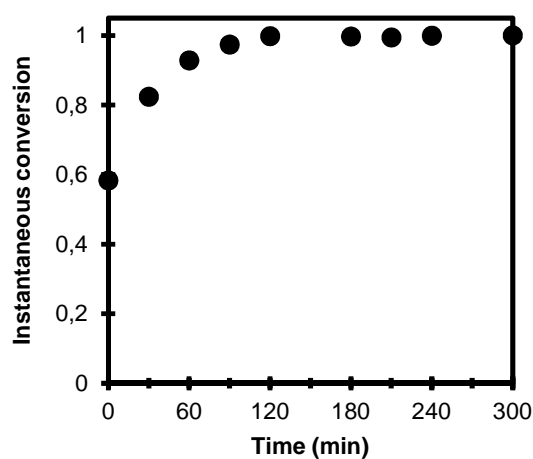


Figure 4.3. Instantaneous conversion during the polymerization time in experiment D60-1B.

Regarding the final particle size of the latexes in all cases almost the target particle size (320 nm) was obtained, which is an indirect proof that the number of polymer particles remained constant during the polymerization time; namely that secondary nucleation or coagulation did not occur during the process. Figure 4.4 shows the predicted (assuming that the number of polymer particles of the seed latex remains constant and that instantaneous conversion was 1) and experimental particle size evolution (measured by DLS) during the polymerization time for the experiments carried out using different surfactants. In all cases the experimental particle size evolution was very close to the predicted one. Furthermore, as it can be observed in Figure 4.5, in all polymerizations latexes with unimodal PSDs were obtained.

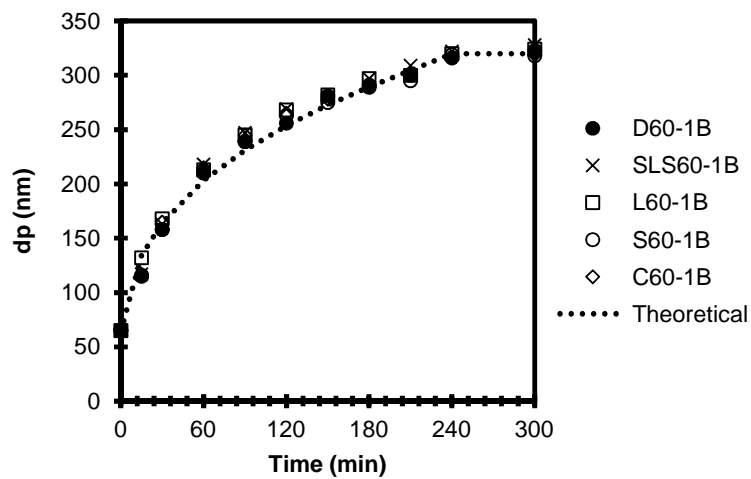


Figure 4.4. Evolution of the experimental (symbols) and predicted (dashed line) particle diameter during the polymerization process.

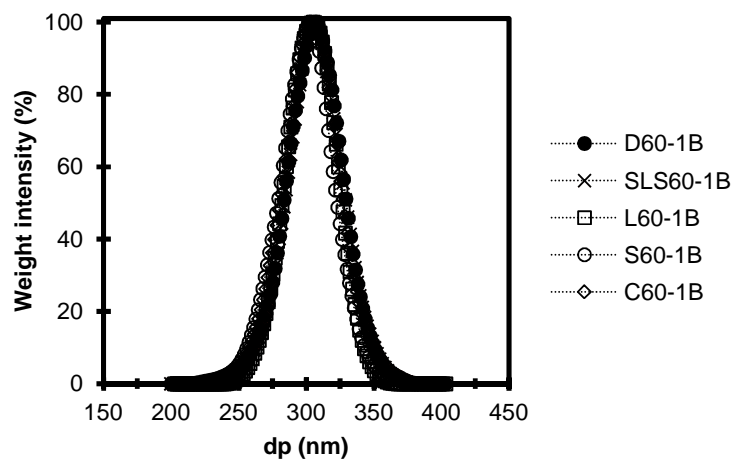


Figure 4.5. Particle size distribution of the final latexes measured by CHDF.

From the results presented above, it can be concluded that when the polymerizations were carried out under basic conditions the surfactant type used during the polymerization process did not have any noticeable effect because in all cases stable latexes without coagulum and with the target particle size were obtained. Therefore, it could be said that polymerizable surfactants/stabilizer employed in this work were as efficient as the conventional surfactants to stabilize the growing polymer particles during the synthesis of high solids content latexes or that the acidic monomer has a strong effect on the stability and hence hinders the difference between conventional and polymerizable surfactants.

At this point, it is worth to point out that in this work the surfactant amount used was considerably reduced in comparison to the work carried out by Mariz et al.²¹. Whereas Mariz et al.²¹ synthesized 60 wt% solids content latexes using 0.4 wbm% of Dowfax[®]2A1 (3.99 mmol), in this work 0.14 wbm% of Dowfax[®]2A1 (0.85 mmol) was used. This reduction in surfactant amount would be beneficial from the application point of view because less surfactant would be present in the final film.

4.3.1.2. Latexes synthesized under acidic conditions

Several polymethyl methacrylate-co-butyl acrylate-co-methacrylic acid (MMA/BA/MAA at weight composition of 49.5/49.5/1) latexes with 60 wt% of solids content and target particle size of 320 nm were synthesized by seeded semi-batch emulsion polymerization under acidic conditions (ammonia was not added to the preemulsion, see Table 4.3). The process variables studied were the surfactant type and surfactant amount. For each surfactant type 7 reactions were carried out varying the surfactant amount from 0.85 mmol to 12.39 mmol (Table 4.4).

Table 4.6 presents the final characteristics of the latexes synthesized under acidic conditions. Note that although 7 reactions were carried out per each surfactant type varying the surfactant amount, in Table 4.6 only the results corresponding to successful reactions (coagulum free) are presented.

Table 4.6. Main characteristics of high solids content latexes synthesized by seeded semi-batch emulsion polymerization under acidic conditions.

Latex	Surfactant	Surfactant amount		SC (wt%)	dp (nm)	Comments
		(mmol)	(wbm%)			
D60-5A		6.2	1.00	60.87	317	---
D60-6A	Dowfax [®] 2A1	9.3	1.50	61.19	318	---
D60-7A		12.39	2.00	61.46	317	---
L60-4A		4.95	2.32	61.37	322	---
L60-5A		6.2	2.91	61.98	320	---
L60-6A	Latemul [®] PD-104	9.3	4.36	62.13	324	Surfactant solution fed in a separated stream
C60-7A	Sipomer [®] Cops-1	12.39	0.75	60.32	319	---
C60-5A (IC)		6.2	0.38	59.75	375	All the stabilizer added in the initial charge
C60-6A (IC)	Sipomer [®] Cops-1	9.3	0.57	59.13	397	
C60-7A (IC)		12.39	0.75	58.21	428	

First of all it is noticeable that regardless of the surfactant type used during the polymerization, it was not possible to obtain stable high solids content latexes using 0.85 mmol of surfactant when the reactions were conducted at acidic conditions contrary to what was observed when the reactions were conducted at basic pH. Furthermore, in all cases increasing the surfactant amount 1.5 or 2.5 times (1.27 mmol and 2.13 mmol, respectively) stable latexes were not obtained either. In order to obtain stable high solids content latexes under acidic conditions the surfactant amount had to be increased to 4.95 mmol or 6.2 mmol depending on the surfactant used during the polymerization process. It is also noticeable that it was not possible to obtain stable high solids content latexes under acidic conditions when the polymerizable surfactant Sipomer[®]Pam-200 was used, not even when the surfactant amount was increased to 12.39 mmol.

As in these reactions ammonia was not added to the preemulsion the pH evolved naturally during the reaction. As a representative example Figure 4.6 presents the evolution of the pH during the synthesis of D60-5A latex. As it can be observed, the reaction started at pH=6 and due to the thermal decomposition of KPS the pH decreased reaching values of around 2 at the end of the process³¹. Since the pKa for MAA is 4.86³², it can be assumed that approximately after 50 minutes of reaction (when the pH is lower than the pKa of MAA) the electrosteric stabilization provided by the polymerized MAA units was reduced and hence, higher surfactant amount was needed to obtain stable latexes in comparison to the reactions carried out under basic conditions. The lack of stabilization observed in the reactions carried out using Sipomer[®]Pam-200 could be explained in terms of surfactant burial or formation of oligomers in the aqueous phase^{33,34}. As Sipomer[®]Pam-200 is very reactive with the monomers

employed in this work (see Chapter 2), it can be speculated that it reacts early in the process becoming buried inside the particles during the particle growth stage and hence not contributing to colloidal stabilization. Furthermore, this polymerizable surfactant homopolymerizes easily in the aqueous phase (see Chapter 2 for details) and therefore part of the surfactant can be lost as water-soluble oligomers. Notably, when this polymerizable surfactant was used the instability started around 120 minutes of reaction (approximately at 50 wt% of solids content) when the pH reached the minimum value.

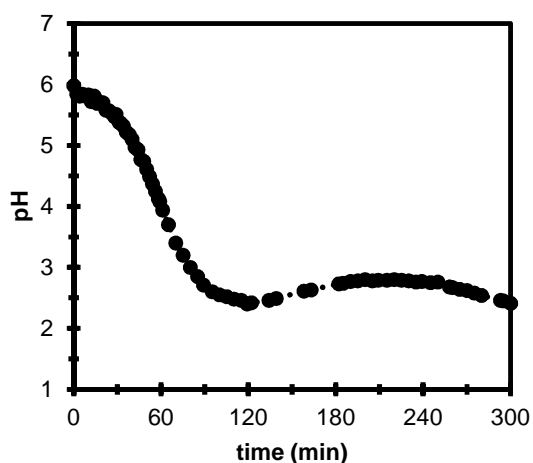


Figure 4.6. Evolution of the pH during the synthesis of D60-5A latex.

Before going into details discussing the results obtained in this work, it should be mentioned that among the surfactants used in this work, the polymerizable surfactant Latemul[®]PD-104 provided the best stabilization in the synthesis of high solids content latexes under acidic conditions. When Latemul[®]PD-104 was used, the minimum amount of surfactant

needed to obtain a stable latex was 4.95 mmol (L60-4A latex), whereas in the other cases was 6.2 mmol (Table 4.6). However, when the amount of Latemul[®]PD-104 was increased to 9.3 mmol, it was not possible to carry out satisfactorily the reaction, due to the high viscosity of the preemulsion (Figure 4.7) and therefore, the polymerization procedure was changed. In L60-6A reaction two separate feeds were used, one containing only the mixture of neat monomers, and the second was an aqueous solution of Latemul[®]PD-104.



Figure 4.7. Small scale preemulsions containing 4.95 and 9.3 mmol of Latemul[®]PD-104.

When Sipomer[®]Cops-1 was used as polymerizable stabilizer a stable latex was only obtained when 12.39 mmol of Sipomer[®]Cops-1 was used (C60-7A latex). However, when the stabilizer was fully added into the initial charge (no stabilizer added to the preemulsion) stable latexes were synthesized using less amount of Sipomer[®]Cops-1, for instance, stable latexes

were obtained using 6.2 and 9.3 mmol (C60-5A (IC) and C60-6A (IC) latexes, respectively). As it was previously mentioned in Chapter 2 and Chapter 3, Sipomer[®]Cops-1 is very hydrophilic so it must react with growing oligoradicals in the aqueous phase in order to produce amphiphilic species that act as surfactant molecules during the polymerization process. Moreover, Sipomer[®]Cops-1 does not copolymerize well with the monomers employed throughout this work (reactivity ratios given by the supplier: $r_{\text{MMA}}=19.62$, $r_{\text{Sipomer}^{\text{®}}\text{Cops-1}}=0.048$; $r_{\text{BA}}=15$, $r_{\text{Sipomer}^{\text{®}}\text{Cops-1}}=0.041$). Therefore, when the stabilizer was fully added to the initial charge it could better copolymerize and hence, the ability to stabilize the growing polymer particles was better obtaining stable latexes using less amount of stabilizer.

From all those observations, the first conclusion could be drawn with respect to the pH used during the polymerization process. In the synthesis of high solids content latexes containing functional monomers such as MAA, when the reactions are carried out under basic conditions the system is mostly stabilized by electrosteric stabilization provided by the functional group, whereas when the reactions are carried out under acidic conditions the system is mostly stabilized by electrostatic stabilization provided by the ionic surfactant. Therefore, contrary to what was observed in the reactions carried out under basic conditions, under acidic conditions the surfactant type used had a strong effect on the synthesis of high solids content latexes.

As in the reactions carried out under basic conditions, in the reactions carried out under acidic conditions full conversion of the monomers was also achieved in all cases except in reactions where the Sipomer[®]Cops-1 was fully added to the initial charge (C60-5A(IC) – C60-

7A(IC)). Therefore, as it can be observed in Table 4.6, C50-5A(IC), C60-6A(IC) and C60-7A(IC) latexes presented lower solids content.

Figure 4.8 presents the evolution of the instantaneous conversion for the reactions carried out using Sipomer[®]Cops-1. As it can be observed, when Sipomer[®]Cops-1 was added to the preemulsion, in C60-7A reaction, full conversion of the monomer was achieved at the end of polymerization due to starved monomer feeding conditions employed. The same behaviour was observed when the polymerizations were carried out using Dowfax[®]2A1 (D60-5A – D60-7A reactions) and Latemul[®]PD-104 (L60-4A – L60-6A reactions). However, in reactions where Sipomer[®]Cops-1 was fully added to the initial charge (C60-5A(IC) – C60-7A(IC) reactions) the instantaneous conversion during the polymerization time was lower. Furthermore, increasing the amount of Sipomer[®]Cops-1 in the initial charge (from 6.2 to 12.39 mmol) the instantaneous conversion decreased which means that the polymerization rate (R_p) decreased. This could be attributed to the differences found between the particle size of the latexes, as explained below.

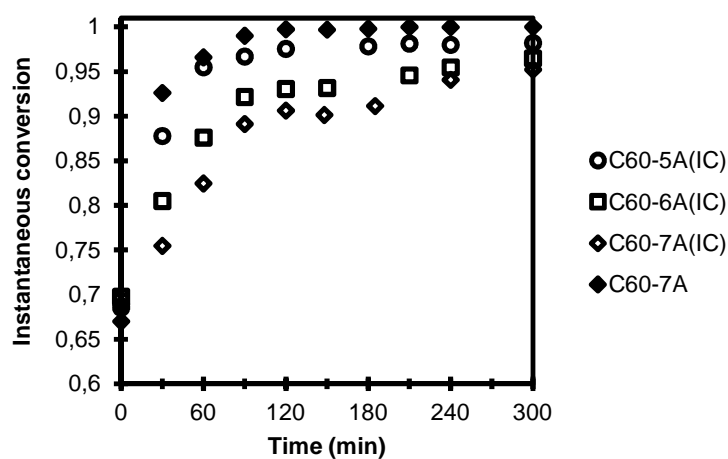


Figure 4.8. Instantaneous conversion during the polymerization time for the experiments carried out using Sipomer®Cops-1.

As it can be observed in Table 4.6, in all cases the target particle size was achieved except in the polymerizations carried out using Sipomer®Cops-1 in the initial charge, in where latexes with larger particle sizes were obtained (C60-5A(IC) – C60-7A(IC) latexes).

Figure 4.9, Figure 4.10 and Figure 4.11 show the predicted and experimental particle size evolution during the polymerization time for the experiments carried out using Dowfax®2A1, Latemul®PD-104 and Sipomer®Cops-1, respectively.

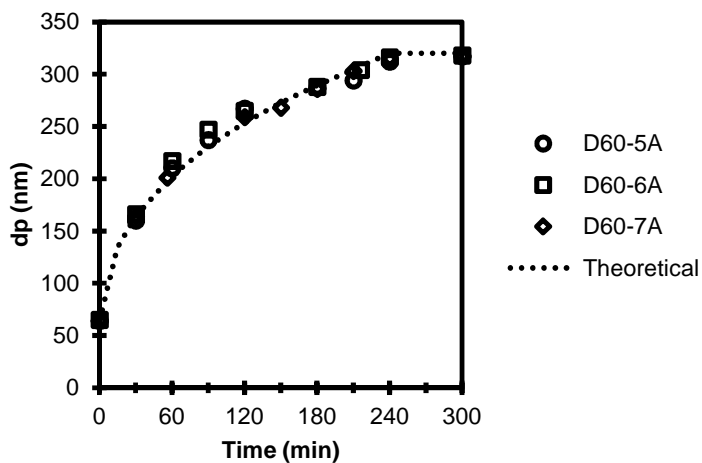


Figure 4.9. Evolution of the experimental (symbols) and predicted (dashed line) particle diameter for reactions carried out using Dowfax[®]2A1.

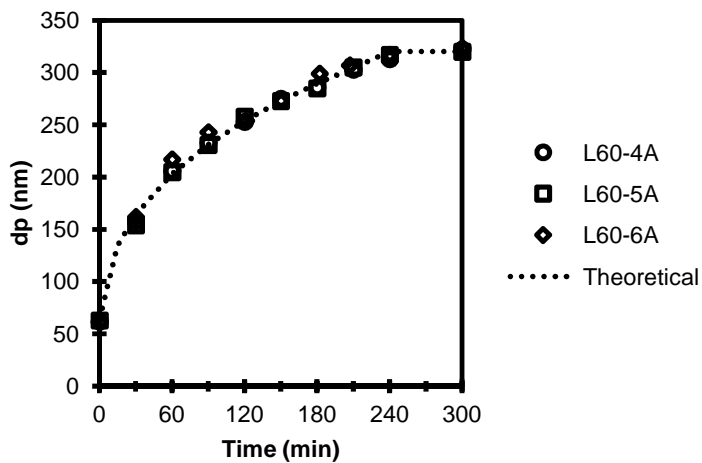


Figure 4.10. Evolution of the experimental (symbols) and predicted (dashed line) particle diameter for reactions carried out using Latemul[®]PD-104.

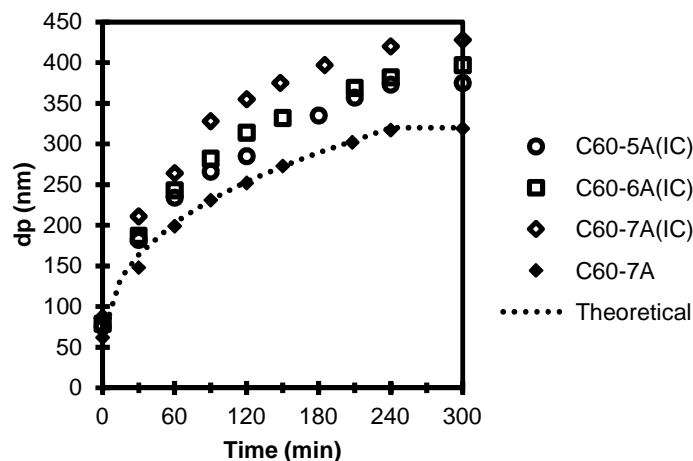


Figure 4.11. Evolution of the experimental (symbols) and predicted (dashed line) particle diameter for reactions carried out using Sipomer[®]Cops-1.

In reactions where Dowfax[®]2A1 (Figure 4.9) and Latemul[®]PD-104 (Figure 4.10) were used the evolution of the particle size was almost the same as the predicted one independently of the surfactant amount used in the polymerization process. However, when Sipomer[®]Cops-1 was used (Figure 4.11) only in the reaction where the stabilizer was added in the preemulsion (C60-7A reaction) the experimental particle size evolution was the same as the predicted one. When this polymerizable stabilizer was fully added to the initial charge (C60-5A(IC), C60-6A(IC) and C60-7A(IC) reactions), the experimental particle sizes were above the predicted one. It is worth to mention that increasing the amount of Sipomer[®]Cops-1 in the initial charge (C60-7A(IC) > C60-6A(IC) < C60-5A(IC)), the experimental particle size was farther from the predicted one, which is the opposite behavior that one could expect. Therefore, it seems that the fact that the target particle size was not achieved was related with the addition of

Sipomer[®]Cops-1 into the initial charge rather than to the ability of Sipomer[®]Cops-1 to stabilize the growing polymer particles.

At this point it is worth to remind that Sipomer[®]Cops-1 is a sodium salt (see Chapter 2). Therefore, when this stabilizer was added to the initial charge the ionic strength of the medium increased. As it has been explained in Appendix III, when the ionic strength of the medium is increased, the electrical double layer thickness around the seed polymer particles is decreased. If the seed latex is not very stable, this situation could lead to coagulation or coalescence of seed polymer particles at the beginning of the reaction.

Table 4.7 presents the measured particle size at the beginning of the reaction ($d_{p,t=0 \text{ min}}$) for the polymerizations carried out using Sipomer[®]Cops-1. As it can be observed, the measured $d_{p,t=0 \text{ min}}$ was higher in reactions where Sipomer[®]Cops-1 was added in the initial charge. Moreover, the higher was the amount of Sipomer[®]Cops-1 in the initial charge, the larger was the measured $d_{p,t=0 \text{ min}}$, suggesting that less number of polymer particles were in the initial stage of the reaction and hence, latexes with larger particle sizes were obtained. As it is discussed in Appendix III, if the particle size of the seed latex measured at the beginning of the reaction differs from that used to make the calculations, the target particle size is not achieved. In this work a seed particle size of 64 nm was considered to make the calculations (see Appendix III for explanations).

Taking into account the particle size measured at the beginning of these reactions the predicted particle size evolution was calculated again, and as it can be observed in Figure 4.12, in all cases the experimental particle size evolution fitted reasonably well with the

predicted particle size evolution; the small differences can be attributed to the lower conversion achieved in these polymerizations (see Figure 4.8).

Table 4.7. Particle size at the beginning of the reaction ($d_{p,t=0 \text{ min}}$) for the polymerizations carried out using Sipomer[®]Cops-1.

Latex	$d_{p,t=0 \text{ min}}$ (nm)
C60-7A	64
C60-5A(IC)	76
C60-6A(IC)	79
C60-7A(IC)	86

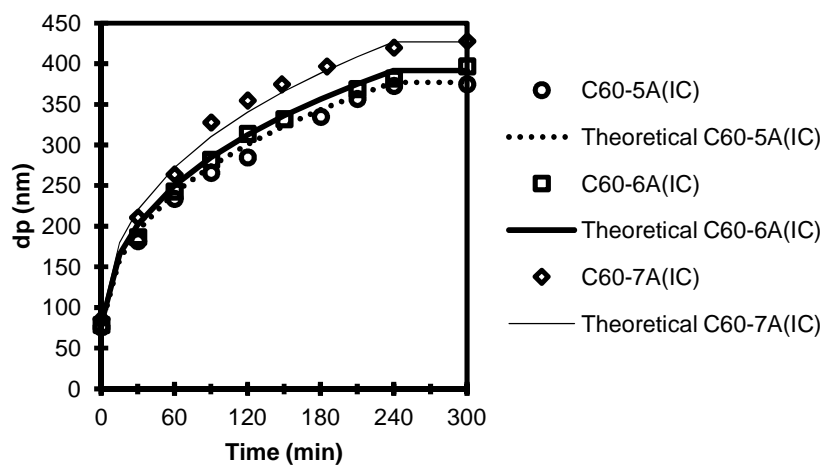


Figure 4.12. Evolution of the experimental (symbols) and predicted (dashed line) particle diameter (calculated using $d_{p,t=0 \text{ min}}$) for reactions carried out using Sipomer[®]Cops-1 in the initial charge.

As mentioned before, increasing the amount of Sipomer[®]Cops-1 in the initial charge (C60-7A(IC) > C60-6A(IC) < C60-5A(IC)), the particle size of the seed latex increased leading to a lower number of particles in the initial stage of the reaction. As the rate of polymerization (R_p) is proportional to the number of polymer particles (assuming Smith-Ewart case II or case III if termination in the aqueous phase is not negligible), increasing the amount of Sipomer[®]Cops-1 in the initial charge the polymerization rate decreased lowering the instantaneous conversion and hence, lower monomer conversion was achieved at the end of the process (Figure 4.8).

4.3.2. Polymer microstructure: gel content

Polymer microstructure of the final latexes was analyzed in terms of gel content (or THF insoluble part) and molecular weight of the sol part. Table 4.8 shows the gel content and the sol molecular weight of the latexes synthesized throughout this work and as it can be observed, in all cases gel was formed. Furthermore, the sol molecular weight decreased as the gel content increased.

Table 4.8. Gel content and sol molecular weight of the final latexes.

Latex	Surfactant	Surfactant (mmol)	Gel (%)	Mw.10 ⁵ (g/mol)	Đ
D60-1B	Dowfax [®] 2A1	0.85	22±1	3.698	3.35
D60-5A		6.2	24±1	3.694	3.77
D60-6A		9.3	23±5	3.452	3.89
D60-7A		12.39	24±1	3.374	3.67
SLS60-1B	SLS	0.85	26±2	3.693	3.20
L60-1B	Latemul [®] PD-104	0.85	24±2	3.628	3.21
L60-4A		4.95	61±5	2.991	3.63
L60-5A		6.2	62±1	2.660	3.35
L60-6A		9.3	64±2	2.835	3.44
S60-1B	Sipomer [®] Pam-200	0.85	20±1	3.866	3.25
C60-1B	Sipomer [®] Cops-1	0.85	24±1	3.605	3.53
C60-7A		12.39	45±3	2.868	3.95
C60-5A (IC)	Sipomer [®] Cops-1	6.2	53±1	2.836	3.91
C60-6A (IC)		9.3	54±2	2.915	4.05
C60-7A (IC)		12.39	55±1	2.995	3.95

These results are in conflict with plenty of work done in our research group, because as mentioned in Chapter 2, in the seeded semi-batch emulsion copolymerization of MMA/BA at 50/50 wt% negligible or little gel was obtained³⁵⁻³⁷. For example, Gonzalez et al.^{36,37} studied

the effect of MMA composition on the gel polymer produced in the seeded semi-batch emulsion copolymerization of MMA/BA/MAA. Figure 4.12 presents the final gel content of MMA/BA copolymer latexes produced with different MMA/BA ratios and 1wt% of MAA³⁷. They observed that as the amount of MMA increased the gel content decreased. When they polymerized MMA/BA at 50/50 wt% the amount of gel content was negligible. This was attributed to the higher stability of the MMA radical (tertiary) compared to that of the BA (secondary) that decreases the probability of having intermolecular chain transfer to polymer and hence, formation of gel polymer, and because the MMA units bound in the polymer chain do not suffer chain transfer to polymer. The results were further supported by a mathematical model that predicted reasonable well these observations³⁵.

However, we found that polymerizing MMA/BA/MAA at weight composition of 49.5/49.5/1 wt% gel was formed. Furthermore, when the reactions were carried out under acidic conditions using Latemul[®]PD-104 (L60-4A – L60-6A) and Sipomer[®]Cops-1 (C60-7A and C60-5A(IC) – C60-7A(IC)) the measured gel content was much higher.

The fact that in this study gel was formed could be due to the differences found in the seeded semi-batch polymerization process conditions between Gonzalez et al.'s^{36,37} work and the present work (Table 4.9). As it can be seen in Table 4.9, in our study higher initiator concentration was used, longer feeding times were employed and latexes with larger particle sizes were obtained.

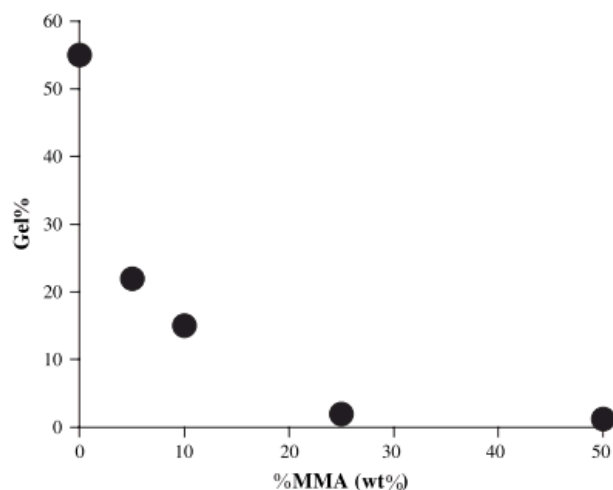


Figure 4.12. Final gel content of MMA/BA/MAA copolymer latexes produced with different MMA/BA ratios and 1 wt% of MAA at 80°C and [KPS]=0.155 wbm%^{36,37}.

Table 4.9. Main differences found in the seeded semi-batch emulsion copolymerization process conditions between Gonzalez et al. 's work and the present work.

Polymerization process conditions	Gonzalez et al. ^{36,37}	Present work
Initiator (wbm%)	0.155	0.5
Feeding time (h)	3	4
dp _{latex} (nm)	< 200	320-430

It is worth to recall that in the emulsion polymerization of acrylates the gel is formed by intermolecular chain transfer to polymer followed by termination by combination³⁸⁻⁴¹. Therefore, it could be expected that in the present system gel was formed due to the higher probability of

having intermolecular chain transfer to polymer and higher rate of bimolecular termination. On the one hand, in the present study the average number of radicals per particle (\bar{n}) could be higher due to the higher amount of initiator used, and also because of the substantially larger particle sizes. The increase in \bar{n} implies higher rate of termination by combination and hence, an increase in the gel content. On the other hand, as in this study longer feeding times were used higher instantaneous conversions were obtained in comparison to the ones observed by Gonzalez et al.^{36,37}. This means that during the polymerization time the concentration of the monomer in the polymer particles was reduced increasing the probability of having intermolecular chain transfer to polymer leading to latexes with higher gel content.

When the latexes were synthesized under acidic conditions using Latemul[®]PD-104 and Sipomer[®]Cops-1, although the polymerization process conditions employed were the same, latexes with even higher gel content were obtained (Table 4.8). Similar results were observed by Suresh and Bartsch⁴² when an anionic polymerizable surfactant, viz., sulfonated 3-pentadecyl phenyl acrylate, was used in the batch emulsion polymerization of styrene. They showed that latexes prepared with 2.31 and 4.52 mol% of polymerizable surfactant (incorporation degree of the surfactant 90% and 80%, respectively) were insoluble in THF due to the association of the polymer chains through sulfonic acid groups. The incorporation of the polymerizable surfactant caused a chain-stiffening effect indicated by an increase of the glass transition temperature and of the elastic modulus. From the results obtained in this study it seems that at least part of Latemul[®]PD-104 and Sipomer[®]Cops-1 were incorporated into the polymer backbone making the polymer insoluble in THF due to ionic association of sulfate/sulfonate head groups of the surfactant/stabilizer.

It is worth mentioning that although C60-7A and C60-7A(IC) latexes were synthesized using the same amount of Sipomer[®]Cops-1, the measured gel content was higher when the stabilizer was added into the initial charge (C60-7A(IC) latex). This could be due to two different reasons. On the one hand, as mentioned before in the synthesis of C60-7A(IC) latex less polymer particles were in the system which could increase the \bar{n} leading to higher gel content. On the other hand, as in the synthesis of C60-7A(IC) latex the Sipomer[®]Cops-1 was fully added to the initial charge, higher incorporation of the stabilizer could be expected and hence, higher ionic association between polymer chains due to higher amount of sulfonate head groups in the polymer backbone that makes the polymer more insoluble in THF.

4.4. Conclusions

In this chapter the feasibility of using polymerizable surfactants/stabilizer to synthesize 60 wt% solids content polymethyl methacrylate-co-butyl acrylate-co-methacrylic acid (MMA/BA/MAA at weight composition of 49.5/49.5/1) latexes was investigated.

It was found that it was possible to obtain stable high solids content latexes using relatively low amount of polymerizable surfactants/stabilizer (0.85 mmol) when the reactions were carried out under basic conditions due to the electrosteric stabilization provided by the methacrylic acid. It was also observed that the surfactant type used did not have any effect during the polymerization process and therefore, latexes with similar characteristics were obtained.

However, when the polymerizations were carried out under acidic conditions, the system was mostly stabilized by electrostatic stabilization provided by the ionic surfactant and hence higher surfactant amount was needed to obtain stable latexes. It was observed that the polymerizable surfactant Latemul[®]PD-104 provided the best stabilization during the synthesis of high solids content latexes under acidic conditions because when Latemul[®]PD-104 was used, the minimum amount of surfactant needed to obtain a stable latex was 4.95 mmol whereas in the other cases was 6.2 mmol. When the polymerizable surfactant Sipomer[®]Pam-200 was used it was not possible to obtain stable latexes probably due to surfactant burial or surfactant lost in the aqueous phase that did not contribute in particle stabilization.

In the polymerizations carried out under acidic conditions, no effect of the surfactant amount in the polymerization process was observed except when the polymerizable stabilizer Sipomer[®]Cops-1 was used. When this stabilizer was used the polymerization strategy was change in order to obtain stable latexes with less stabilizer amount, namely, all the stabilizer was added to the initial charge. However, when this stabilizer was added to the initial charge the target particle size (320 nm) was not obtained and latexes with larger particle sizes were obtained due to the increase of the ionic strength of the medium at the beginning of the reaction which led to coagulation or flocculation of seed latex particles. Increasing the amount of stabilizer in the initial charge the ionic strength also increased and hence larger particle sizes were measured at the beginning of the reaction meaning that less polymer particles were at the beginning of the reaction and hence obtaining larger particle sizes at the end of the reaction.

Unexpectedly and contrary to what was obtained in another works carried out in our research group, gel was formed in the seeded semi-batch emulsion copolymerization of

MMA/BA/MAA (at weight composition of 49.5/49.5/1 wt%). This was attributed to the differences found in the polymerization process conditions (higher initiator concentration, longer feeding times and more likely, due to the fact that latexes with larger particle sizes were targeted) that favored higher average number of radicals per particle and hence the gel formation. Furthermore, it was observed that when the polymerizations were carried out under acidic conditions using Latemul[®]PD-104 and Sipomer[®]Cops-1, the measured gel content was even higher, probably due to the ionic association of sulfate/sulfonate ionic head groups of the surfactant/stabilizer incorporated into the polymer backbone.

4.5. References

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Chapter 5. Water sensitivity and mechanical properties of water-borne coatings produced with polymerizable surfactants

5.1. Introduction

As discussed in Chapter 1, the use of polymerizable surfactants in emulsion polymerization has been considered to be a promising way to reduce the negative effects caused by conventional surfactants. The absence of surfactant desorption or migration imparts substantial benefits to film-forming latexes, such as better colloidal stability under high ionic strength and freezing conditions¹⁻⁶, improved water resistance⁶⁻¹³ and mechanical properties⁸. A possible downside to the use of polymerizable surfactants is that their price is higher than that of conventional ones, due to the more complicated synthesis pathway and lower tonnage. Therefore, the use of polymerizable surfactants instead of conventional ones is only rational if there is an improvement in latex or film properties that justifies their cost. However, in the future, the increased use of polymerizable surfactants may lead to an increase in the production of them reducing the operating costs.

In Chapter 4 it has been shown that the polymerizable surfactants Latemul[®]PD-104 and Sipomer[®]Pam-200 as well as the polymerizable stabilizer Sipomer[®]Cops1 can be used to synthesize 60 wt% solids content acrylic latexes. Therefore, this chapter is focused in comparing the performance of high solids content latexes stabilized by polymerizable surfactants/stabilizer with that of latexes stabilized by conventional surfactants (Dowfax[®]2A1 and SLS).

For this purpose, first of all the latex stability against freeze-thaw cycles is considered. Most commercially available water-borne coating materials need to pass three to five freeze-thaw cycles¹⁴. When a latex is frozen, ice crystals tend to undergo phase separation from the colloidal system; therefore, the concentration of the particles in the fluid phase continuous to increase with the progress of the freezing process. Sooner or later, phase inversion will occur and the probability for the coagulation of polymer particles to take place increases significantly. This is especially true for polymer particles with a glass transition temperature lower than the freezing temperature or with insufficient stabilization by surfactants or by protective colloids¹⁴.

Secondly, the water sensitivity of the films formed from high solids content latexes stabilized either by polymerizable surfactants/stabilizer or by conventional surfactants is discussed. The water sensitivity depends on the distribution of hydrophilic and hydrophobic species in the final film, which in turn is dictated by the mechanism governing film formation¹⁵. The film formation process is divided in four main stages (Figure 5.1): the concentration of the latex, the sintering or deformation of the particles, the coalescence and rupture of interparticle membranes, and the interdiffusion of polymer chains to form a coherent film¹⁵⁻¹⁸. During film formation, surfactants that are physically adsorbed to the polymer particles may either remain

at the particle surface or phase separate from the polymer particle¹⁹. If phase separation occurs, the water flux may carry it to the air-film surface. Alternatively, it may accumulate along the particle-particle boundaries^{18,20} and from there it will migrate to the film-air or film-substrate interface through a long-term exudation process^{9,21–25}. The surfactant may also segregate from the matrix and form aggregates or pockets^{26–28}. In some cases, if the surfactant is similar to the polymer it will dissolve and plasticize the polymer^{29,30}.

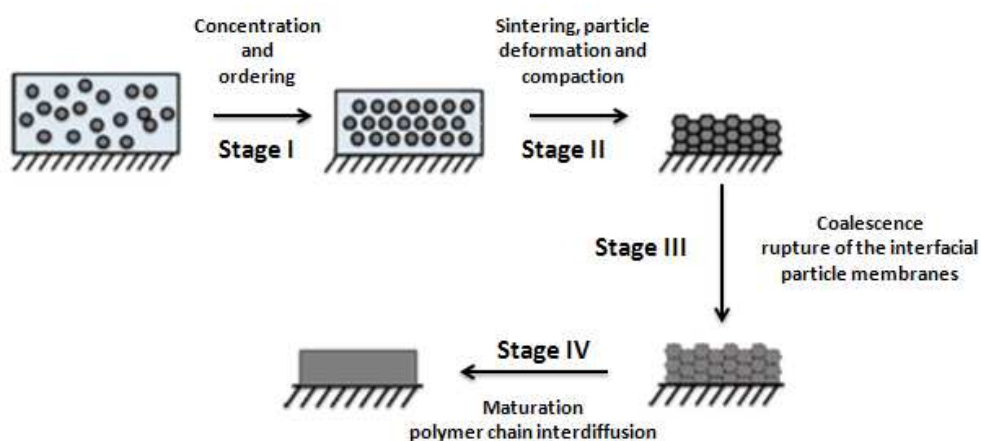


Figure 5.1. Film formation process¹⁵.

If the surfactant (or low molecular weight species such as salts) migrates to the air-film interface, the contact angle value of the film will be reduced as a consequence of the increased hydrophilicity of the film surface. Whereas the contact angle value is only affected by the hydrophilicity of the air-film interface, the water uptake of the films results from the interplay between the existence of hydrophilic pockets or aggregates inside the film, the capacity of those pockets for water absorption and their accessibility¹¹. When the film is in contact with

water, hydrophilic pockets inside the film provide a strong osmotic driving force for the diffusion of water through the film leading to a prolonged water absorption¹⁵.

A possible drawback of using polymerizable surfactants is that they could provide a continuous pathway through the film for water penetration, because there will be entrapped along particle-particle boundaries creating hydrophilic pathways in the film¹⁸. This would depend on the surface density of surfactant chains on the polymer particle surface and whether the density is high enough to form such a pathway.

Another possible disadvantage of using polymerizable surfactants is that the lack of desorption may hinder the particle deformation and interdiffusion¹⁸. As a consequence, the mechanical properties of the films might be affected because a good cohesion of the film is not achieved until the polymers from neighbouring particles have interdiffused across particle-particle boundaries^{31,32}. Therefore, it seems that a sufficient amount of polymerizable surfactant is needed to warrant colloidal stabilization, but not too much to create hydrophilic pathways nor to hinder film formation.

The last part of this chapter is focused on the mechanical properties of the films cast from high solids content latexes stabilized by polymerizable surfactants and conventional ones. It has been reported that the tensile strength of latexes stabilized by conventional surfactants was lower than that of the films containing polymerizable surfactants, because free surfactant within the film led to the weakening of the interaction between molecular chains⁸.

5.2. Experimental

The performance of high solids content acrylic latexes (MMA/BA/MAA at weight composition of 49.5/49.5/1) synthesized with polymerizable surfactants/stabilizer and conventional surfactants was studied. Table 5.1 summarizes the final characteristics of these latexes. Note that latexes made with conventional surfactants Dowfax[®]2A1 and SLS are designated as D60 and SLS60, respectively. Those made with polymerizable surfactants Latemul[®]PD-104 and Sipomer[®]Pam-200, L60 and S60, respectively, and latexes synthesized using the polymerizable stabilizer Sipomer[®]Cops-1 as C60. Latexes synthesized under basic conditions are designated with the letter B and those synthesized under acidic conditions with the letter A. Latexes with the same number were synthesized using the same number of moles of surfactant. For the sake of clarity, films were designated in the same way as the latexes that were coming from.

The final pH of the latexes synthesized under basic conditions (B) was around 7.5 whereas the pH was around 2.5 for the latexes synthesized under acidic conditions (A). Before analyzing the colloidal stability of the latexes and the water resistance and mechanical properties of the films, the pH of the latexes synthesized under acidic conditions was set to 7.5 by adding ammonia in order to increase the electrosteric stabilization provided by the copolymerized MAA units.

The colloidal stability of latexes was assessed by freeze-thaw cycles. Freeze-thaw stability was determined by placing the latex (20 g) in a freezer at -20 °C for 24 hours and leaving at room temperature for another 24 hours. Afterwards the coagulum amount was

measured by filtering the latex through a 85 μm nylon mesh and the particle size was measured by Dynamic Light Scattering (DLS).

Table 5.1. Main characteristics of high solids content latexes synthesized by seeded semi-batch emulsion polymerization under basic (B) and under acidic (A) conditions.

Latex	Surfactant	Surfactant amount		SC (wt%)	dp (nm)	Gel (%)
		(mmol)	(wbm%)			
D60-1B		0.85	0.14	60.95	323	22 \pm 1
D60-5A	Dowfax [®] 2A1	6.2	1.00	61.38	317	24 \pm 1
D60-6A		9.3	1.50	61.14	318	23 \pm 5
D60-7A		12.39	2.00	60.71	317	24 \pm 1
SLS60-1B		SLS	0.85	0.07	60.94	328
L60-1B		0.85	0.4	61.11	324	24 \pm 2
L60-4A	Latemul [®] PD-104	4.95	2.32	62.13	322	61 \pm 5
L60-5A		6.2	2.91	61.98	320	62 \pm 1
L60-6A		9.3	4.36	61.37	324	64 \pm 2
S60-1B		Sipomer [®] Pam-200	0.85	0.12	61.06	318
C60-1B		0.85	0.05	60.88	319	24 \pm 1
C60-5A (IC)	Sipomer [®] Cops-1	6.2	0.38	59.75	375	53 \pm 1
C60-6A (IC)		9.3	0.57	59.13	397	54 \pm 2
C60-7A (IC)		12.39	0.75	58.21	428	55 \pm 1

In order to check the water resistance of the films produced from high solids content latexes, water static contact angle values and water uptake measurements were carried out. Tensile test experiments were also performed. The experimental procedures are explained in Appendix II.

5.3. Results and discussion

5.3.1. Colloidal stability against freeze-thaw cycles

All the latexes synthesized under acidic conditions (A) were able to stand three freeze-thaw cycles without coagulating and without any significant variation in the particle size, independently if they were stabilized by conventional surfactant (Dowfax[®]2A1) or by polymerizable surfactants/stabilizer (Latemul[®]PD-104, Sipomer[®]Pam-200 and Sipomer[®]Cops-1).

However, some differences were observed in the freeze-thaw stability of the latexes synthesized under basic conditions (B) depending on the surfactant type used to stabilize the latex. It is worth to mention that these latexes were synthesized using the lowest surfactant amount, namely, 0.85 mmol. As it can be observed in Table 5.2, latexes synthesized using polymerizable surfactants Latemul[®]PD-104 and Sipomer[®]Pam-200 and polymerizable stabilizer Sipomer[®]Cops-1, exhibited excellent freeze-thaw stability, whereas latexes synthesized using conventional surfactants Dowfax[®]2A1 and SLS coagulated after the first freeze-thaw cycle. The fact that latexes synthesized under acidic conditions using Dowfax[®]2A1 showed excellent stability against freeze-thaw cycles, could be attributed to the higher surfactant amount used in

the polymerizations (see Table 5.1) which may impart higher electrostatic stabilization to the latex.

Table 5.2. Results from latex stability against freeze-thaw cycles for the latexes synthesized under basic conditions.

Latex	Surfactant	Surfactant amount (mmol)	1 st cycle	2 nd cycle	3 rd cycle
D60-1B	Dowfax [®] 2A1	0.85	65 % coagulum	---	---
SLS60-1B	SLS	0.85	100 % coagulum	---	---
L60-1B	Latemul [®] PD-104	0.85	Stable	Stable	Stable
S60-1B	Sipomer [®] Pam-200	0.85	Stable	Stable	Stable
C60-1B	Sipomer [®] Cops-1	0.85	Stable	Stable	Stable

5.3.2. Water sensitivity

5.3.2.1. Films cast from latexes synthesized under basic conditions

Figure 5.2 presents the evolution of water uptake for films obtained from latexes synthesized under basic conditions using 0.85 mmol of surfactant.

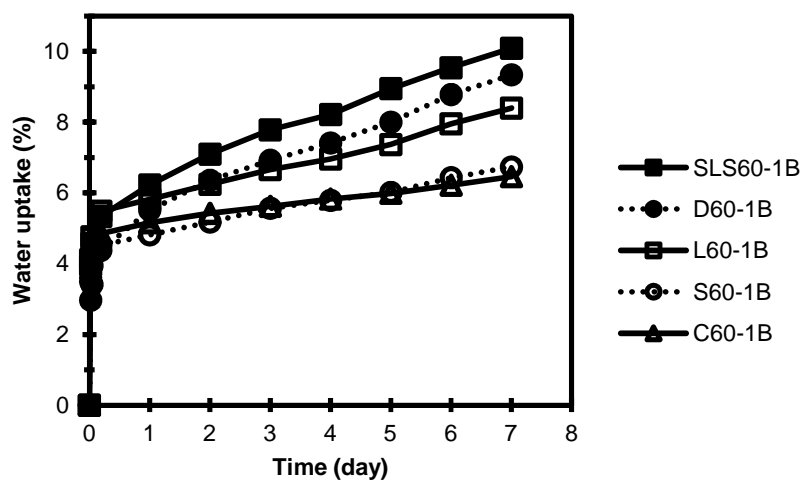


Figure 5.2. Evolution of water uptake for films formed from latexes synthesized under basic conditions.

As it can be observed in Figure 5.2, the behavior of the films was identical, namely, high amount of water was absorbed at the beginning of the experiment and during the rest of the days a moderate increase was observed. This behavior could be attributed to the presence of high amount of water-soluble oligomers within the films. It is known that, during the emulsion polymerization process, the pH affects the distribution of the methacrylic acid groups due to the dissociation of the carboxylic groups above the pK_a ($pK_a, \text{methacrylic acid} = 4.86^{33}$); increasing the pH the methacrylic acid would polymerize preferentially in the aqueous phase producing water-soluble oligomers³⁴⁻³⁷. As these latexes were synthesized under basic pH (at $pH = 7.5$, see Chapter 4 for further details) the formation of water-soluble oligomers during the synthesis was favored. Hence, during the film formation process of the latexes, the water-soluble oligomers may remain trapped within the film. As the water uptake of the films results from the interplay

between the existence of hydrophilic pockets or aggregates inside the film, the capacity of those pockets for water absorption and their accessibility, it may be assumed that at the beginning of the water uptake experiment the osmotic driving force for water absorption was enhanced due to the facile access of water to the hydrophilic pockets and high capacity of the pockets for water absorption. Consequently, very fast water absorption was observed at the beginning of the experiment. However, the capacity of the hydrophilic pockets for water absorption reduced with time because the osmotic driving force for water absorption lowered and hence, after the fast absorption at the beginning of the experiment a moderate absorption was observed during the rest of the experiment.

Although the kinetics of water absorption was similar for all the films, the amount of absorbed water at the end of the experiment varied significantly depending on the surfactant used to synthesize the latex; films containing SLS and Dowfax[®]2A1 (SLS60-1B film and D60-1B film, respectively) were the ones absorbing more water whereas films containing polymerizable surfactants/stabilizer (L60-1B, S60-1B and C60-1B films) absorbed less water during the experiment (Figure 5.2).

In order to shed more light on these results, the weight lost of the films after the water uptake experiment was analyzed. Table 5.3 presents the weight lost of the films at the end of the experiment (drying the films in the oven until a constant weight of the film was obtained). In Table 5.3 the weight percent (wt%) of surfactant in each film has been also included. It is worth to mention that although the amount of surfactant used during the polymerization was equivalent in moles (0.85 mmol), the weight percent (wt%) of surfactant in the films was not the

same because the molecular weight of the surfactants differs from one to another (see Chapter 2).

Table 5.3. Results of the experimental weight lost of the films after water uptake experiment.

Film	Surfactant in the film (wt %)	Lost weight (wt %)
D60-1B	0.14	1.407 ± 0.091
SLS60-1B	0.07	1.335 ± 0.005
L60-1B	0.4	1.612 ± 0.022
S60-1B	0.12	1.717 ± 0.046
C60-1B	0.05	1.866 ± 0.016

After water uptake experiments all the films lost weight. The fact that the films lost weight in water implies that water-soluble species (oligomers, salts and surfactant) diffused to the water phase during the water uptake experiment. In all cases the weight lost was much higher than the amount of surfactant in the films, meaning that water-soluble oligomers produced during the synthesis (due to the high pH) diffused from the film to the water. Unfortunately, the amount of water-soluble oligomers lost was only measured at the end of the water uptake experiment and it is not possible to know when they were desorbed from the film. Likely, the water-soluble oligomers were trapped within the film, but it cannot discard that a fraction was also on the surface of the films. In principle, the hydrophilic material present at the air-film interface would not play any negative role in water absorption because they would be quickly solubilised when the film is immersed in water.

A support for the mentioned hypothesis is provided by water static contact angle measurements as well as by AFM topography images of the surface of the films (air-film interface). In order to mimic what happened at the beginning of the water uptake experiment, contact angle values were measured before and after rinsing the films with water and AFM topography images were taken before and after rinsing the films with water.

Figure 5.3 presents the contact angle values of the initial and rinsed films. As it can be observed no differences were observed in the contact angle values of the different films before rinsing them with water, meaning that the initial hydrophilicity of the surface was similar in all the cases. After rinsing them with water, in all cases higher contact angle values were obtained indicating that at least some hydrophilic material was removed from the surface of the films and hence they become more hydrophobic. The contact angle values of the rinsed films containing different surfactants were almost the same (around 69-70°C). Therefore, these results confirm that at least some water-soluble oligomers were present at the air-film interface and that these water-soluble oligomers were easily removed from the film probably not contributing in the water absorption of the films.

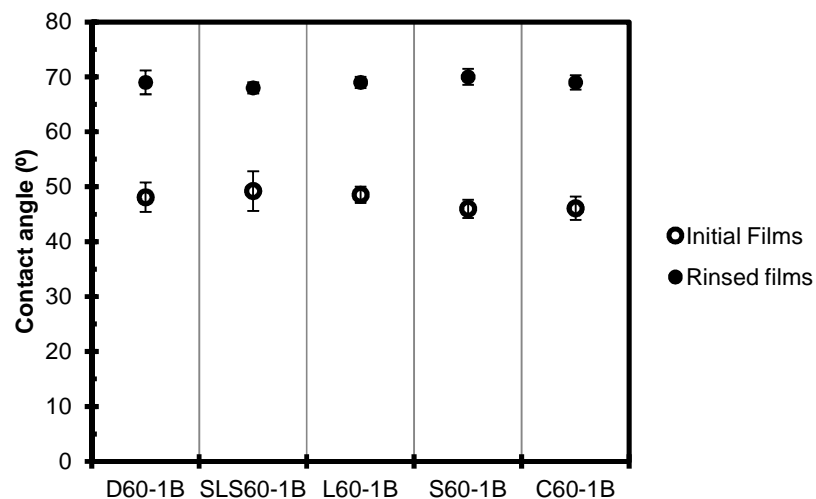


Figure 5.3. Water static contact angles of the films obtained from high solids content latexes synthesized under basic conditions using different surfactants.

As a representative example Figure 5.4 shows the AFM height images of the air-film interface of SLS60-1B and C60-1B films, which were the films showing the highest and the lowest water absorption, respectively. It could be clearly observed that in the initial films (Figure 5.4 top side) the contour of the particles could not be observed likely because water-soluble oligomers were obscuring the individual particle identities. However, after rinsing the films with water (Figure 5.4 bottom side) the morphology of the films changed, and particles can be clearly distinguished due to the elimination of water-soluble species from the air-film interface.

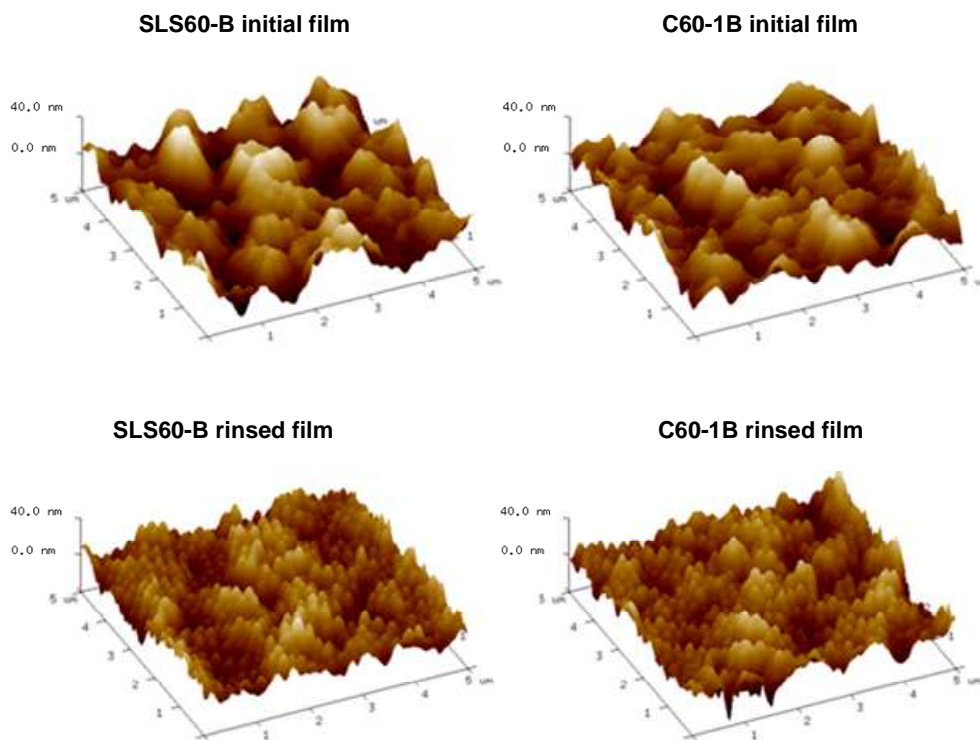


Figure 5.4. AFM height images of the air-film surface of SLS60-1B and C60-1B films before (top) and after rinsing with water (bottom).

Given that all the latexes were synthesized using the same amount of MAA and same pH, it could be expected that in all reactions roughly the same amount of water-soluble oligomers were formed, and therefore, during the water uptake experiment all the films should have lost the same weight. However, as it can be observed in Table 5.3 depending on the surfactant used the weight lost of the films after the water uptake experiment was different. Unexpectedly, the films containing polymerizable surfactants/stabilizer (L60-1B, S60-1B and

C60-1B films) were the ones losing more weight which in turn were the ones absorbing less water at the end of the experiment. As it can be observed in Figure 5.5, almost a linear correlation was obtained between the water uptake at the end of the experiment (7 days) and the lost weight of the films. In principle, this observation seems to be reasonable because when the film loses weight the hydrophobicity of the bulk material increases, decreasing the amount of absorbed water. However, it is not straightforward to know why the films containing polymerizable surfactants/stabilizer lost higher amount of hydrophilic species. Admitting that is speculative, a possible explanation could be that the water-soluble oligomers produced during the synthesis were different depending on the surfactant type used. When polymerizable surfactants or stabilizer were used, there is a possibility of having incorporated surfactant units in the water-soluble oligomers and hence, the weight lost during water-uptake experiment was higher.

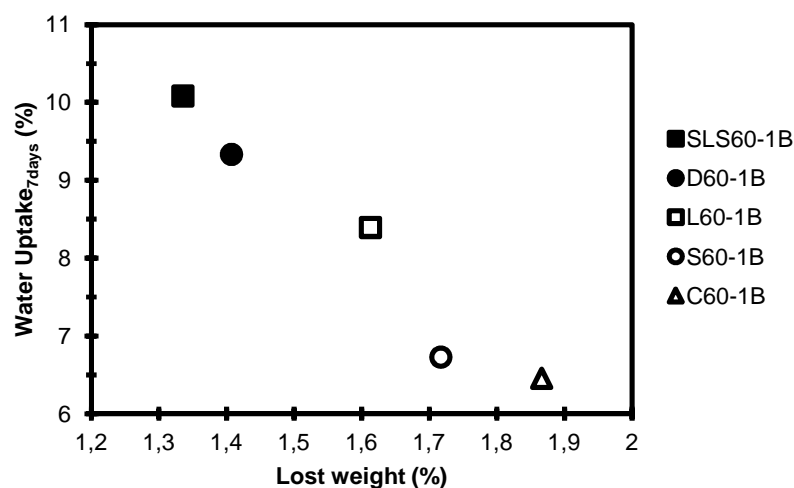
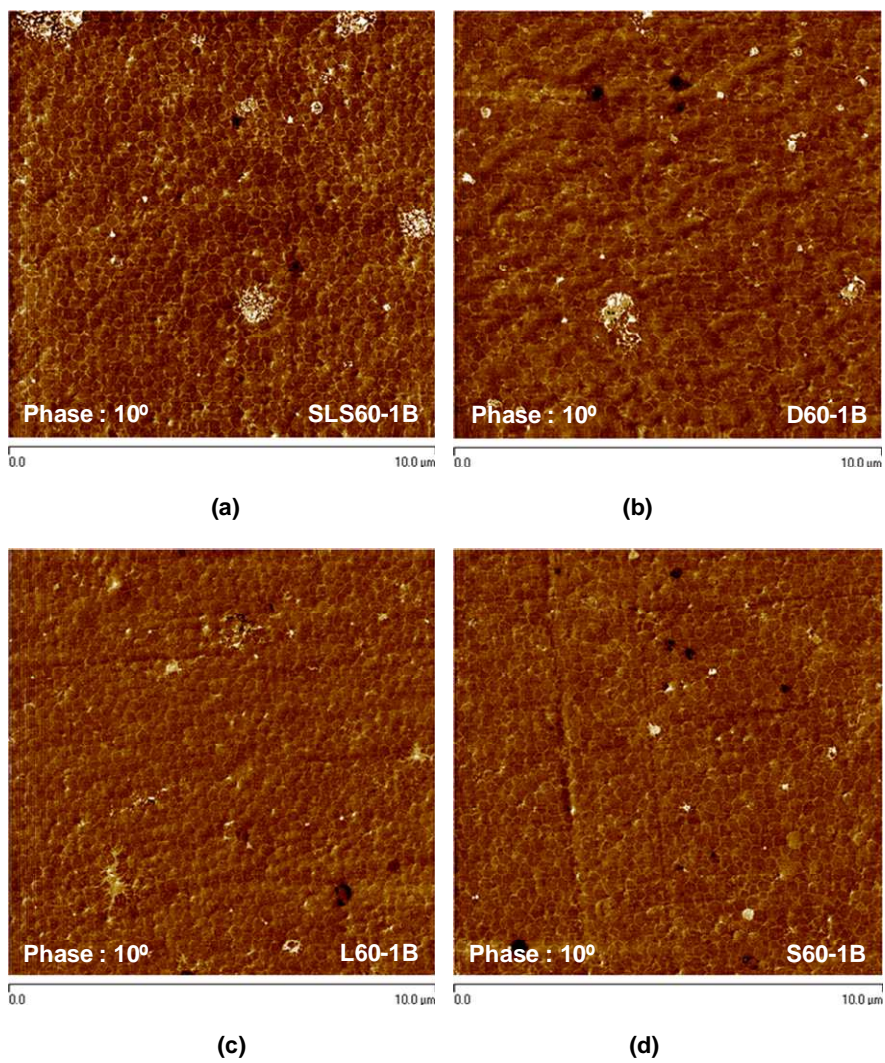
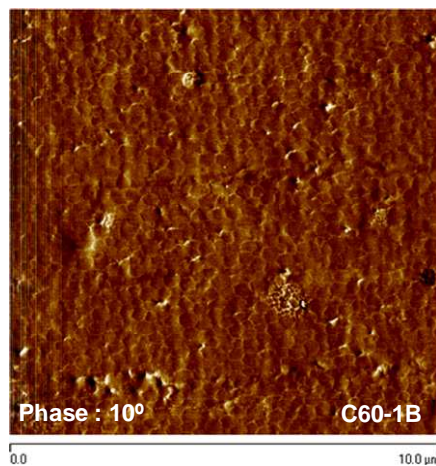


Figure 5.5. Water uptake at the end of the experiment (7 days) as a function of lost weight.

As it has been previously mentioned, water absorption of the films increases by the existence of hydrophilic pockets or aggregates inside the film^{11,15}. Therefore, from the correlation between absorbed water and lost weight of the films (Figure 5.5) the following hypothesis can be formulated: when polymerizable stabilizer (Sipomer[®]Cops-1) and polymerizable surfactants (Sipomer[®]Pam-200 and Latemul[®]PD-104) were used, less hydrophilic pockets or aggregates were formed within the film due to the higher amount of hydrophilic material lost during water uptake experiment whereas when conventional surfactants (SLS and Dowfax[®]2A1) were used, more aggregates were formed within the films increasing the osmotic driving force for water absorption. In order to verify this hypothesis cross-section of the films were analyzed by AFM.

Figure 5.6 presents the AFM phase images of the cross-section of the films made from latexes synthesized under basic conditions using different surfactants. As it can be observed, although in all cases pockets or aggregates (white domains) could be observed within the films, in the films containing SLS and Dowfax[®]2A1 (Figure 5.6a and Figure 5.6b, respectively) the size of the aggregates was much larger. Furthermore, it seems that the lower the water uptake (C60-1B < S60-1B < L60-1B < D60-1B < SLS60-1B) the less aggregates were observed within the film. However, it is hard to believe that the big aggregates observed in SLS60-1B and D60-1B films were only composed with surfactant molecules, because the amount of SLS and Dowfax[®]2A1 in the films was low (0.07 and 0.14 wt%, respectively). Therefore, it can be speculated that the big aggregates observed in SLS60-1B and D60-1B should be a mixture of water-soluble oligomers and surfactant molecules. These large aggregates may increase the water absorption of the films containing the conventional surfactants.





(e)

Figure 5.6. AFM cross-section phase images of films formed from latexes synthesized under basic conditions.

5.3.2.2. Films cast from latexes synthesized under acidic conditions

As a representative example, Figure 5.7 presents the evolution of water uptake for films obtained from latexes synthesized under acidic conditions using different amount of conventional surfactant Dowfax[®]2A1. For comparison purposes the result of D60-1B film was also included. Note that D60-1B latex was synthesized under basic conditions using 0.85 mmol of Dowfax[®]2A1, whereas D60-5A, D60-6A and D60-7A latexes were synthesized under acidic conditions using 6.2 mmol, 9.3 mmol and 12.39 mmol of Dowfax[®]2A1, respectively.

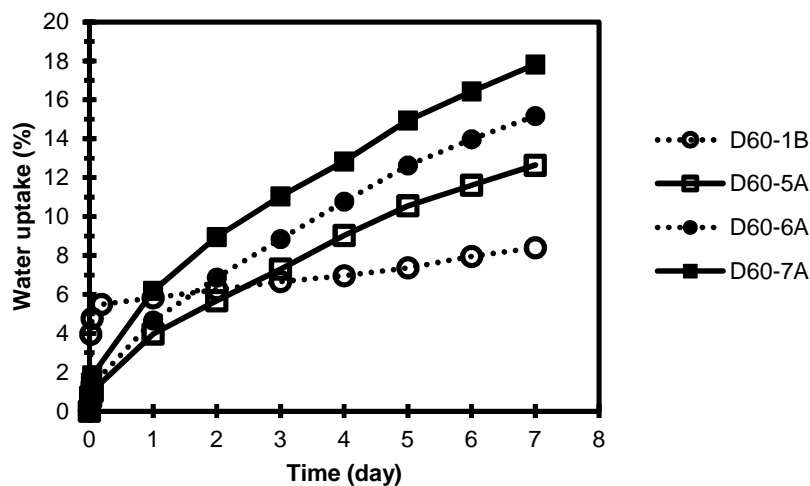


Figure 5.7. Evolution of water uptake for films formed from latexes synthesized using different amounts of conventional surfactant Dowfax[®]2A1.

First of all, it is noticeable that the kinetics of water absorption was different depending on the pH used to synthesize the latex. When the latexes were synthesized under acidic conditions the formation of water-soluble oligomers was less favoured and hence, films formed from these latexes (e.g. D60-5A – D60-7A) absorbed less water at the beginning of the experiment comparing to the films formed from latexes synthesized under basic conditions (e.g. D60-1B). However, independently of the pH used to synthesize the latex, the water uptake of the films at the end of the experiment was proportional to the surfactant amount used during the polymerization; namely, the higher the surfactant amount the higher the final water uptake. Same behaviour was observed by Tang et al.⁸. They showed that increasing the amount of the polymerizable stabilizer 3-allyloxy-2-hydroxyl-propane-sulfonic salt (AHPS) the

water uptake of MMA/BA films increased, which was attributed to the presence of more hydrophilic groups into the film. In this study the same conclusion could be drawn: the higher the surfactant amount, the higher the hydrophilicity of the film and hence, the higher the water uptake of the film.

As a consequence, it seems unreasonable to make the comparison of films containing the same amount of mmoles but different surfactant type, because the molecular weight of the surfactants was different and hence, the weight fraction of surfactant in the final film was also different. Comparison of water uptake of the films as a function of weight percent of surfactant seems to be more realistic.

Figure 5.8 presents the water uptake of the films at the end of the experiment (7 days) as a function of surfactant weight percent in the films. As it can be observed, films containing the conventional surfactant Dowfax[®]2A1 were the ones with the highest water uptake and when polymerizable surfactant Latemul[®]PD-104 and polymerizable stabilizer Sipomer[®]Cops-1 were used, for the same surfactant content, the water uptake was reduced.

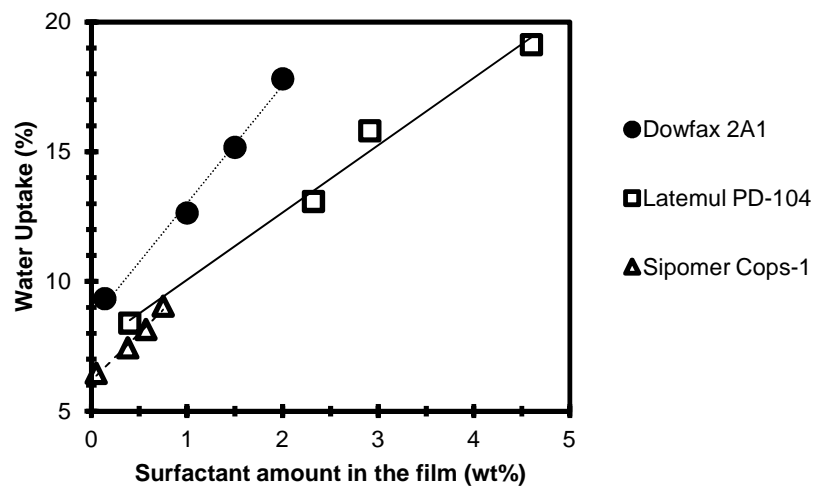


Figure 5.8. Water uptake at the end of the experiment (7 days) for films containing different surfactants as a function of surfactant weight percent (wt%) in the films.

Table 5.4 presents the weight lost of the films formed from latexes synthesized under acidic conditions using different surfactants. It is worth mentioning that the weight lost of those films was much lower than that of the films formed from latexes synthesized under basic conditions (Table 5.3), which supports the hypothesis that when latexes were synthesized under acidic conditions the formation of water-soluble oligomers was substantially reduced. In all the cases the weight lost of the films was lower than the amount of surfactant (in wt%) in the films, suggesting that independently of the surfactant type used part of the surfactant remained in the film after water uptake experiment.

Table 5.4. Results of the experimental weight lost after water uptake experiments for the films formed from latexes synthesized under acidic conditions using different surfactants.

Film	Surfactant in the film (wt %)	Lost weight (wt %)	Surfactant lost (%)^{a)}
D60-5A	1.00	0.277 ± 0.012	27.7
D60-6A	1.50	0.403 ± 0.001	26.9
D60-7A	2.00	0.601 ± 0.010	30.1
L60-4A	2.32	0.229 ± 0.006	9.9
L60-5A	2.91	0.349 ± 0.004	11.9
L60-6A	4.36	0.623 ± 0.008	14.3
C60-5A(IC)	0.38	0.237 ± 0.028	62.4
C60-6A(IC)	0.57	0.398 ± 0.009	69.8
C60-7A(IC)	0.75	0.590 ± 0.017	78.7

^{a)} Assuming that the lost weight of the films after water uptake experiment was only related with the lost of surfactant.

Assuming that the weight lost in the films was only related to the lost of surfactant during the water uptake experiment an idea about the surfactant migration could be obtained. As it can be observed in Table 5.4, in the films containing the conventional surfactant Dowfax[®]2A1 (D60-5A – D60-7A) at the very most 26-30% of the initial surfactant amount diffused to the aqueous phase during water uptake experiment, suggesting that at least 70-75% of the initial surfactant amount get trapped within the film during film formation and was not solubilised during water uptake experiment (7 days). In the films containing Latemul[®]PD-104 at most 9-14% of the initial surfactant diffused to the water phase, suggesting that most of the surfactant remained in the film after the water uptake experiment. In the films containing Sipomer[®]Cops-1

at most 62-78% of the initial surfactant migrated to the aqueous phase during water uptake experiment, indicating that at least 22-38% of the initial surfactant remained within the film after water uptake experiment. It is worth mentioning that Aguirreurreta et al.³⁸ (see Chapter 7) found that the incorporation degree (determined by High Performance Liquid Chromatography, HPLC) of Sipomer[®]Cops-1 in the emulsion copolymerization of MMA/BA/AA (at weight composition of 9.9/89.1/1) was 50%. Knowing that the reactivity ratios of Sipomer[®]Cops-1 with MMA and BA were similar ($r_{\text{MMA}}=19.62$, $r_{\text{Sipomer}^{\text{®}}\text{Cops-1}}=0.048$; $r_{\text{BA}}=15$; $r_{\text{Sipomer}^{\text{®}}\text{Cops-1}}=0.041$) it could be expected that the incorporation degree of this stabilizer in the emulsion copolymerization of MMA/BA/MAA (at weight composition of 49.5/49.5/1) should be approximately the same. Therefore, it could be expected that the percentage of surfactant lost during water uptake experiment is overestimated because, as mentioned before, it is assumed that all the weight lost was only related with the lost of surfactant.

In order to see if some surfactant migrated to the air-film interface water static contact angle measurements were carried out before and after rinsing the films with water. Figure 5.9 presents the water static contact angle values for the films cast from latexes synthesized under acidic conditions using different surfactants.

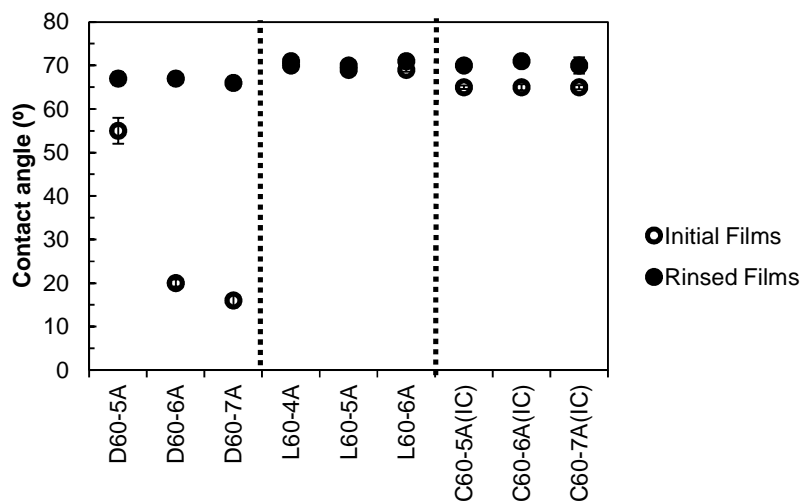


Figure 5.9. Water static contact angles of the films obtained from high solids content latexes synthesized under acidic conditions using different surfactants.

In the films containing the conventional surfactant Dowfax[®]2A1, increasing the surfactant amount (D60-5A < D60-6A < D60-7A) lower contact angle values were obtained, suggesting that when Dowfax[®]2A1 was used surfactant migration to the air-film interface occurred and that increasing the amount of surfactant in the film higher amount of surfactant was in the air-film interface, yielding a more hydrophilic interface. When the films were rinsed with water, higher contact angle values were obtained, indicating that the migrated surfactant was removed from the air-film interface.

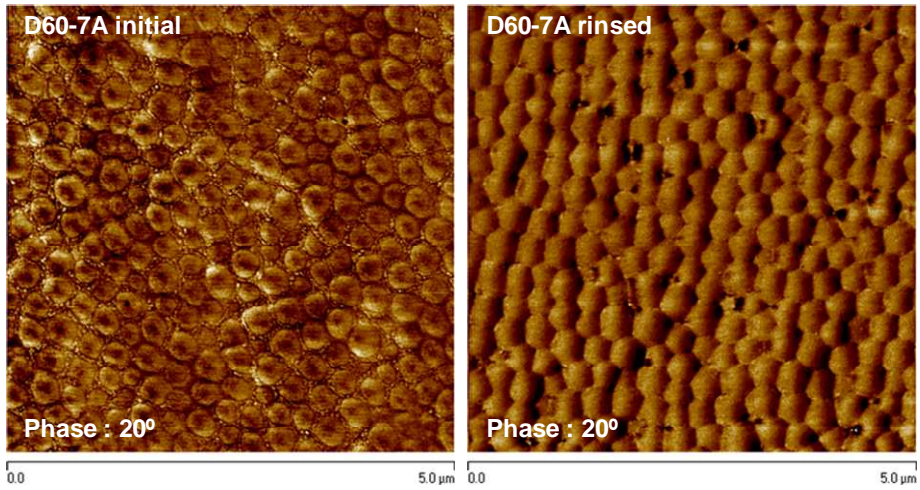
In the films containing Latemul[®]PD-104 (L60-4A – L60-6A) no differences were observed between films containing different amount of surfactant neither between the initial

and rinsed films. These results indicate that no migration of Latemul[®]PD-104 occurred to the air-film interface.

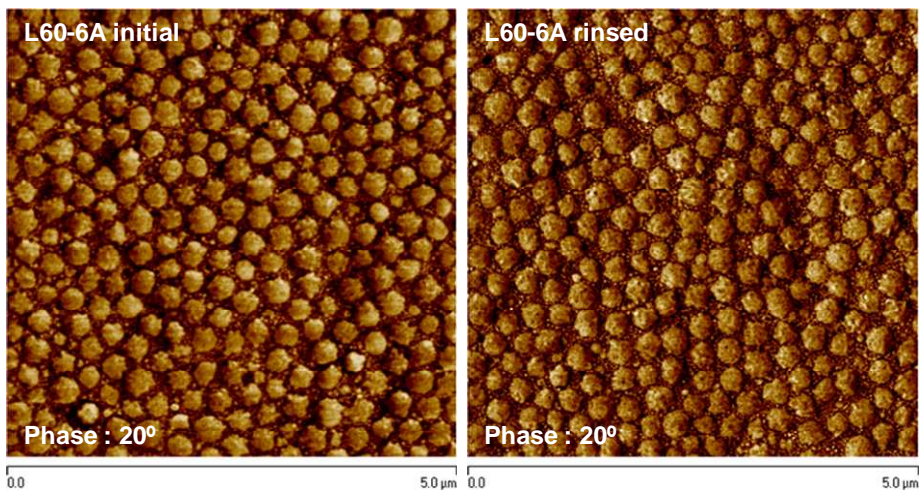
In the films containing the polymerizable stabilizer Sipomer[®]Cops-1, independently of the surfactant amount used, the contact angle values of the initial films were similar and, in all cases, after rinsing the films with water some hydrophilic species were removed from the surface yielding films with higher contact angle values. These results may suggest that part of Sipomer[®]Cops-1 migrated to the air-film interface during film formation.

The results obtained from contact angle measurements were corroborated by AFM. Although AFM technique does not provide a quantitative characterization, it has been widely used to qualitatively characterize surfactant migration within the film^{23,25,38-40}. Aramendia et al.²⁵ showed that the interpretation of surfactant migration made by AFM correlated well with the results obtained from Rutherford Backscattering Spectrometry (RBS) analysis. More recently, Aguirreurreta et al.³⁸ (see also Chapter 7) showed a good correlation between the incorporation of polymerizable surfactants/stabilizer determined by High Performance Liquid Chromatography (HPLC) and the qualitative analysis of surfactant migration observed by AFM. Therefore, AFM technique is a powerful tool to study the surfactant migration within the film.

As a representative example Figure 5.10 presents the AFM phase images of the air-film interfaces for D60-7A, L60-6A and C60-7A(IC) films before (left side) and after rinsing them with water (right side).



(a)



(b)

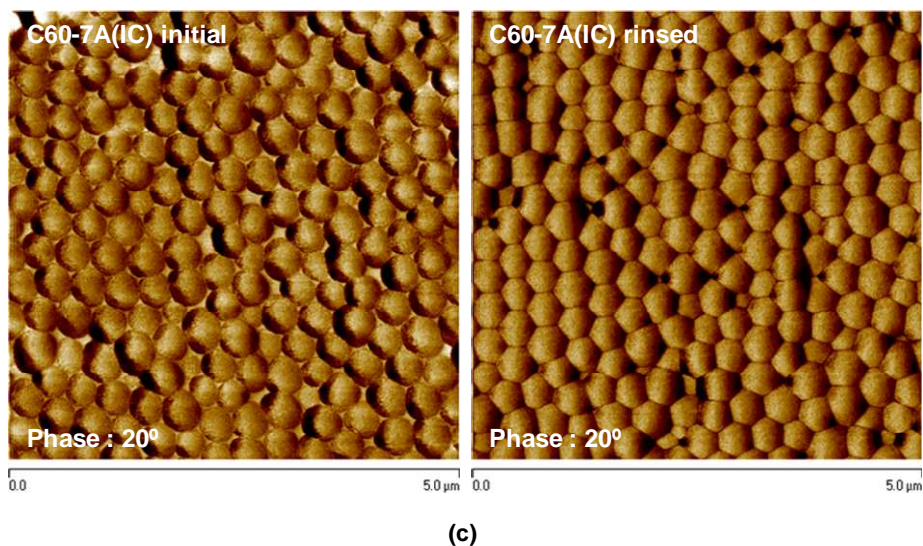


Figure 5.10. AFM phase images of the air-film interface of films containing different surfactants before (left side) and after rinsing them with water (right side). (a) D60-7A film, (b) L60-6A film and (c) C60-7A(IC) film.

As it can be observed in Figure 5.10a, in the film containing the highest surfactant amount of Dowfax[®]2A1 (2 wt%), the polymer particles seem to be floating in a pool of exuded surfactant which increases the hydrophilicity of the air-film interface decreasing the contact angle value of the initial film as observed in Figure 5.9. When the film was rinsed with water the exuded surfactant was removed from the air-film interface.

In the film containing the highest amount of Latemul[®]PD-104 (4.36 wt%), as it can be observed in Figure 5.10b, the air-film interface was exactly the same before and after rinsing the film with water and therefore same contact angle values were obtained (Figure 5.9). Therefore it could be said that Latemul[®]PD-104 was incorporated into the polymer backbone or

that desorption of this polymerizable surfactant from particle surface did not occur. It seems that polymer particles were surrounded by a continuous network formed by Latemul[®]PD-104, probably due to the high amount of surfactant used during the synthesis of L60-6A latex.

In the film containing the polymerizable stabilizer Sipomer[®]Cops-1 (Figure 5.10c), a surfactant layer could not be observed in the surface of the film as it was shown in the film containing Dowfax[®]2A1 (Figure 5.10a). However, as in the case of D60-7A film, after rinsing C60-7A(IC) film with water the shape of the particles changed, suggesting that some hydrophilic species were removed from the surface of the film and therefore the contact angle value increased (Figure 5.9).

As mentioned at the beginning of this chapter, the water uptake of the films results from an interplay between the existence of hydrophilic pockets or aggregates inside the film, the capacity of those pockets for water absorption and their accessibility¹¹. Therefore, in principle the migration of surfactant to the air-film interface would not play any negative role in water absorption and indeed, it would reduce water absorption due to the presence of less hydrophilic material within the film.

It has been observed that in all cases the weight lost after water uptake experiment was less than the initial amount of surfactant (in wt%) in the films. Therefore, in order to know if the surfactant that remained inside the film was forming hydrophilic pockets or aggregates the cross-sections of the films were analyzed by AFM. Figure 5.11, Figure 5.12 and Figure 5.13 show the AFM phase images of the cross-sections of the films containing Dowfax[®]2A1, Latemul[®]PD-104 and Sipomer[®]Cops-1, respectively.

Figure 5.11 shows that the conventional surfactant Dowfax[®]2A1 that did not migrate to the air-film interface, remained within particles interstices and that increasing the amount of surfactant (D50-5A < D60-6A < D60-7A) the aggregation of surfactant within particle interstices increased. This behaviour was not observed in the films containing Latemul[®]PD-104 and Sipomer[®]Cops-1. As it can be observed in Figure 5.12, no aggregation of Latemul[®]PD-104 could be observed in any of the films suggesting that Latemul[®]PD-104 was incorporated or that desorption from particle surface was impeded. However, it seems that the lack of surfactant desorption was hindering particle deformation during film formation because spherical particles were clearly observed. In the films containing the polymerizable surfactant Sipomer[®]Cops-1 no stabilizer aggregation was observed within particle interstices suggesting that at least part of this stabilizer was incorporated into the polymer backbone. Contrary to what was observed in the films containing Latemul[®]PD-104, in the films containing Sipomer[®]Cops-1 it seems that particle deformation was not hindered probably due to the lower surfactant amount (in wt%) present in the films compared to the films containing Latemul[®]PD-104.

It can be concluded that for films containing the same weight percent of surfactant, the ones with Dowfax[®]2A1 absorbed more water due to surfactant aggregation within particle interstices. When polymerizable surfactant and polymerizable stabilizer were used hydrophilic pockets were not formed and, as a consequence, the water absorption was substantially reduced.

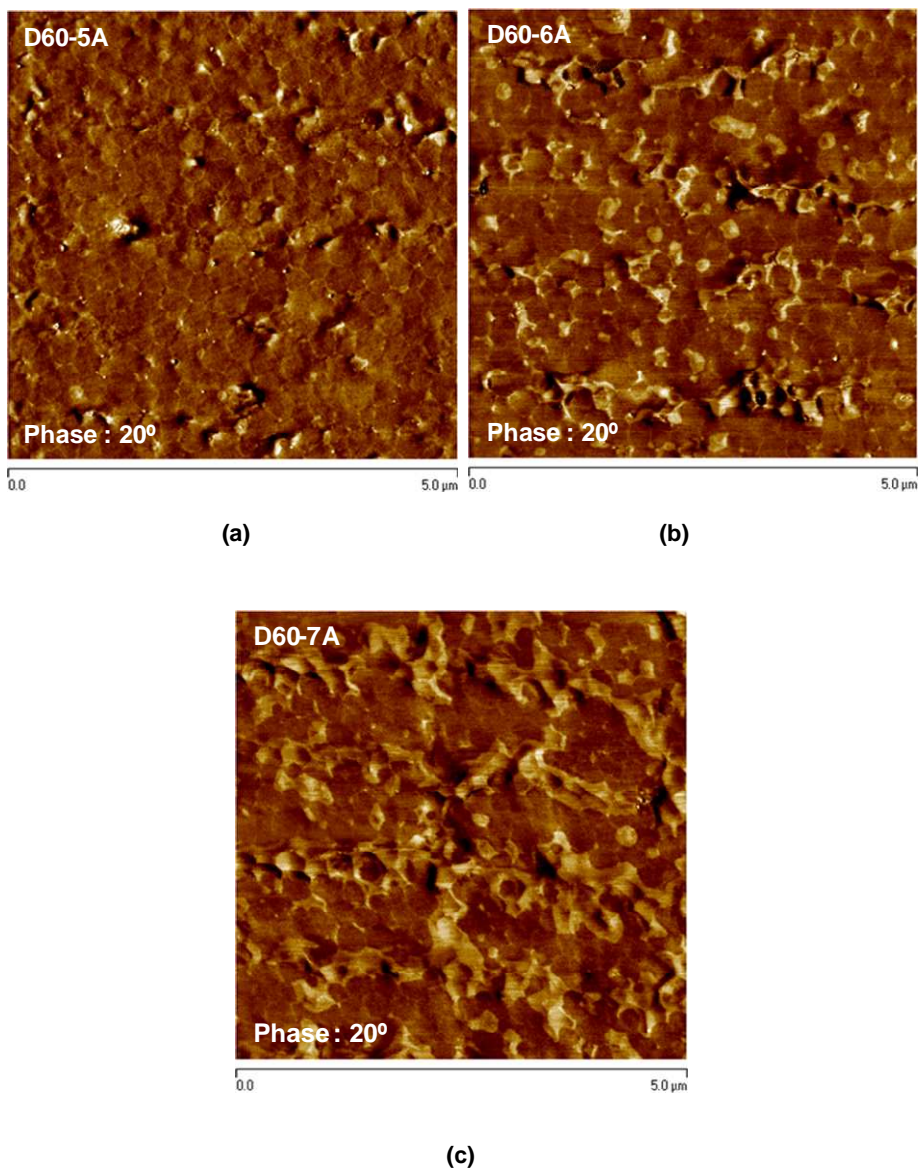


Figure 5.11. AFM phase images of the cross-section of the films containing different amounts of the conventional surfactant Dowfax[®] 2A1.

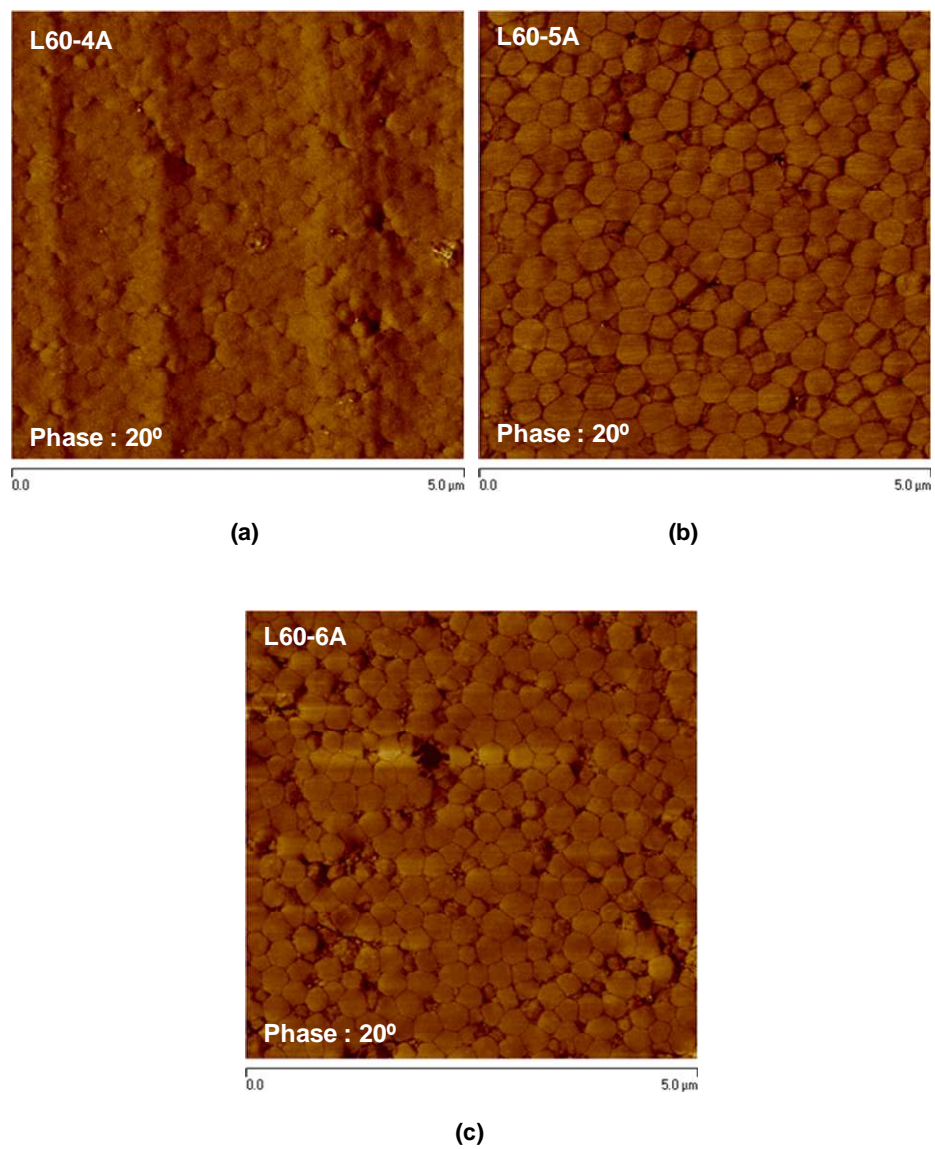


Figure 5.12. AFM phase images of the cross-section of the films containing different amounts of the polymerizable surfactant Latemul®PD-104.

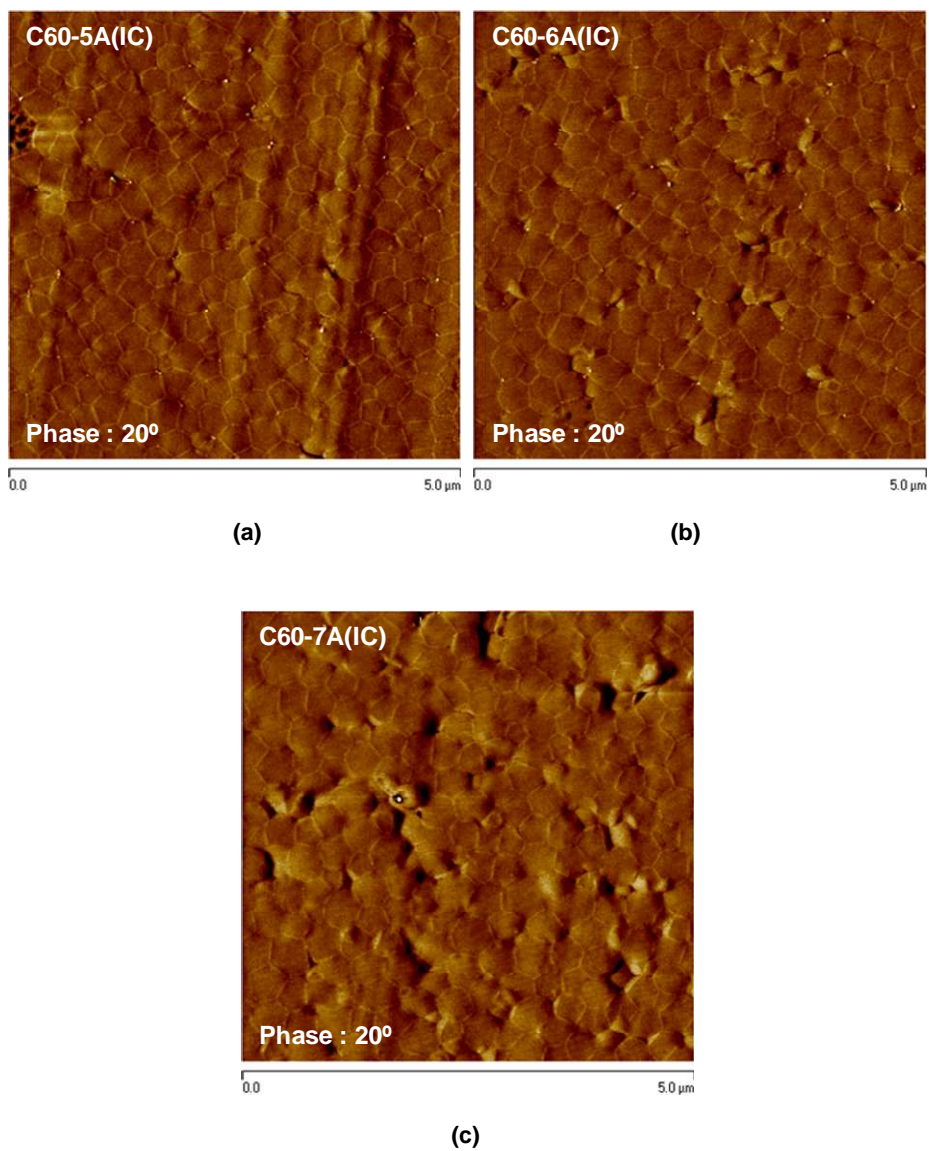


Figure 5.13. AFM phase images of the cross-section of the films containing different amounts of the polymerizable stabilizer Sipomer®Cops-1.

5.3.3. Mechanical properties

5.3.3.1. Films cast from latexes synthesized under basic conditions

The mechanical properties of the films cast from latexes synthesized under basic conditions using 0.85 mmol of surfactant are summarized in Table 5.5. Figure 5.14 shows the stress-strain curves of the films. It is worth to recall that all the latexes synthesized under basic conditions contain almost the same gel content (between 20 and 26 % of gel, Table 5.1).

Table 5.5. Mechanical properties of the films casted from latexes synthesized under basic conditions using 0.85 mmol of surfactant.

Film	Elongation@Break $\times 10^{-2}$ (%)	Ultimate Strength (MPa)	Young's Modulus $\times 10^{-2}$ (MPa)	Toughness $\times 10^{-6}$ (J.m ⁻³)
D60-1B	3.64 ± 0.59	8.53 ± 0.24	0.24 ± 0.13	33.72 ± 4.97
SLS60-1B	3.96 ± 0.07	8.16 ± 0.08	0.28 ± 0.04	34.09 ± 1.12
L60-1B	3.81 ± 0.16	8.51 ± 0.12	0.24 ± 0.05	32.43 ± 2.45
S60-1B	3.62 ± 0.38	8.86 ± 0.70	0.21 ± 0.04	33.65 ± 5.16
C60-1B	3.59 ± 0.17	8.72 ± 0.88	0.23 ± 0.05	34.97 ± 3.80

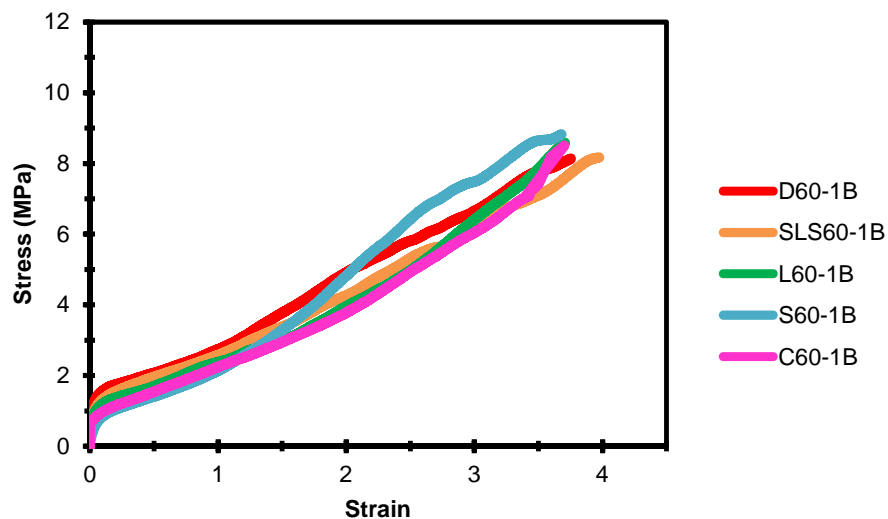


Figure 5.14. The stress-strain behavior of the films cast from latexes synthesized under basic conditions using 0.85 mmol of surfactant.

Contrary to what was observed in the freeze-thaw stability test and water uptake experiment, as it can be clearly seen in Table 5.5 and Figure 5.14, the surfactant type employed in the polymerizations did not have any effect on the mechanical properties of the films. Therefore, it can be concluded that the small amounts of surfactants used are enough to alter latex stability and water sensitivity of the films, but they do not play any role on the stress-strain behavior of the films.

5.3.3.2. Films cast from latexes synthesized under acidic conditions

The mechanical properties of the films cast from latexes synthesized under acidic conditions using different amounts of surfactant are summarized in Table 5.6. The stress-strain behavior of films containing different amounts of Dowfax[®]2A1, Latemul[®]PD-104 and Sipomer[®]Cops-1 are presented in Figure 5.15, Figure 5.16 and Figure 5.17, respectively.

Table 5.6. Mechanical properties of the films cast from latexes synthesized under acidic conditions using different amounts of surfactant.

Film	Gel (%)	Elongation@Break $\times 10^{-2}$ (%)	Ultimate Strength (MPa)	Young's Modulus $\times 10^{-2}$ (MPa)	Toughness $\times 10^{-6}$ (J.m ⁻³)
D60-5A	24±1	2.82 ± 0.12	11.88 ± 2.09	0.97 ± 0.3	34.62 ± 3.95
D60-6A	23±5	3.43 ± 0.21	8.42 ± 1.36	0.68 ± 0.33	27.06 ± 2.71
D60-7A	24±1	3.91 ± 0.33	7.61 ± 0.27	0.51 ± 0.088	24.50 ± 1.74
L60-4A	61±5	3.17 ± 0.31	4.21 ± 0.8	0.52 ± 0.11	16.95 ± 2.95
L60-5A	62±1	2.71 ± 0.33	3.45 ± 0.19	0.31 ± 0.08	11.58 ± 1.45
L60-6A	64±2	2.44 ± 0.16	2.40 ± 0.24	0.21 ± 0.08	8.16 ± 0.18
C60-5A (IC)	53±1	2.66 ± 0.36	7.24 ± 0.57	0.71 ± 0.11	20.69 ± 4.89
C60-6A (IC)	54±2	2.86 ± 0.40	7.99 ± 0.46	0.70 ± 0.05	23.50 ± 3.05
C60-7A (IC)	55±1	2.68 ± 0.43	7.63 ± 0.18	0.73 ± 0.07	21.57 ± 4.23

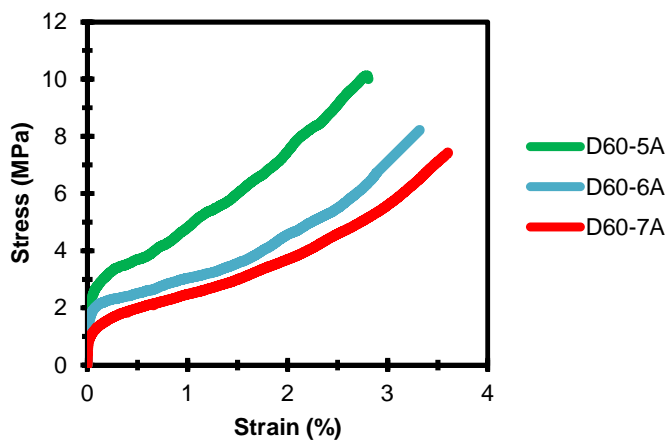


Figure 5.15. The stress-strain behavior of the films cast from latexes synthesized under acidic conditions using different amounts of Dowfax[®]2A1.

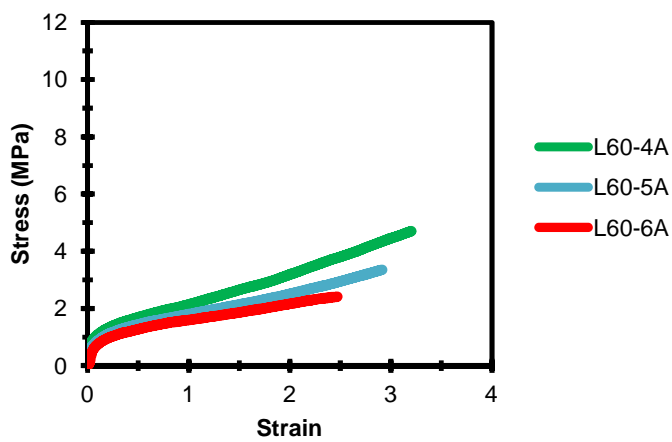


Figure 5.16. The stress-strain behavior of the films cast from latexes synthesized under acidic conditions using different amounts of Latemul[®]PD-104.

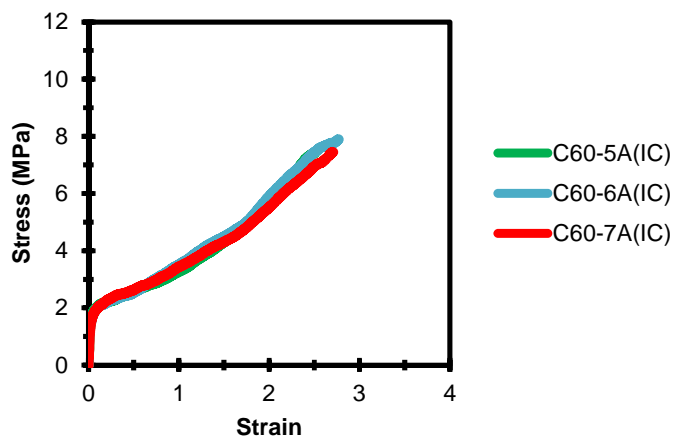


Figure 5.17. The stress-strain behavior of the films cast from latexes synthesized under acidic conditions using different amounts of Sipomer®Cops-1.

It can be clearly seen that the mechanical properties were considerably affected by the surfactant type used during the polymerization process. In Chapter 4, it has been discussed that depending on the surfactant type used during the polymerization process latexes with different gel content were obtained (Table 5.6). Therefore and unfortunately, a direct comparison between films containing different surfactants could not be done due to the different gel content of the latexes that strongly affects the mechanical properties of the films.

It is worth to point out that the films were dried at ambient temperature (just few degrees above the glass transition temperature). Therefore, it could be expected that a good cohesion of the films was not achieved in any case, because polymer chain mobility is limited and hence,

the interdiffusion of polymer chains across the interface of the particles is hindered which is necessary for having good cohesion in the film^{18,31}.

For each surfactant type, latexes with similar gel content were obtained independently of the surfactant amount used during the polymerization process. Therefore, the effect of the surfactant amount on the mechanical properties of the films containing the same surfactant will be discussed.

In the films containing Dowfax[®]2A1, as it can be observed in Table 5.6 and Figure 5.15, the amount of surfactant used to synthesize the latex had a strong influence on the mechanical properties of the films. It can be seen that whereas the elongation at break increased the ultimate strength, Young's modulus (the slope obtained at low strains) and toughness (the area under the curve) decreased with increasing surfactant amount (D60-5A < D60-6A < D60-7A). These results suggest that the conventional surfactant trapped within the film was acting as a plasticizer and that increasing the surfactant amount the plasticizing effect of the surfactant was higher probably due to a higher surfactant aggregation within the film (Figure 5.11). If the surfactant acts as a plasticizer the free volume of the polymer is increased resulting in a reduction of the Young's modulus⁴¹. As the molecular mobility of the polymeric network is increased the flexibility of the chains increased and as a consequence the films elongate more before breaking.

In the films containing Latemul[®]PD-104, the mechanical properties were also affected by the surfactant amount (Table 5.6 and Figure 5.16). It can be observed that the elongation at break, ultimate strength, Young's modulus and toughness decreased with increasing surfactant

amount. The fact that the Young's modulus decreased could be due to the plasticizing effect of the surfactant. However, the elongation at break and the ultimate strength decreased with increasing surfactant concentration, which means that weaker films were obtained. This could be due to the lack of surfactant desorption from the particle surface during film formation (no migration of Latemul[®]PD-104 was observed, see Figure 5.12) that hinders particle deformation and as a consequence, retards interdiffusion between adjacent particles which is necessary for having a good cohesion of the film^{31,32}. Hence, during film formation the higher the surfactant amount surrounding the polymer particles the slower the interdiffusion between adjacent particles leading to weaker films.

Contrary to what was observed in the films containing the conventional surfactant Dowfax[®]2A1 and the polymerizable surfactant Latemul[®]PD-104, in the films containing the polymerizable stabilizer Sipomer[®]Cops-1 the amount of the stabilizer used during polymerization did not have any effect on the mechanical properties of the films. This, could be due to the low surfactant amount present in the films (less than 0.75 wt%) that was not enough to alter the mechanical properties of the films.

5.4. Conclusions

In this chapter the performance of high solids content acrylic latexes synthesized using polymerizable surfactants/stabilizer and conventional surfactants were analyzed.

It has been observed that the freeze-thaw stability of the latexes synthesized under basic conditions was improved by using polymerizable surfactants (Sipomer[®]Pam-200 and Latemu[®]PD-104) and polymerizable stabilizer (Sipomer[®]Cops-1).

The kinetics of water absorption was different depending on the pH used to synthesize the latex. It was observed that the films formed from latexes synthesized under acidic conditions absorbed less water at the beginning of water uptake experiments due to the lower amount of water-soluble species present in the final films. However, independently of the pH used to synthesize the latex, the water uptake of the films at the end of the experiment was proportional to the surfactant amount used during the polymerization.

It has been concluded that for films containing the same weight percent of surfactant, the ones with Dowfax[®]2A1 absorbed more water due to surfactant aggregation within particle interstices and that the water absorption was substantially reduced when Latemu[®]PD-104 and Sipomer[®]Cops-1 were used.

It was shown that the mechanical properties were considerably affected by the surfactant used during the polymerization process, because depending on the surfactant type

used the gel content of the final latexes was different as explained in Chapter 4. Therefore, it was not possible to make a direct comparison between films containing different surfactants.

It was concluded that the conventional surfactant Dowfax[®]2A1 acted as a plasticizer and consequently, increasing the surfactant amount the Young's modulus decreased and the elongation at break increased. In the films containing Latemul[®]PD-104, the increase in surfactant amount led to weaker films, likely, due to the lack of surfactant desorption from the particle surface during film formation that hinders interdiffusion of polymer chains between adjacent particles. In the films containing polymerizable stabilizer Sipomer[®]Cops-1, probably due to the low surfactant amount used during the polymerization process, no effect of the stabilizer amount on the mechanical properties was observed.

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Chapter 6. Synthesis of water-borne pressure-sensitive adhesives (PSAs) using polymerizable surfactants

6.1. Introduction

Pressure-sensitive adhesives (PSAs) are viscoelastic materials which can adhere to solid surfaces when a small pressure is applied¹. In the production of PSAs, acrylic water-borne PSAs have become more attractive than solvent based acrylic due to their intrinsic advantages: environmentally safe (solvent-free), high solids content, ease of handling and economical reasons (low cost)^{2,3}. However, when water-borne PSAs are applied as film forming polymers often poorer properties compared to their counterpart solvent-borne PSAs have been reported due to the presence of surfactant in the final films⁴⁻⁹. Previous studies showed that adhesion strength⁵, shear strength⁸, peel strength^{7,10} and water resistance^{4,9} of PSAs can be adversely affected by the surfactant migration.

Although the use of polymerizable surfactants has been considered to be a promising approach to improve the performance of water-borne PSAs, to our best knowledge, only a few

scientific studies can be found in the open literature reporting the use of polymerizable surfactants in the synthesis of water-borne PSAs¹¹⁻¹⁵.

In this chapter, the feasibility of using polymerizable surfactants/stabilizer (Latemu[®]PD-104, Sipomer[®]Pam-200 and Sipomer[®]Cops-) to produce 50 wt% solids content acrylic PSAs is studied. To this end, poly(butyl acrylate-co-methyl methacrylate-co-acrylic acid) model latexes were synthesized by seeded semi-batch emulsion polymerization. As mentioned in Chapter 4, in the synthesis of high solids content latexes (50-60wt%) the amount of surfactant needed can be substantially reduced without jeopardizing the stability of the latexes if functional monomers such as methacrylic acid or acrylic acid are used and, the polymerization is carried out at basic pH¹⁶. However, as shown in Chapter 4, when the polymerizations are conducted at basic pH water-soluble oligomers are produced, which may alter the final properties of the films (e.g. water absorption kinetics). Therefore, first of all, the effect that the pH had on the polymerization process as well as on the microstructure of the polymer was studied. Then, the effect of the surfactant concentration and type (polymerizable or not) on the polymerization process and polymer microstructure was studied.

6.2. Experimental

6.2.1. Materials

Methyl methacrylate (MMA, BASF SE), n-butyl acrylate (BA, BASF SE) and acrylic acid (AA, BASF SE) were used as supplied. Sodium persulfate (NaPS, Fluka) was used as thermal initiator. Dowfax[®]2A1 (The Dow Chemical Company) was used as conventional surfactant. Anionic polymerizable surfactants Latemul[®]PD-104 (Kao Corporation) and Sipomer[®]Pam-200 (Solvay) were used. Sipomer[®]Cops-1 (Solvay) was used as polymerizable stabilizer. Deionized water was used throughout the work. To increase the pH of the dispersions, 25% solution of ammonia (Fluka) was used.

6.2.2. Emulsion polymerization

50 wt% solids content acrylic latexes (MMA/BA/AA at weight composition of 9.9/89.1/1) stabilized with different surfactants were synthesized by seeded semi-batch emulsion polymerization. Polymerizations were carried out in a 2L glass reactor fitted with a reflux condenser, a nitrogen inlet, feeding inlet, temperature probes and a stainless steel anchor type stirrer. Reaction temperature and inlet flow rate of the feed were controlled by an automatic control system. The formulation used to prepare the seed is given in Table 6.1 and that of the seeded semi-batch reactions in Table 6.2.

The seed was prepared by semi-continuous emulsion polymerization at 80°C and 150 rpm. An initial charge of water, surfactant and ammonia were added to the reactor. After reaching the desired temperature (80°C) a shot of thermal initiator was added. Then the

preemulsion containing water, monomers and surfactant was fed during 2 hours. After that, the temperature was increased to 90°C and the latex was let to react batchwise during 1 hour. A seed latex with 29.1 wt% of solids content and 62 nm of particle diameter was obtained (measured by Dynamic Light Scattering). The final pH of the seed was 9.5.

Table 6.1. Formulation used to synthesize the seed latex.

Compound	Initial Charge (g)	Stream (g)
MMA	---	30.69
BA	---	276.21
AA	---	3.10
Dowfax [®] 2A1 ^{a)}	6.89	10.33
Water	608.00	104.9
Na ₂ S ₂ O ₈ ^{b)}	22.14	---
Ammonia ^{c)}	12.40	---

^{a)} 45% aqueous solution. ^{b)} 7% aqueous solution. ^{c)} 25% aqueous solution.

Seeded semi-batch emulsion polymerizations were carried out at 80°C and 150 rpm. An initial charge containing the seed latex, water and a small amount of monomers were added to the reactor. After reaching the desired temperature (80°C) a shot of thermal initiator was added. Then the preemulsion containing the monomers, the surfactant and water was fed during 3 hours. After that, the temperature was increased to 90°C and kept batchwise 2 hours.

Table 6.2. General formulation used in the seeded semi-batch emulsion polymerizations.

Compound	Initial Charge (g)	Stream (g)
Seed latex	18.04	---
MMA	0.50	49.00
BA	4.50	441.05
AA	---	4.95
Na ₂ S ₂ O ₈ ^{a)}	35.71	---
Water	351.5	110.75-124.79 ^{b)}
Surfactant	---	variable

^{a)} 7% aqueous solution. ^{b)} The amount of water used was varied in order to adjust the formulation to 50 wt% of final solids content. The amount of water corresponds to the total amount of water added (added water + water coming from surfactant solutions).

6.2.3. Characterization

The final solids content and monomer conversion were measured gravimetrically. The amount of coagulum, if any, was measured by filtering the final latex through a 85 µm nylon mesh followed by gravimetry. The average particle size was measured by Dynamic Light Scattering (DLS) and the particle size distribution (PSD) of the latexes was analyzed by Capillary Hydrodynamic Fractionation chromatography (CHDF). The gel fraction and swelling capacity were determined by Soxhlet extraction of the dried latex using tetrahydrofuran (THF) and the absolute molecular weight of the soluble fraction was analyzed by Size Exclusion chromatography (SEC) using a Multi Angle Light Scattering (MALS) and Refractive Index (RI) detectors. The details of the characterization procedures and methods are given in Appendix I.

6.3. Results and discussion

6.3.1. Synthesis of high solids content acrylic PSAs by emulsion polymerization

A total number of 21 polymethyl methacrylate-co-butyl acrylate-co-acrylic acid (MMA/BA/AA at weight composition of 9.9/89.1/1) latexes at 50 wt% of solids content and target particle size of 300 nm were synthesized by seeded semi-batch emulsion copolymerization. The process variables studied were the pH, the surfactant concentration and surfactant type. The process variables and the main characteristics of the final latexes are shown in Table 6.3.

In Table 6.3 and throughout this chapter, latexes made with conventional surfactant Dowfax[®]2A1 are designated as D50. Those made with the polymerizable surfactants Latemul[®]PD-104 and Sipomer[®]Pam-200, L50 and S50, respectively, and latexes synthesized using the polymerizable stabilizer Sipomer[®]Cops-1 as C50. For each surfactant system, five reactions were carried out, which are designated with a different number (1 – 5). Reactions with the same number were synthesized using the same number of moles of surfactant (Table 6.4). As the molecular weight of the surfactants differs from one to another (see Chapter 2), surfactant concentrations present in Table 6.3 are little bit different because the amount of surfactant was considered as solids content in the formulation. Therefore, the amount of water used was slightly varied in each reaction (Table 6.2) in order to adjust the final solids content to 50 wt%.

Table 6.3. Main characteristics of the formulation used to synthesize high solids content PSAs and main characteristics of the final latexes.

Latex	Surfactant concentration ^{a)} (mM)	Comments	Conversion (%)	dp ^{b)} (nm)	pH	Gel (%)
D50-1b	3.40	1 wbm% of ammonia (20g) added in the preemulsion	96.7	299	9.7	1 ± 0
D50-1	3.40	---	99.8	304	1.8	27 ± 0
D50-2	6.78	---	99.9	299	2.1	30 ± 3
D50-3	10.22	---	99.9	292	2	38 ± 0
D50-4	13.58	---	99.9	285	2	41 ± 2
D50-5	16.94	---	98.5	290	1.9	38 ± 1
L50-1	3.39	---	99.8	295	2	34 ± 1
L50-2	6.77	---	98.5	286	2.3	38 ± 0
L50-3	10.11	---	97.1	265	2.3	45 ± 0
L50-4	13.38	---	96.7	264	2.2	43 ± 0
L50-5	16.67	---	95.9	262	2.1	47 ± 1
S50-1	3.42	---	99.0	302	2.1	33 ± 0
S50-2	6.84	---	99.0	305	2.1	32 ± 0
S50-3	10.24	---	96.7	297	2.4	36 ± 2
S50-4	13.60	---	99.3	290	2.6	45 ± 0
S50-5	16.98	---	99.6	294	2.8	44 ± 0
C50-1	3.61	All the stabilizer and water added in the initial charge. Only mixture of monomers fed	99.6	303	2.1	27 ± 5
C50-2	6.73		99.6	295	2.2	29 ± 2
C50-3	9.04		99.2	296	2.2	33 ± 1
C50-4	13.64		99.2	294	2.2	37 ± 0
C50-5	17.15		99.6	292	2	40 ± 1

^{a)} Per liter of water (mmol/L). ^{b)} Measured by DLS.

Table 6.4. Amount of surfactant used in the seeded semi-batch experiments described in Table 6.2.

Run	Surfactant amount (mmol)
1 ^{a)}	1.7
2	3.4
3 ^{a)}	5.2
4	6.9
5	8.7

^{a)} In C50-1 and C50-3 reactions, 1.8 and 4.6 mmol were used, respectively.

6.3.1.1. Effect of the pH

In order to study the effect of the pH on the polymerization process, D50-1b and D50-1 latexes were synthesized using the same amount of the conventional surfactant Dowfax[®]2A1 in both experiments, but with ammonia in the preemulsion for reaction D50-1b. In both polymerizations stable latexes without coagulum were obtained and the target particle size was achieved. However, in reaction D50-1b full conversion of the monomer was not achieved (96.7%).

The pH affects the distribution of the acrylic acid groups during the emulsion polymerization due to the dissociation of the carboxylic groups above the pK_a ($pK_{a, \text{acrylic acid}}=4.25^{17}$); hence, increasing the pH the acrylic acid would preferentially polymerize in the aqueous phase producing water-soluble polymer¹⁸⁻²¹. The amount of water-soluble species was determined for both dispersions and results are presented in Table 6.5. When ammonia

was added to the preemulsion (D50-1b) the amount of water-soluble species was substantially higher.

Table 6.5. Amount of water-soluble species in the aqueous phase determined by ultracentrifugation (at 50000 rpm for 16 hours) and followed by gravimetric analysis.

Latex	Water-soluble species (wt%)
D50-1B	1.5
D50-1	0.3

Formation of water-soluble species implies higher termination of oligoradicals in the aqueous phase and hence a reduction in the average number of radicals per particle (\bar{n})^{20,22}, leading to a lower monomer conversion at the end of the polymerization process when ammonia was used (D50-1b reaction).

Apart from the reduction in the final monomer conversion due to a high pH during the polymerization process, as it can be observed in Table 6.3, the pH also had a strong influence on the polymer microstructure; when the reaction was carried out under basic conditions (D50-1b) the obtained gel content (1%) was negligible, whereas when the same reaction was carried out under acidic conditions (D50-1) 27% of gel was obtained. In order to discard that the difference found in the final gel content was due to the final pH of the latex, the final pH of D50-1 was set to 9.7 and the gel content was measured again. However, the gel content did not change noticeable when the pH of the final dispersion was increased to 9.7. Therefore, the key to modify the microstructure of the latex should be related with the effect that the pH had during the polymerization process. As it was discussed above, when the polymerization was

conducted at basic conditions (D50-1b) high amount of water-soluble species were formed leading eventually to a reduction in the average number of radicals per particle (\bar{n}). In emulsion polymerization of acrylates, gel is formed by intermolecular chain transfer to polymer followed by termination by combination. Therefore, lower values of \bar{n} , lead to a reduction of the rate of bimolecular termination between large molecules in the polymer particles, which reduced the gel formation. Furthermore, the gel content tends to decrease the sol molecular weight because the long polymer chains have a higher probability to suffer intermolecular chain transfer to polymer and therefore to incorporate into the gel. Indeed the average molecular weight of the soluble fraction for D50-1b was higher than for D50-1 (612 kDa against 573 kDa, respectively).

In order to produce PSAs with enhanced adhesive performance (good balance of adhesive properties) it is well known that some degree of cross-linking or gel content is needed^{3,23}. Therefore, as polymerizations carried out at high pH led to negligible amount of cross-linked polymer, the polymerizations carried out to assess the impact of the polymerizable surfactant or stabilizer were conducted at acidic pH.

6.3.1.2. Effect of the surfactant concentration and surfactant type

20 latexes were synthesized under acidic conditions (the pH was allowed to evolve naturally) using different surfactants. On the one hand, the conventional surfactant Dowfax[®]2A1 was used (D50-1 – D50-5). On the other hand, polymerizable surfactants Latemul[®]PD-104 (L50-1 – L50-5) and Sipomer[®]Pam-200 (S50-1 – S50-5) as well as the

polymerizable stabilizer Sipomer®Cops-1 (C50-1 – C50-5) were also used. For each surfactant type the effect of the surfactant concentration was analyzed.

In all polymerizations stable latexes with low amounts of coagulum (< 0.1 wt%) were obtained. It is worth to point out that when the polymerizable stabilizer Sipomer®Cops-1 was used, contrary to the procedure used with the other surfactants, the stabilizer was fully added into the initial charge and no stabilizer was added in the preemulsion (C50-1 – C50-5 reactions). Sipomer®Cops-1 does not copolymerize well with the monomers used throughout this work (reactivity ratios given by the supplier: $r_{\text{MMA}}=19.62$, $r_{\text{Sipomer}^{\circ}\text{Cops-1}}=0.048$; $r_{\text{BA}}=15$, $r_{\text{Sipomer}^{\circ}\text{Cops-1}}=0.041$). Furthermore, as this stabilizer is very hydrophilic it must react with growing oligoradicals in the aqueous phase in order to produce amphiphilic species that act as a surfactant molecules during the polymerization process. Therefore, when this stabilizer was added in the preemulsion high amount of coagulum was obtained (between 25 to 75 wt% of coagulum) because Sipomer®Cops-1 did not form enough amphiphilic species. However, when the stabilizer was added to the initial charge it could copolymerize and hence, it was able to stabilize the growing polymer particles during the polymerization process.

As in these reactions ammonia was not added almost full conversion of the monomer was achieved in all polymerizations. However, special attention has to be paid in the series of reactions carried out using Latemul®PD-104 (L50-1 – L50-5). When this polymerizable surfactant was used, the final monomer conversion decreased when the surfactant concentration was increased (Table 6.3). It has been reported that chain transfer can occur in polymerizations where allylic polymerizable surfactants²⁴⁻²⁶ or block copolymers containing poly(ethylene oxide) (PEO) groups^{27,28} are used, and as a consequence the polymerization

rate decreases due to the generation of tertiary radicals which are quite stable, propagates slowly^{26,28} and can only react with other radicals leading to termination^{29,30}.

In order to verify if chain transfer to polymerizable surfactant Latemul[®]PD-104 was an important event in the case under study, solution polymerization of MMA/BA/Latemul[®]PD-104 was carried out using toluene as solvent. The recipe is given in Table 6.6. As a reference, the same reaction was carried out without adding Latemul[®]PD-104 and the reaction kinetics and molecular weights were compared.

Table 6.6. Formulation used in the solution polymerization.

Compound	Charge (wt%)
MMA	14.9
BA	14.9
AIBN	0.3
Toluene	69.3
Latemul [®] PD-104 ^{a)}	0.6

^{a)} Active matter obtained by evaporating the water of the surfactant solution in the oven.

Figure 6.1 presents the evolution of the conversion in the absence and presence of Latemul[®]PD-104 in solution polymerization and Figure 6.2 shows the final molecular weight distributions. A clear evidence of chain transfer to Latemul[®]PD-104 was not found because, although the conversion evolved slightly below when Latemul[®]PD-104 was added (Figure 6.1), no substantial difference was observed in the final molecular weight distribution (Figure 6.2).

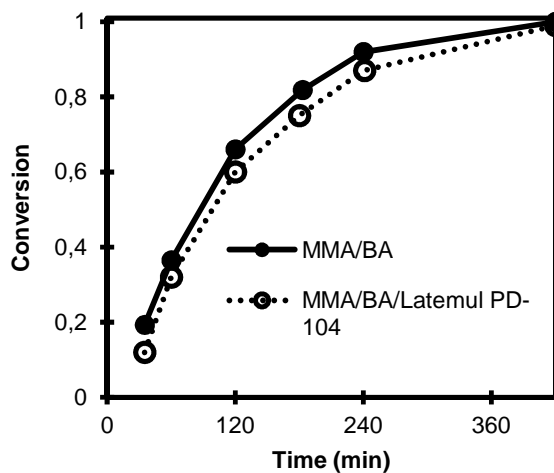


Figure 6.1. Evolution of the conversion in the absence and presence of Latemul®PD-104 in solution polymerization of MMA/BA.

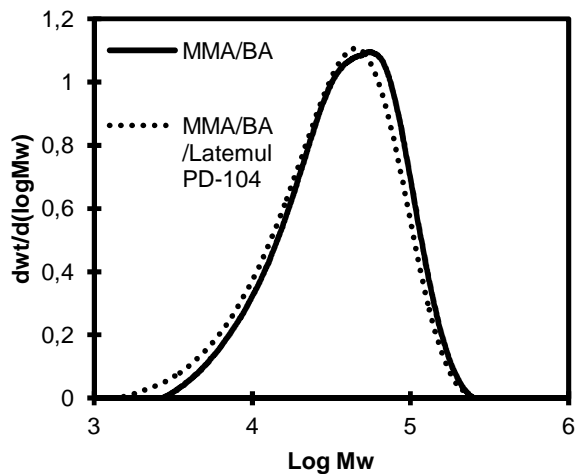


Figure 6.2. Final molecular weight distribution obtained in the absence and presence of Latemul®PD-104 in solution polymerization.

Therefore a plausible explanation for this behavior (lower monomer conversion increasing the concentration of Latemul[®]PD-104, Table 6.3) could be that increasing the amount of Latemul[®]PD-104, the polymerization rate decreased due to mass transfer limitations for radical entry created by the dense hairy layer formed by the surfactant^{26,31,32}. Same trend was observed by Aramendia et al.³³ when a non-ionic polymerizable surfactant was used. Although Latemul[®]PD-104 is an anionic surfactant its molecular weight (1674 g/mol) is comparable to that of nonionic ones.

Regarding the final particle size of the latexes (see Table 6.3), in all cases almost the target particle size (300 nm) was obtained, except in the latexes synthesized using Latemul[®]PD-104 (L50-1 – L50-5 latexes). There, the final particle size decreased with increasing surfactant concentration suggesting that secondary nucleation occurred during the polymerization process. Although in the latexes synthesized using Dowfax[®]2A1, Sipomer[®]Pam-200 and Sipomer[®]Cops-1 almost the target particle size was achieved at the end of the polymerization, increasing the surfactant concentration a slight decrease in the final particle size was observed too. The number of polymer particles (N_p) was calculated from the z-average particle diameter of the particle size distribution obtained by DLS technique. Note that for bimodal distributions the N_p calculated based on the z-average diameter is an approximate value. As it can be observed in Figure 6.3, increasing the surfactant concentration the final number of polymer particles increased, suggesting that not only in the reactions were Latemul[®]PD-104 was used, but also in the reactions were Dowfax[®]2A1, Sipomer[®]Pam-200 and Sipomer[®]Cops-1 were used secondary nucleation occurred. Particle size distributions (PSDs) obtained from CHDF analysis (Figure 6.4) revealed that in all cases some extent of secondary

nucleation occurred when the highest surfactant concentration was used during the polymerization process and that for Latemul[®]PD-104 the number of small particles was relevant.

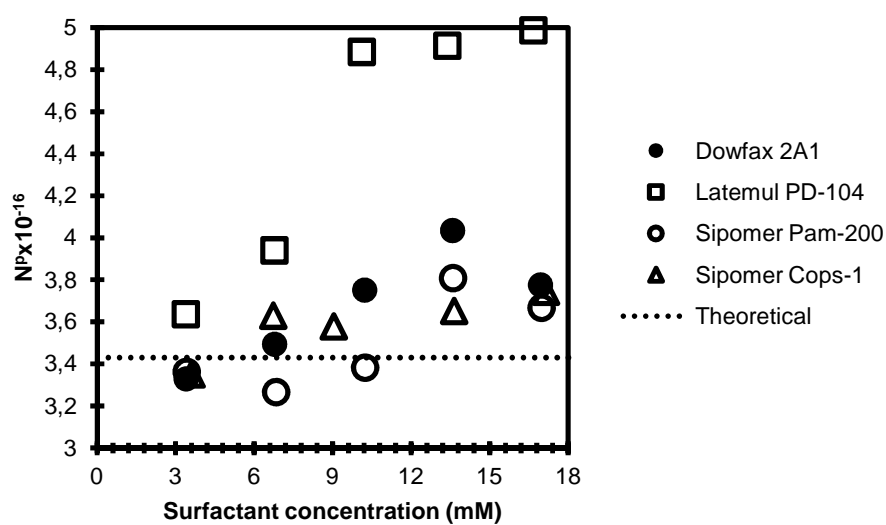


Figure 6.3. Number of polymer particles in the final latexes synthesized with different surfactant concentration.

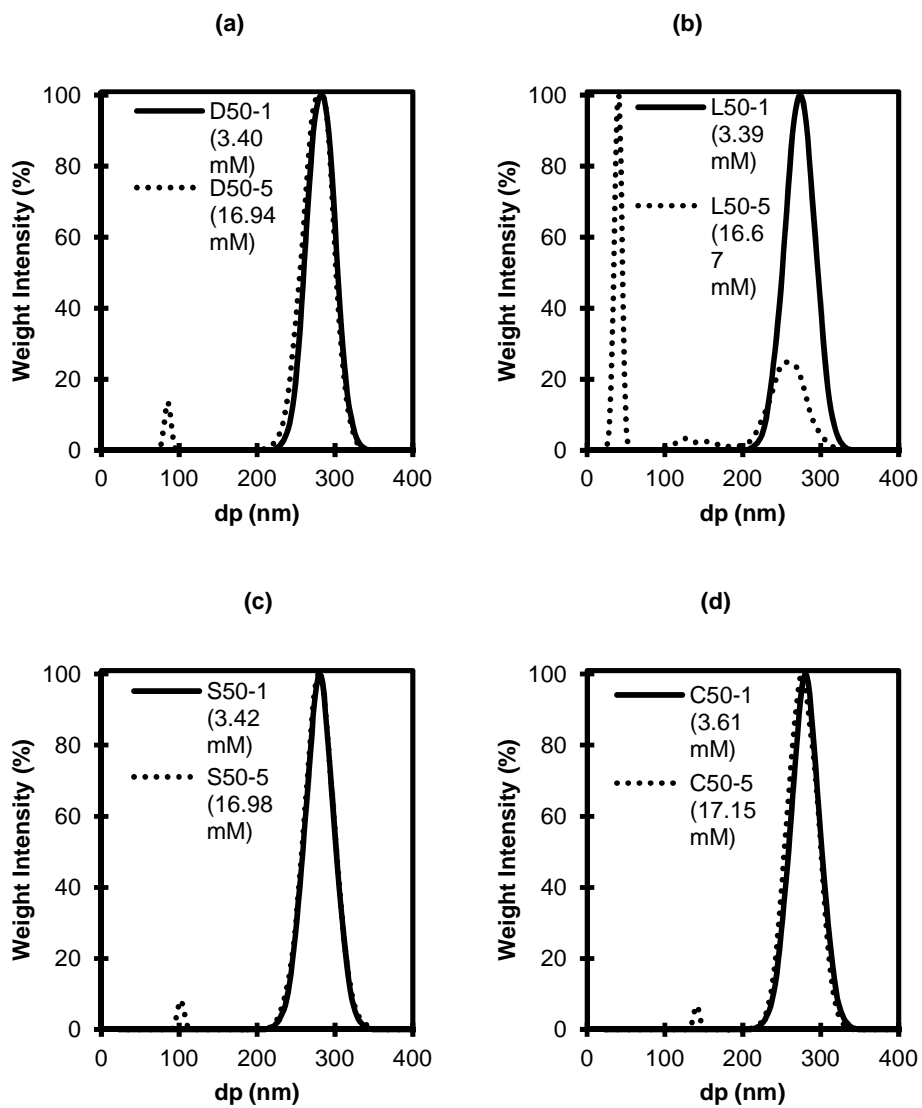


Figure 6.4. PSD of final latexes synthesized using different surfactant concentration and surfactant type: (a) Dowfax[®]2A1, (b) Latemul[®]PD-104, (c) Sipomer[®]Pam-200 and (d) Sipomer[®]Cops-1.

6.3.2. Polymer microstructure

Table 6.3 presents the gel content of the final latexes. Unexpectedly, the amount of gel produced depends on the surfactant concentration used during the synthesis.

Figure 6.5 shows the final gel content of the latexes synthesized using different surfactant and surfactant concentrations. As it can be seen in Figure 6.5, the gel content increased with the surfactant concentration, independently of the surfactant type used in the polymerization process. Same behavior was observed by Gonzalez et al.¹¹ when Sipomer[®]Pam-100 was used as a functional monomer of MMA/BA/MAA/AAEMA with Abex[®]2005 as surfactant; latexes with higher gel content were obtained (the gel content varied from 20% to 50% when the concentration of Sipomer[®]Pam-100 was increased from 0 to 5 wt%). They reported that the increase of the gel content was most likely due to the presence of impurities (divinyl ester phosphate) produced during the synthesis of Sipomer[®]Pam-100 that acted as a cross-linker. However, this hypothesis does not hold here because the same trend was observed for other surfactants that do not imply the presence of diacrylates in their synthesis.

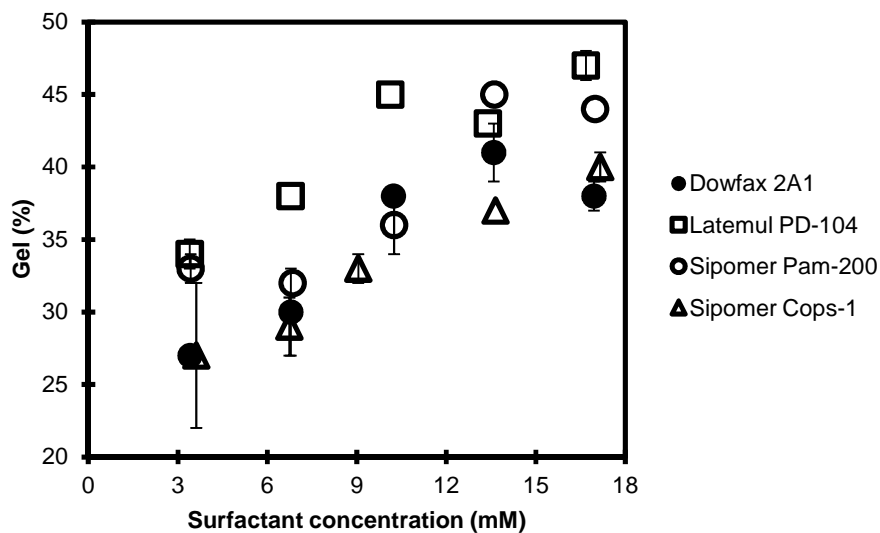


Figure 6.5. Gel content of the final latexes synthesized using different surfactant and surfactant concentrations.

Figure 6.6 shows the effect of the surfactant concentration on the sol molecular weight. As it has been described in previous works, the sol molecular weight decreases when the gel content increases (increasing surfactant concentration) due to the preferential incorporation of the large polymer chains into the gel^{34,35}.

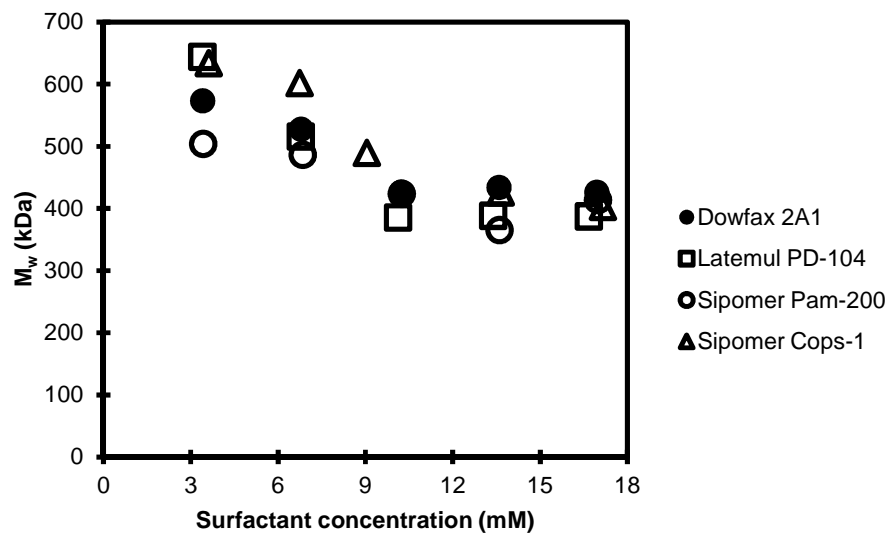


Figure 6.6. Sol molecular weight (M_w) of the final latexes synthesized using different surfactant and surfactant concentrations.

In emulsion polymerization of acrylates the increase in the gel content is mostly related to an increase in the cross-linking density (higher chain transfer to polymer followed by termination by combination). However, Figure 6.7 shows that this is not the case for the experiments carried out varying the surfactant concentration because swelling increased with the gel content. This means that the increase in the gel content when the surfactant concentration increased, was not related to the increase in the cross-linking density in the polymer microstructure (swelling is inversely proportional to the cross-linking density).

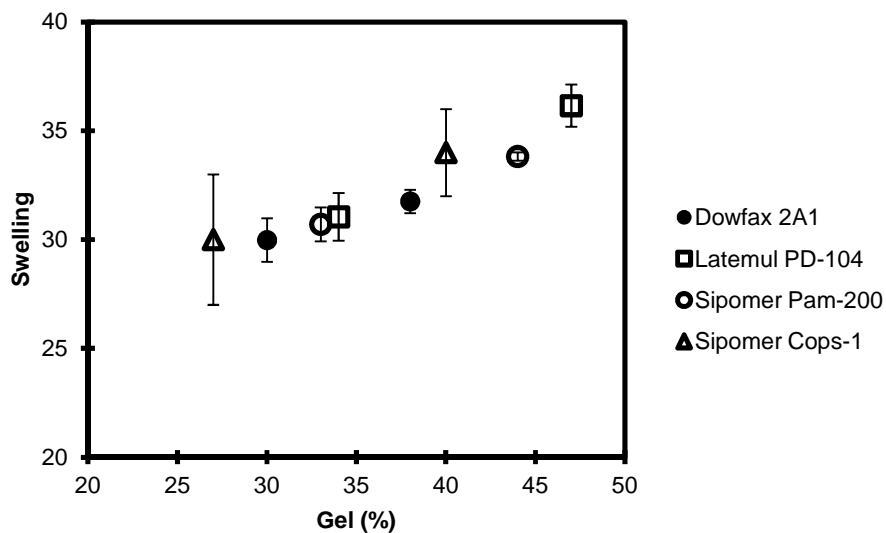


Figure 6.7. Effect of the gel content on the swelling capacity of the final latexes synthesized using different surfactants.

Therefore, a potential explanation for the increase in the gel with surfactant concentration could be an enhanced incorporation of the acidic monomer (AA) into the polymer backbone due to the higher number of polymer particles, that could decrease the solubility of the polymer in THF during Soxhlet extraction and hence increase the measured gel content. To verify this hypothesis, D50-5 polymer was modified by methylation of the carboxylic acid groups using trimethylsilyldiazomethane (TMS, Sigma-Aldrich) as shown elsewhere³⁶ and gel content of the methylated D50-5 latex was measured. It was observed that the gel content was reduced from 38 % to 26 % when the carboxylic acid groups were methylated.

6.4. Conclusions

In this chapter the effect of the pH and the effect of the surfactant concentration and type in the synthesis of high solids content pressure-sensitive adhesives were studied.

It was found that the pH used during the polymerization process had a strong influence on the kinetics and microstructure of the polymer produced. When basic pH was used during the polymerization process, more water-soluble species were formed and as a consequence lower monomer conversion was obtained. Furthermore, the polymer microstructure was also affected by the high pH leading to a polymer with negligible gel content (due to low conversion/monomer flooded conditions).

Also noticeable was that the surfactant concentration had an effect on the polymer microstructure. Increasing the surfactant amount (independently of the surfactant type used but more pronounced for Latemul[®]PD-104) a new population of polymer particles was produced increasing the total number of polymer particles. This increase in the number of polymer particles led to an increase of gel content that was attributed to an enhanced incorporation of the acidic monomer (AA) into the polymer backbone. Thus all the latexes synthesized at acid pH presented a substantial amount of gel polymer, the higher the surfactant concentration, the higher the gel content.

Part of this work was carried out in BASF SE (Ludwigshafen, Germany) during the internship and part of it has been published or will be published soon:

- Aguirreurreta, Z.; Dimmer, J.-A.; Willerich, I.; de la Cal, J. C.; Leiza, J. R. Water Whitening Reduction in Waterborne Pressure-Sensitive Adhesives Produced with Polymerizable Surfactants. *Macromol. Mater. Eng.* **2015**, *300*, 925–936.
- Aguirreurreta, Z.; Dimmer, J.-A.; Willerich, I.; Leiza, J. R.; de la Cal, J. C. Improving the Properties of Water-Borne Pressure Sensitive Adhesives by Using Non-Migratory Surfactants. *Accepted in International Journal of Adhesion and Adhesives*, **2016**.

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Chapter 7. Improving the properties of water-borne pressure-sensitive adhesives (PSAs) produced with polymerizable surfactants

7.1. Introduction

Pressure-sensitive adhesives (PSAs) are used in different applications such as tapes, labels, protective films, and medical products¹. Adhesives that are exposed to any of the following conditions will need some level of water whitening resistance: pasteurization process, retort process, water soak, dishwasher, shower/water spray, rain and high humidity environment². These types of conditions occur in different markets and applications such as filmic labels (bottle labels, shampoo labels, and food labels). For example, bottles labelled with PSAs when they are exposed to pasteurization conditions or exposed to long-term immersion in cool water (beer and beverage bottles), the label is expected to remain clear³. For these demanding applications, solvent-based adhesives have been used due to their excellent water resistance⁴. However, as environmental regulations favour the elimination of solvents, acrylic water-borne PSAs have become more attractive. As mentioned in Chapter 6, water-borne PSAs often have poorer properties when they are applied as film forming polymers due to migration of surfactant present in the final film.

Water whitening of PSAs is caused due to the presence of aggregates or hydrophilic pockets throughout the film. As water is drawn into the film by osmotic forces, the existence of hydrophilic pockets can result in localized defects such as discoloration and blistering because the hydrophilic pockets will swell when exposed to water^{2,5}. The swollen pockets usually have a refractive index different from that of the polymer, and hence they scatter light and the film becomes cloudy or white^{5,6}.

Several patents can be found where polymerizable surfactants have been claimed in order to improve water whitening resistance of PSAs⁷⁻⁹. However, to our best knowledge, the analysis of water whitening phenomena in PSAs in the open literature is scarce^{2,5}. Therefore, this chapter addresses the factors affecting the water whitening resistance of films made from poly(butyl acrylate-co-methyl methacrylate-co-acrylic acid) latexes that have been synthesized in Chapter 6.

Apart from studying the water whitening phenomena, the effect of the surfactant concentration and type (polymerizable or not) on the adhesive properties of PSAs is also investigated in this chapter. Tack, peel strength and shear strength are usually the three adhesive properties used to determine the performance of PSAs¹⁰. Tack measures how easily a PSA can stick to a substrate, peel strength test measures the force necessary to remove a PSA from a substrate and shear strength is related to the cohesive strength of the adhesive and is defined as the holding time of a PSA before falling from testing panel after application of a load.

Before going into detail analysing the adhesive properties and the water whitening phenomena, the surfactant migration within PSA films is studied in order to understand how surfactant migration affects the final properties of PSAs.

7.2. Experimental

The adhesive properties and water whitening resistance of acrylic PSAs synthesized with polymerizable surfactants/stabilizer (Latemul[®]PD-104, Sipomer[®]Pam-200 and Sipomer[®]Cops-1) and conventional surfactant (Dowfax[®]2A1) were studied. The synthesis of these latexes was presented in Chapter 6. Table 7.1 presents the main characteristics of these latexes. It is worth to remind that latexes made with conventional surfactant Dowfax[®]2A1 are designated as D50. Those made with polymerizable surfactants Latemul[®]PD-104 and Sipomer[®]Pam-200, L50 and S50, respectively, and latexes synthesized using the polymerizable stabilizer Sipomer[®]Cops-1 as C50. For the sake of clarity, PSA films were designated in the same way as the latexes that were coming from.

Table 7.1. Main characteristics of the formulation used to synthesize high solids content PSAs and main characteristics of the final latexes.

Latex	Surfactant concentration ^{a)} (mM)	SC (wt%)	dp ^{b)} (nm)	pH	Gel (%)	Surfactant incorporation degree (%) ^{c)}
D50-1b	3.40	47.9	299	9.7	1 ± 0	None
D50-1	3.40	50.2	304	1.8	27 ± 0	None
D50-2	6.78	49.9	299	2.1	30 ± 3	None
D50-3	10.22	49.9	292	2	38 ± 0	None
D50-4	13.58	50.1	285	2	41 ± 2	None
D50-5	16.94	49.2	290	1.9	38 ± 1	None
L50-1	3.39	49.9	295	2	34 ± 1	N/D
L50-2	6.77	49.3	286	2.3	38 ± 0	N/D
L50-3	10.11	48.6	265	2.3	45 ± 0	N/D
L50-4	13.38	48.4	264	2.2	43 ± 0	N/D
L50-5	16.67	48.0	262	2.1	47 ± 1	N/D
S50-1	3.42	49.5	302	2.1	33 ± 0	100
S50-2	6.84	49.5	305	2.1	32 ± 0	100
S50-3	10.24	47.4	297	2.4	36 ± 2	100
S50-4	13.60	49.6	290	2.6	45 ± 0	100
S50-5	16.98	49.8	294	2.8	44 ± 0	100
C50-1	3.61	49.8	303	2.1	27 ± 5	50
C50-2	6.73	49.8	295	2.2	29 ± 2	49
C50-3	9.04	49.6	296	2.2	33 ± 1	56
C50-4	13.64	49.6	294	2.2	37 ± 0	50
C50-5	17.15	49.6	292	2	40 ± 1	50

^{a)} Per litter of water (mmol/L). ^{b)} Measured by DLS. ^{c)} Measured by HPLC-ELSD.

Ultracentrifugation (at 50000 rpm for 16 h) was used to accomplish the separation of the aqueous phase from the polymer particles. The aqueous phase was dried in the oven and then redispersed in water (1.5 – 1.9 wt% of solids content) and directly analyzed by High Performance Liquid chromatography (HPLC) coupled with an Evaporative Light Scattering detector (ELSD) in order to determine the amount of unreacted surfactant.

Topography and phase images of the latex films were analyzed using atomic force microscope (AFM) of type Dimension Icon from Bruker in combination with Nanoscope V controller. For all measurements standard AFM Si₃N₄-tips AC160-TS from Olympus were used (K=26 N/m, f₀=300 Hz). All images were obtained using tapping mode with constant amplitude attenuation. To analyze the surface morphology 200 µm wet thick films were cast on a PET foil at room temperature. Cross-cuts of the latex films were prepared using a commercial cryo-microtome Ultracut-S from Leica/Reichert. Small droplets of the dried latex films were cooled down to a temperature of -80°C and then cut using a diamond knife. Afterward, the samples were measured at room temperature. AFM cross-section images of the films were taken in the middle of the film, as it is represented by the black square in Figure 7.1. AFM images of the air-film interface were also taken.

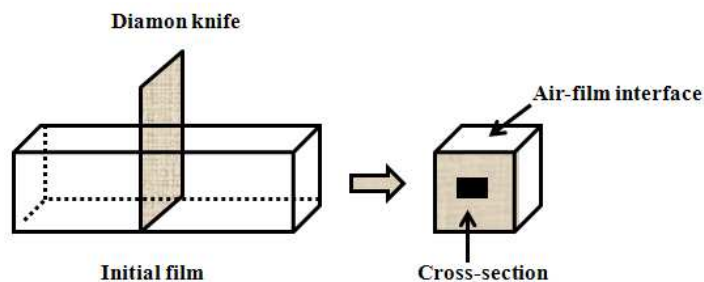


Figure 7.1. Schematic representation of the cross-cut of the films.

For the measurements of water static contact angle, 120 μm wet thick films were cast onto glass substrate, at 22°C and 55 % relative humidity during one day. The measurements were carried out in a Contact Angle System OCA (Dataphysics) equipment, taking an average value from 20 measurements. The contact angles were measured at the air-film interface before and after rinsing the films with water.

Shear adhesion failure temperature (SAFT) tests were carried out in a Binder oven (Sneep Industries) using stainless steel as the backing and as the substrate. The dispersions were coated to a level of 0.029 g/cm^2 (280 μm wet thick films) on the stainless steel backing and dried at 22°C and 55% relative humidity during 24 hours. Four samples per latex were tested and the average is reported.

The probe tack tests were carried out on a Stable Micro Systems TA HD Plus Texture Analyser using the Avery Adhesive Tape (ADH7_P1S) and the 1" stainless steel ball probe. For the preparation of the samples, 120 μm wet thick films were cast onto stainless steel

substrate and dried for 24 hours at 22°C and 55% of relative humidity. Three experiments were performed for each sample. The stainless steel ball probe was cleaned in between measurements.

Peel resistance was measured at 180° angle at speed of 300 mm/min in the Stable Micro Systems TA HD Plus Texture Analyser. 120 µm wet thick films were cast onto treated PET sheet and dried for 24 hours at 22°C and 55% of relative humidity. The dry films were attached in a stainless steel panel. The reported values are the average peel force obtained during the peel process.

To perform water whitening resistance test, the dispersions were coated to a level of 18.5-19.5 g/m² on a clear oriented polypropylene and dried at 90°C in an oven for 3 minutes. UV/VIS spectroscopy using a Specord S 300 UV/VIS spectrophotometer (Analytik Jena) was used to determine the opacity of the films. The films were placed in cuvettes which were filled with water at time zero. The absorbance between 300 and 650 nm was measured (see Appendix II for an example of the absorption data in latex stabilized with Dowfax®2A1 surfactant). Percentage opacity was used to evaluate water whitening resistance of the PSAs. Percentage opacity was determined from the average of the normalized absorbance as follows:

$$Opacity(\%) = \frac{\int_{300}^{650} A(\lambda)d\lambda}{650-300} \times 100 \quad (7.1)$$

where $A(\lambda)$ is the normalized absorbance with respect to a sample with light transmission lower than 0.1% and λ is the wavelength. Lower opacity numbers correspond to higher water whitening resistance.

Adaptive Speckle Imaging Interferometry (ASII) optical technique, which is based on the diffusive wave spectroscopy (DWS), was used to analyse the film formation process^{11,12}. The Horus[®] (Formulation) was used to perform the analyses. The principle of the measurements consists of sending laser light into the film. Part of incident coherent light is absorbed by the sample and the other part is scattered back and detected by the video camera through an interference image, also called Speckle image. During film formation the sample undergoes some changes such as particle movement or refractive index changes; this activity causes temporal fluctuations in the scattered light and, consequently, random changes of light intensity on the Speckle image. The speed of light fluctuations (the Speckle rate) during the drying process is directly related to the motion of the scatterers inside the sample. The motion of the particles is strongly dependent on the viscosity of the film in the way that as water evaporates, viscosity rises and the scatterers motion (Speckle rate) slows down. The main stages during film formation can thereof be associated with changes in the Speckle rate as shown in Figure 7.2. To study the effect of the pH on the drying kinetics 60 μm wet thick films were cast onto glass substrate. To study the effect of the surfactant amount all the samples were diluted to the same solids content (45 wt%) and then the samples were drawn on a glass substrate with a wet thickness of 120 μm . In all the cases the measurements were done at a relative humidity of 55% and a temperature of 22°C.

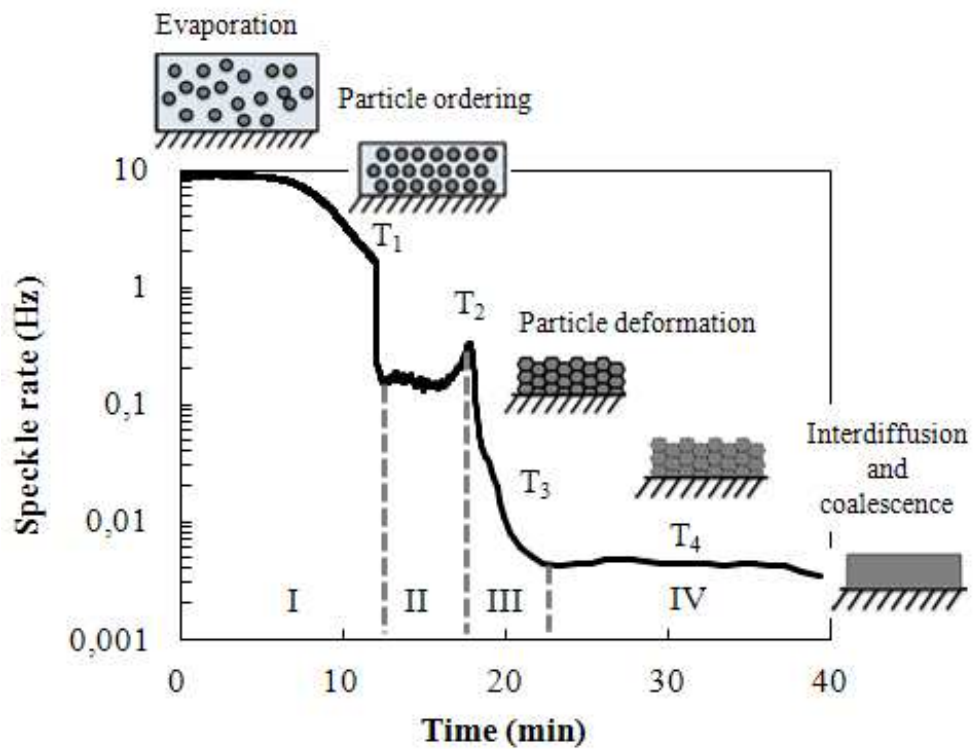


Figure 7.2. Drying kinetics of water-borne PSA as interpreted in the application notes of the Horus® (<http://www.formulation.com/microrheology-horus.html>).

To perform gravimetric analysis of water loss during latex drying, 60 μm wet films were cast onto glass substrate (10cm x 5cm) and immediately, samples were placed on a digital balance and the weight was recorded every minute during 1 hour.

7.3. Results and discussion

7.3.1. Assessing surfactant migration in PSA films

7.3.1.1. Incorporation degree of polymerizable surfactants into the polymer backbone

In order to determine the degree of incorporation of the polymerizable surfactants/stabilizer into the polymer backbone, the aqueous phase was analyzed by HPLC-ELSD. The unreacted amount of surfactant in the aqueous phase was measured and assuming that the rest of surfactant is in the polymer particle, the degree of incorporation was determined (Table 7.1).

When Sipomer[®]Pam-200 was used, unreacted surfactant was not found in the aqueous phase. Consequently, incorporation of Sipomer[®]Pam-200 was complete. This polymerizable surfactant has a methacrylic function in the structure; hence it copolymerizes well during the reaction.

Knowing that Sipomer[®]Cops-1 does not copolymerize well with the monomers used in this study, it was not surprising to find that only 50% of the stabilizer amount was incorporated into the polymer backbone. Similar results were obtained by Aramendia et al.¹³ when an alkenyl-based nonionic surfactant was used. The degree of incorporation of this alkenyl-based surfactant was around 40-60% depending on the polymerization process used.

In the case of Latemul[®]PD-104 it was not possible to track the unreacted amounts by HPLC due to the overlapping of relevant peaks. No attempt was made to change the separation protocol and hence improve separation.

7.3.1.2. Surfactant migration to the air-film interface

The surfactant migration to the air-film interface was assessed by water static contact angle measurements. Figure 7.3 presents the water static contact angles of the films formed from latexes stabilized using different amount of surfactant. Measurements made after immersing the films in water are also presented.

As it was expected, in the films made from latexes synthesized using the conventional surfactant Dowfax[®]2A1 (Figure 7.3a), increasing the surfactant concentration lower contact angle values were obtained due to the presence of higher amount of surfactant in the air-film interface yielding a more hydrophilic interface. In all cases cleaned films presented higher contact angle values indicating that at least part of the surfactant was removed from the air-film surface. The migration of the conventional surfactant was corroborated by the AFM images of the air-film interfaces (Figure 7.4). Figure 7.4 shows that by increasing the concentration of Dowfax[®]2A1 from 3.40 to 16.94 mM more surfactant was present in the air-film interface.

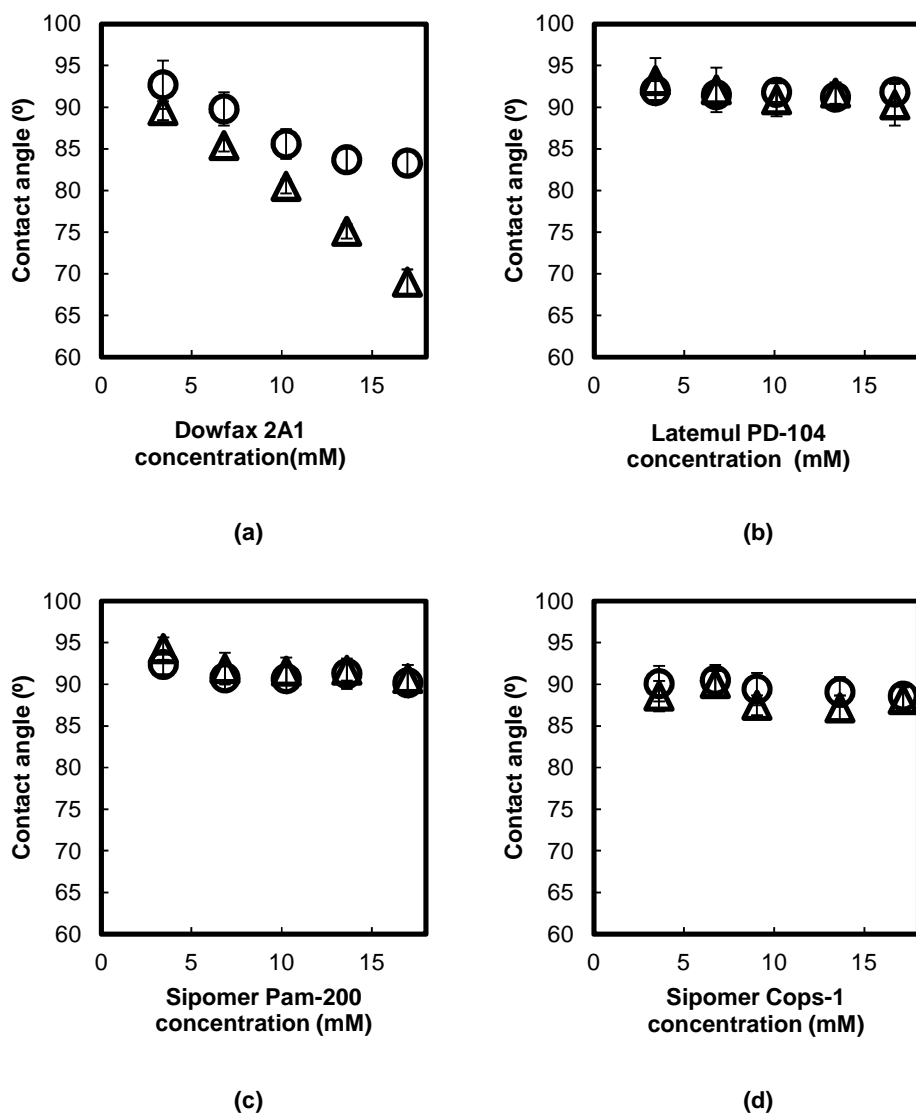


Figure 7.3. Water static contact angles of initial films (Δ) and cleaned films (\circ) stabilized with different surfactant concentration and type: (a) Dowfax[®]2A1, (b) Latemul[®]PD-104, (c) Sipomer[®]Pam-200 and (d) Sipomer[®]Cops-1.

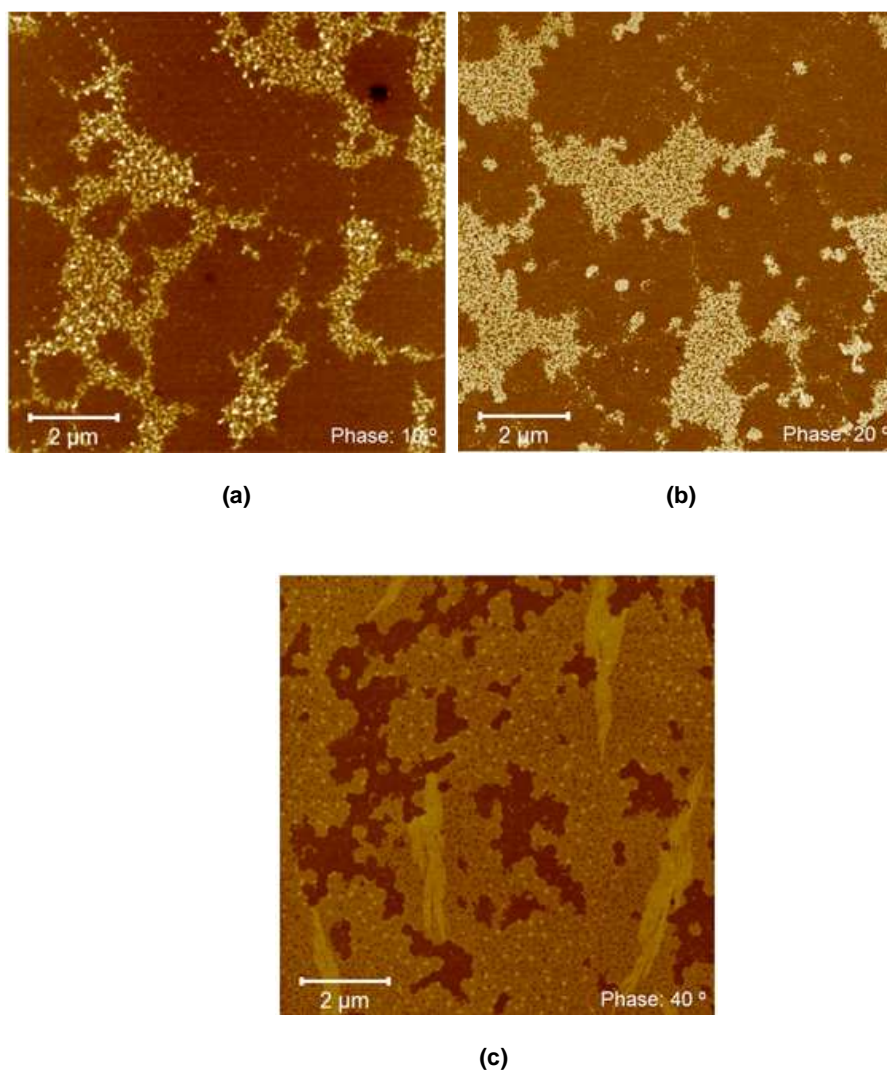


Figure 7.4. AFM phase images of the air-film surface of the films containing different Dowfax[®]2A1 concentrations. (a) 3.4 mM, (b) 10.22 mM and (c) 16.94 mM. The pH of the dispersion was adjusted to pH 8.5 before the film formation.

When polymerizable surfactants were used (Figure 7.3b and Figure 7.3c), the measured contact angle values were almost the same when the surfactant amount was increased. Furthermore, after rinsing with water contact angle values did not change. Due to the incorporation of the polymerizable surfactants to the polymer backbone the surfactant migration to the air-film interface was impeded. Incorporation of Sipomer[®]Pam-200 was complete (determined by HPLC of the serum) as it can be observed in Table 7.1. Although for the latexes synthesized with Latemul[®]PD-104, the degree of incorporation could not be determined; these observations suggest that at least part of Latemul[®]PD-104 was incorporated into the polymer backbone or that migration to surface was impeded.

When the polymerizable stabilizer Sipomer[®]Cops-1 was used (Figure 7.3d) a similar trend was observed; increasing the surfactant amount, almost the same contact angle value was measured. The contact angle values of the films containing this stabilizer were slightly lower than the values obtained in the films containing polymerizable surfactants. Furthermore, after rinsing with water it seems that some hydrophilic material was removed from the surface, because the contact angle values measured after rinsing were slightly higher. Taking into account that the degree of incorporation of this stabilizer was around 50%, some migration to the air-film interface of this stabilizer could be expected.

Figure 7.5 presents the AFM images of the air-film surface of the films made from latexes synthesized using polymerizable surfactant or stabilizer with the highest surfactant concentration (~17 mM). AFM images support the results obtained from water static contact angle measurements. Whereas no surfactant migration could be observed when the polymerizable surfactants were used (Figure 7.5a and Figure 7.5b), when the polymerizable

stabilizer was used, stabilizer migration to the air-film interface could be observed (Figure 7.5c).

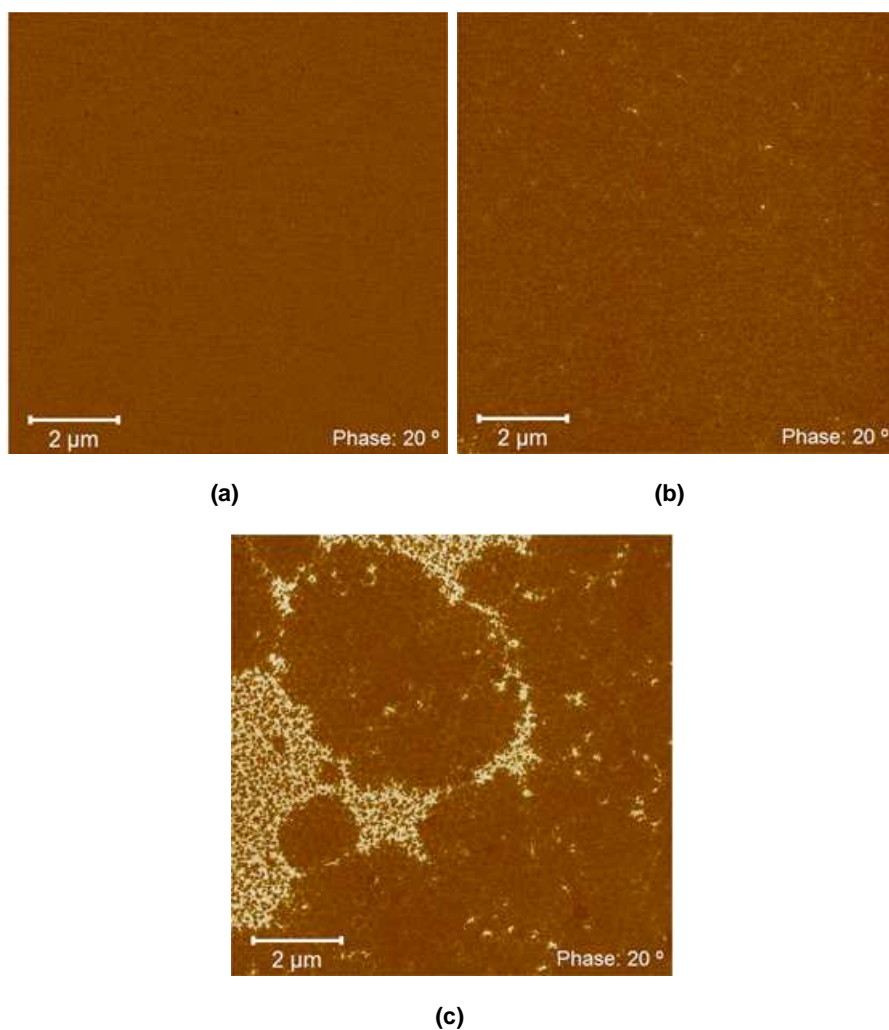


Figure 7.5. AFM phase images of the air-film surface of the films containing the highest surfactant concentration (~ 17 mM). (a) Latemul®PD-104, (b) Sipomer®Pam-200 and (c) Sipomer®Cops-1. The pH of the dispersion was adjusted to pH 8.5 before the film formation.

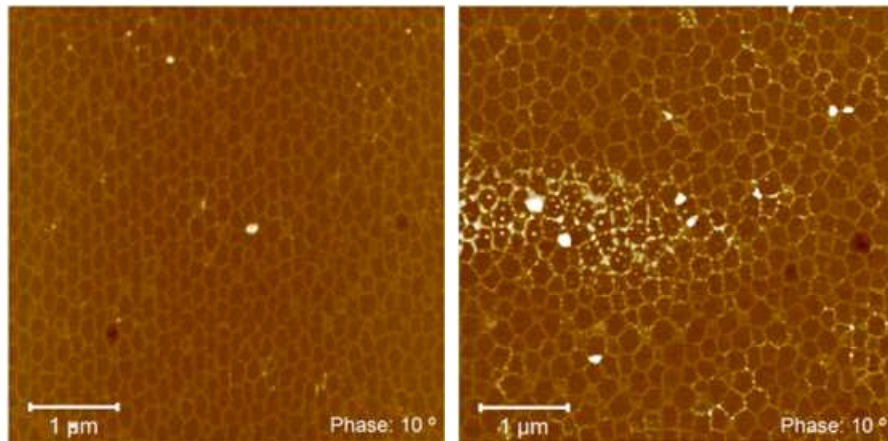
7.3.1.3. Surfactant aggregation within the film

In order to know if non-covalently bonded surfactant tended to aggregate forming hydrophilic pockets within the film, cross-section of the films were analyzed by AFM. Figure 7.6 presents the AFM images of the cross-section of the films with the lowest and the highest surfactant concentrations (~3.4 mM and ~17 mM, respectively).

AFM images of the cross-section of the films clearly showed that, surfactant aggregation between particle interstices only occurred when the conventional surfactant Dowfax[®]2A1 was used. It is noticeable that the higher the amount of Dowfax[®]2A1, the higher the surfactant aggregation within the film (Figure 7.6e).

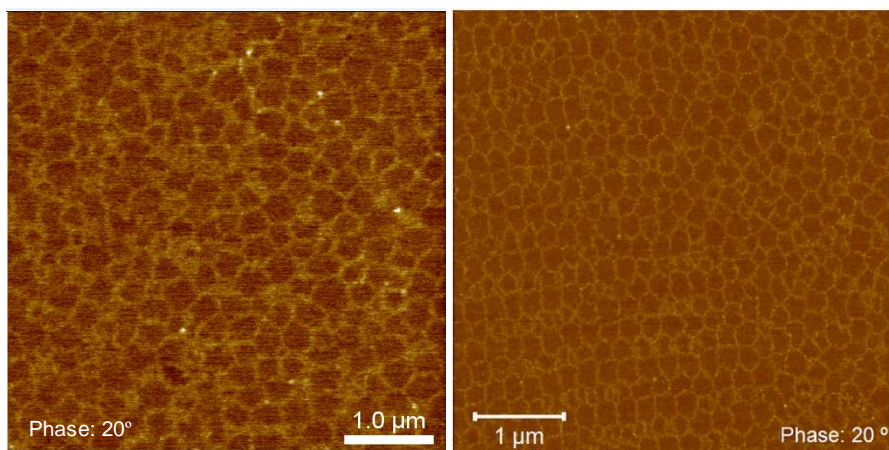
When polymerizable surfactants/stabilizer were used, due to the incorporation of the surfactant/stabilizer in the polymer backbone, the formation of surfactant pockets or aggregates within the film was avoided.

It is worth mentioning that, although surfactant migration to the air-film interface was observed when Sipomer[®]Cops-1 was used (Figure 7.5c), no aggregation was observed within the film (Figure 7.6d and Figure 7.6h). It seems that the unreacted stabilizer tended to migrate to the air-film interface and not to accumulate between particle interstices, probably due to its low molecular weight (218 g/mol).



(a)

(e)



(b)

(f)

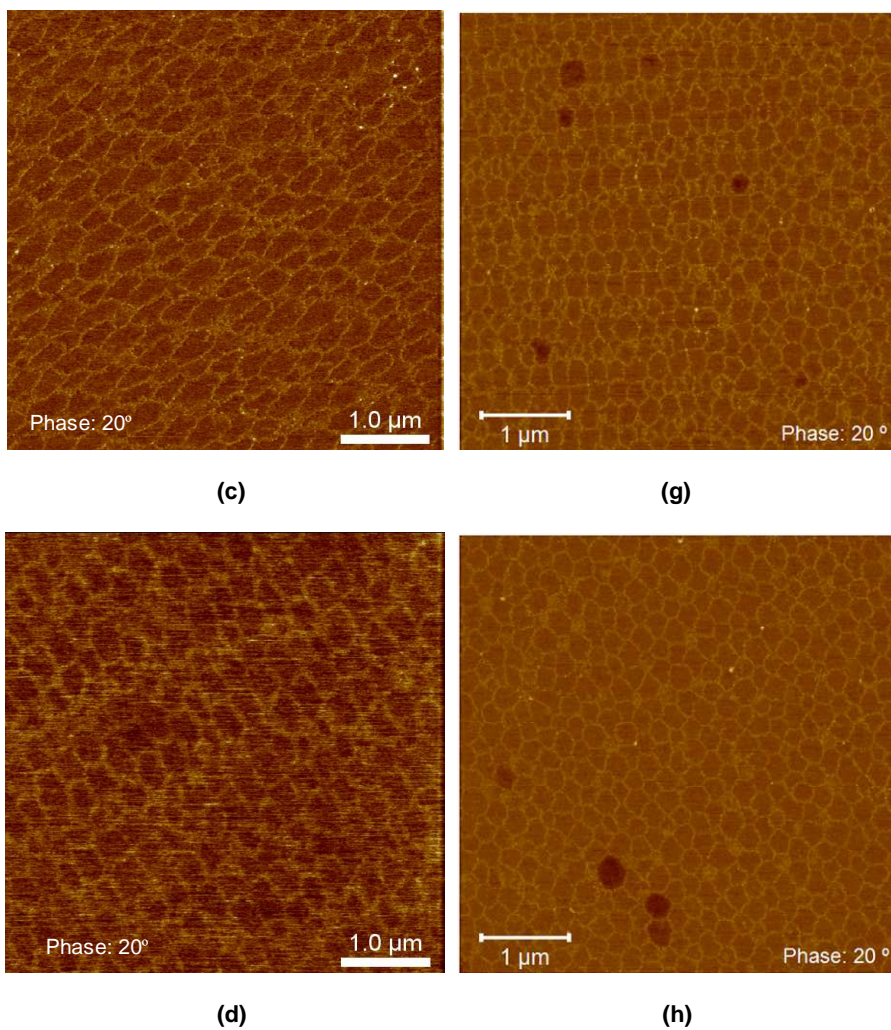


Figure 7.6. AFM phase images of the cross-section of the films with the lowest surfactant concentration (~ 3.4 mM): (a) Dowfax[®]2A1, (b) Latemul[®]PD-104, (c) Sipomer[®]Pam-200 and (d) Sipomer[®]Cops-1. Films containing the highest surfactant concentration (~ 17 mM): (e) Dowfax[®]2A1, (f) Latemul[®]PD-104, (g) Sipomer[®]Pam-200 and (h) Sipomer[®]Cops-1. The pH of the dispersion was adjusted to pH 8.5 before the film formation.

7.3.2. Adhesive properties of PSAs

The microstructure of the polymer^{14–18}, defined by the molecular weight distribution (MWD), cross-linking density and gel content, as well as the presence of functional monomers¹⁹ strongly affects the adhesive properties. In the previous chapter (Chapter 6) it was shown that increasing the surfactant concentration the gel content increased and sol molecular weight decreased, but interestingly swelling increased. As the major differences were found in the gel content of the latexes (see Table 7.1), the effect of the surfactant concentration and type on the adhesives properties of the latexes will be discussed as a function of the gel content of the latexes. It is worth mentioning that the sol molecular weight of latexes having similar gel content, were similar (Figure 7.7). Shear adhesion failure temperature (SAFT) measurements, peel resistance and probe tack analysis were carried out to assess the adhesive performance of the films obtained from the latexes synthesized in Chapter 6 and listed in Table 7.1.

Before measuring the adhesive properties all the latexes were diluted to 45 wt% of solids content and the final pH of the latex was set to 8.5 by adding ammonia (when necessary).

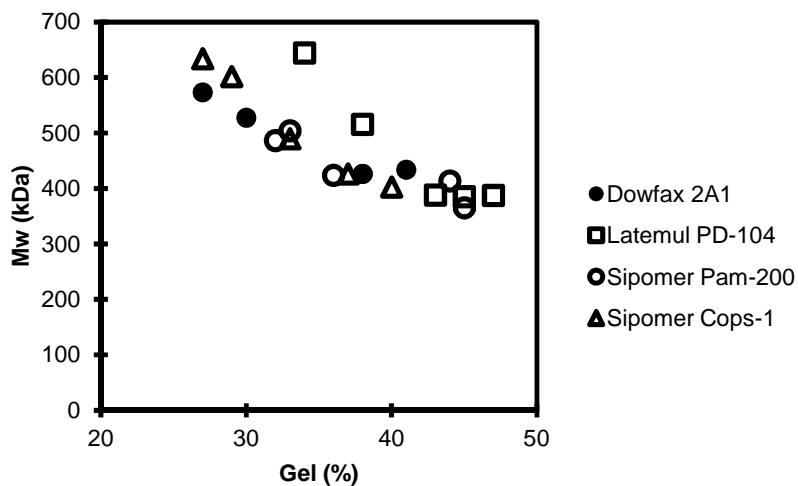


Figure 7.7. Sol molecular weight of latexes as a function of gel content.

7.3.2.1. Adhesive properties of latexes synthesized using the conventional surfactant Dowfax[®]2A1

Figure 7.8 presents the effect of the gel content on SAFT, peel strength and work of adhesion for the latexes synthesized using Dowfax[®]2A1 (D50-1b – D50-5). Figure 7.8a shows that the SAFT is affected by the gel content; the higher the gel content the higher was the SAFT due to a higher cohesion of the film, which is necessary for having cohesive strength^{17,20,21}. Tackiness, measured by the work of adhesion (Figure 7.8b) decreased with increasing gel content (above 30%) due to a decrease in chain mobility which is necessary for good tack^{14,20}.

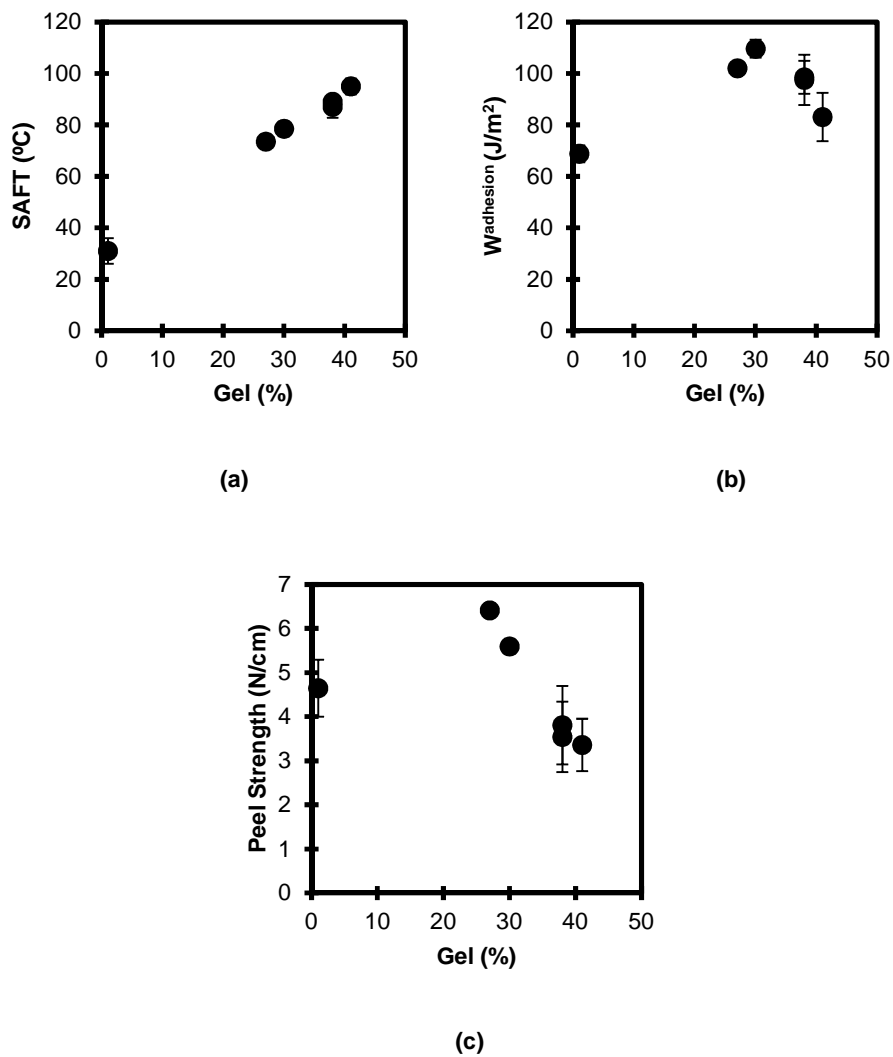


Figure 7.8. Effect of gel content on the adhesive properties for the latexes synthesized using Dowfax[®]2A1: (a) SAFT, (b) work of adhesion and (c) peel strength.

The fact that the latex having no gel (D50-1b) showed the lower work of adhesion could be related to a different adhesive failure as it is shown in Figure 7.9 where the stress-strain curves obtained in the probe tack test for the films made from latexes D50-1b (1 % of gel content) and D50-1 (27 % gel content) are presented. D50-1 latex showed adhesive failure, which is the typical behavior of cross-linked materials and is characterized by a maximum in the stress followed by a pronounced shoulder (fibrillation plateau) and a slight increase in the stress just before the final detachment due to the strain hardening of the material²². On the contrary, D50-1b showed cohesive failure (residual polymer was left on the probe), namely, typical behavior corresponding to liquid like materials where fibrils are formed, but as the material did not have any cross-link the fibril broke up easily. The peel strength (Figure 7.8c) showed similar trends as the work of adhesion.

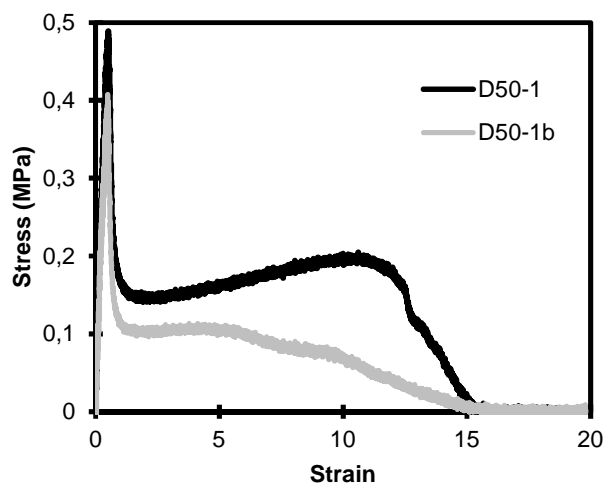


Figure 7.9. Stress-strain curves obtained in the probe tack test for latexes D50-1 and D50-1b.

7.3.2.2. Adhesive properties of latexes synthesized using polymerizable surfactants or polymerizable stabilizer

Figure 7.10 shows the effect of gel content on the SAFT of the latexes synthesized using Latemul[®]PD-104 (L50-1 – L50-5), Sipomer[®]Pam-200 (S50-1 – S50-5) and Sipomer[®]Cops-1 (C50-1 – C50-5). Results of the latexes synthesized using Dowfax[®]2A1 have been also included for the sake of comparison.

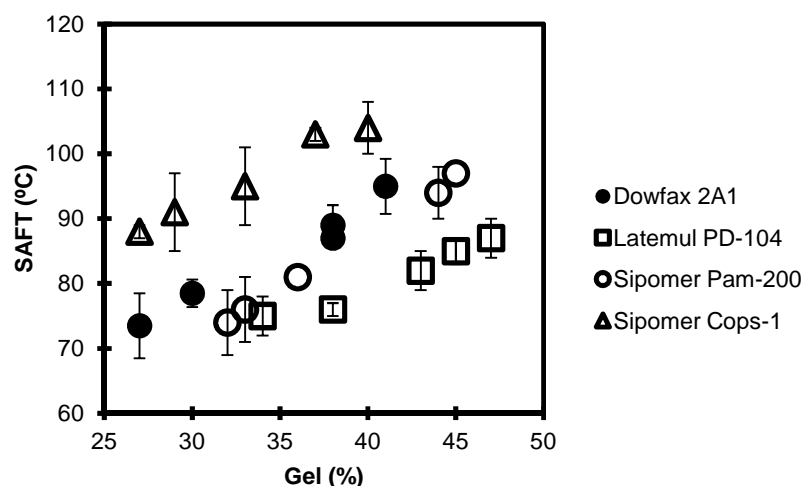


Figure 7.10. Effect of the gel content on the SAFT for the films obtained from latexes synthesized using different surfactant type.

In the films containing Latemul[®]PD-104, Sipomer[®]Pam-200 and Sipomer[®]Cops-1 SAFT increased with the gel content as in the films obtained from latexes synthesized using the conventional Dowfax[®]2A1. Whereas the SAFT values of the films containing Sipomer[®]Pam-

200 were somewhat similar to the films containing Dowfax[®]2A1, films containing the polymerizable stabilizer Sipomer[®]Cops-1 showed an improvement on SAFT for latexes with similar gel content. On the other hand, films made with Latemul[®]PD-104 showed lower SAFT.

It has been previously demonstrated that when polymerizable surfactants Latemul[®]PD-104 and Sipomer[®]Pam-200 were used, due to the incorporation of these polymerizable surfactants to the polymer backbone (determined by HPLC) no surfactant migration to the air-film interface nor surfactant aggregation within the film was observed in the AFM images (Figure 7.5 and Figure 7.6, respectively). When Sipomer[®]Cops-1 was used as stabilizer, due to a lower incorporation degree (~ 50%) surfactant migration to the air-film interface was observed (Figure 7.5c), but in a lower extent than the conventional surfactant Dowfax[®]2A1 did (Figure 7.4). Therefore, it could be said that the surfactant migration was not playing a role on the differences found on SAFT because when migration of the surfactant was not observed (films containing Latemul[®]PD-104 and Sipomer[®]Pam-200) similar or lower SAFT values compared to those obtained in the films containing Dowfax[®]2A1 were obtained. However, in Figure 7.10 it seems that the molecular weight of the surfactant used during the synthesis had an effect on the SAFT: the lower the molecular weight of the surfactant, the higher the SAFT.

Admitting that is speculative, a possible explanation for this observation could be found in the interdiffusion of the polymer chains across the interface of the particles in the final stages of the film formation process. In this regard, the structure of the species located at the particle interface might affect the bulk properties of the adhesive. The interdiffusion of the polymer chains may be less difficult for lower molecular weight emulsifiers improving cohesive strength. A similar effect was reported by Gonzalez et al.²³ for poly(acrylic acid)-*block*-poly(butyl

acrylate) (PAA-*b*-PBA) block copolymers of different molecular weights used as surfactants in the synthesis of acrylic polymers. They found that the interdiffusion of polymer between particles (measured by Fluorescence Resonance Energy Transfer (FRET)) and the mechanical properties of the films produced substantially decreased as the molecular weight of the block copolymers increased.

Regarding the work of adhesion (Figure 7.11), in the films containing Latemul[®]PD-104, Sipomer[®]Pam-200 and Sipomer[®]Cops-1 the work of adhesion decreased with increasing the gel content as in the films containing the conventional surfactant Dowfax[®]2A1.

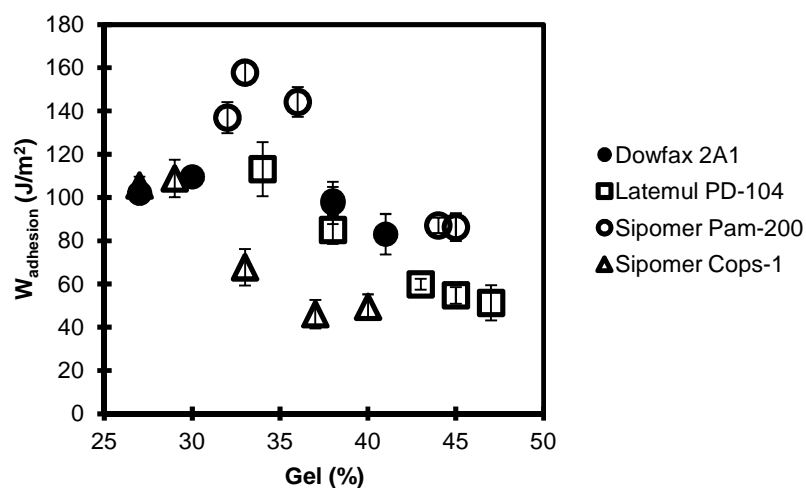


Figure 7.11. Effect of the gel content on the work of adhesion of the films obtained from latexes synthesized using different surfactant type.

As a representative example, Figure 7.12 presents the stress-strain curves obtained in the probe tack test for the films made from latexes synthesized using polymerizable surfactant Latemu[®]PD-104. As it can be observed in Figure 7.12, in all cases the maximum stress and the stress required to deform the fibrils was similar and therefore, the decrease of the work of adhesion with increasing gel content was due to a much shorter fibrillation plateau, which is in agreement with the data reported by Zosel²⁴. This result indicates that increasing the gel content the adhesive can be drawn in fibrils to lower strains before detaching.

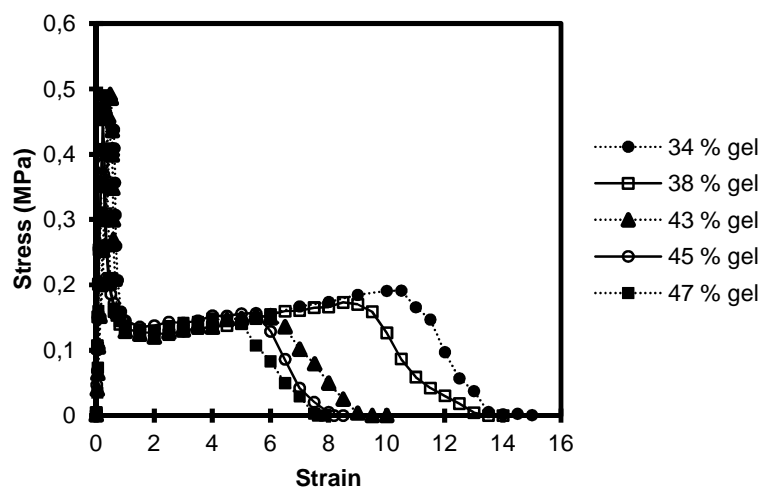


Figure 7.12. Stress-strain curves obtained in the probe tack test for adhesives with different gel content and synthesized using polymerizable surfactant Latemu[®]PD-104.

For samples with similar gel content (Figure 7.11), the films containing Sipomer[®]Cops-1 were the ones with the lower work of adhesion. Films containing Latemu[®]PD-104 behaved as

the ones containing Dowfax[®]2A1 whereas the films containing Sipomer[®]Pam-200 were the ones with the highest work of adhesion.

Figure 7.13 presents the stress-strain curves for the latexes having similar gel content (between 36 and 38% of gel content and, similar sol molecular weight) but containing different surfactant type. As it can be observed, the fact that the latexes having similar gel content but different surfactant type presented different work of adhesion seems to be mostly related to the difference in the fibrillation plateau.

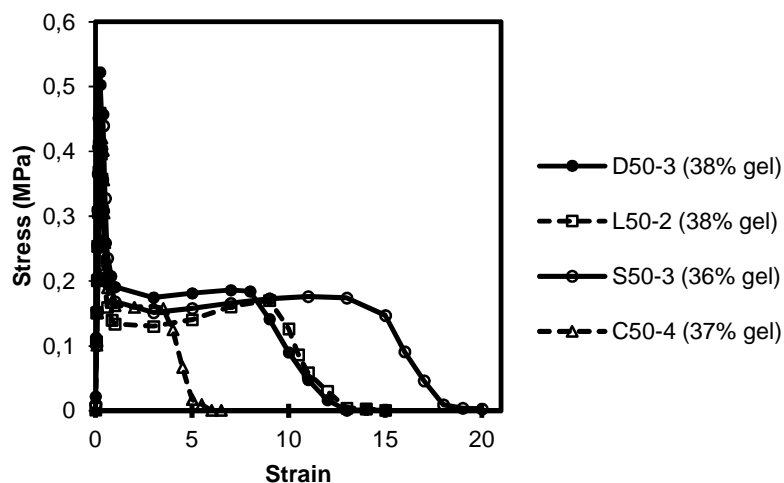


Figure 7.13. Stress-strain curves obtained in the probe tack test for adhesives with similar gel content but synthesized using different surfactants.

In the case of Sipomer[®]Pam-200 (S50-3) the enhanced work of adhesion was achieved through a higher plateau stress and a longer strain before failure (detaching from the probe).

Sipomer[®]Pam-200 has a phosphate group in its structure that it is known to improve the adhesion to metal substrates due to the chemical interactions established with the metal surface^{25,26}, which likely explained the higher values obtained for these latexes at different levels of gel polymer.

Figure 7.14 shows that in all cases the peel strength decreased with the gel content. However, it is noticeable that the effect of the surfactant system in the peel strength differs from that observed previously in the work of adhesion.

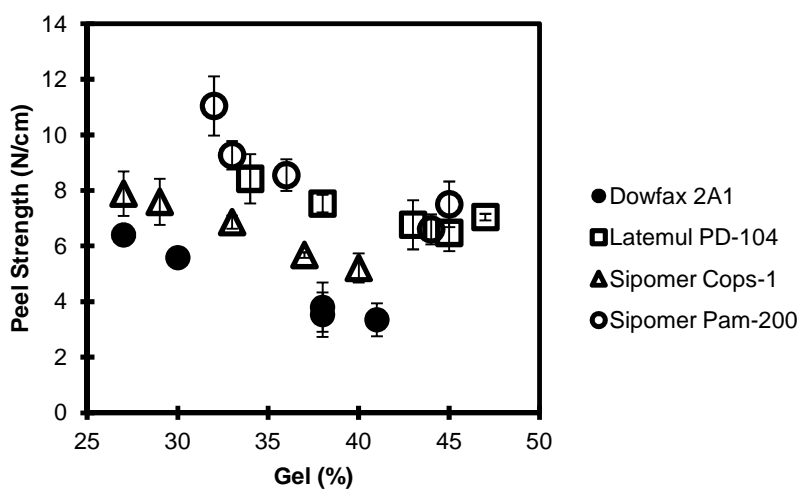


Figure 7.14. Effect of the gel content on the peel strength of the films obtained from latexes synthesized using different surfactant type.

Films containing the conventional surfactant Dowfax[®]2A1 presented the lowest peel strength whereas films containing the polymerizable surfactants Sipomer[®]Pam-200 and Latemul[®]PD-104 presented the highest peel strength. These results might suggest that the migration of the surfactant to the air-film interface had a negative effect on the peel strength. When the polymerizable surfactants Latemul[®]PD-104 and Sipomer[®]Pam-200 were used, no migration to the air-film interface was observed (Figure 7.5a and Figure 7.5b, respectively) and as a consequence films with improved peel strength were obtained. When Sipomer[®]Cops-1 was used, some extent of migration was observed (Figure 7.5c), but as the migration was reduced comparing to that of the Dowfax[®]2A1 (Figure 7.4) the peel strength was also improved.

Although in essence, the debonding mechanism in probe tack and peel test is similar (the energy required to debond and adhesive from a substrate) due to the different test conditions (dwell time, sample geometry and debonding rate) the viscoelastic behavior of these adhesives can change during debonding leading to a higher relative influence of the interfacial adhesion and/or interfacial cracks for the 180° peel test.

7.3.3. Water whitening resistance of PSAs

7.3.3.1. Effect of the pH

Figure 7.15 presents the results of water whitening resistance test for the films obtained from D50-1b and D50-1 latexes. The difference between both latexes was that whereas D50-1b latex was synthesized under basic conditions (pH=9.7), D50-1 latex was synthesized at acidic conditions. For comparison purposes, the final pH of D50-1 latex was increased to 9.7 before making the film.

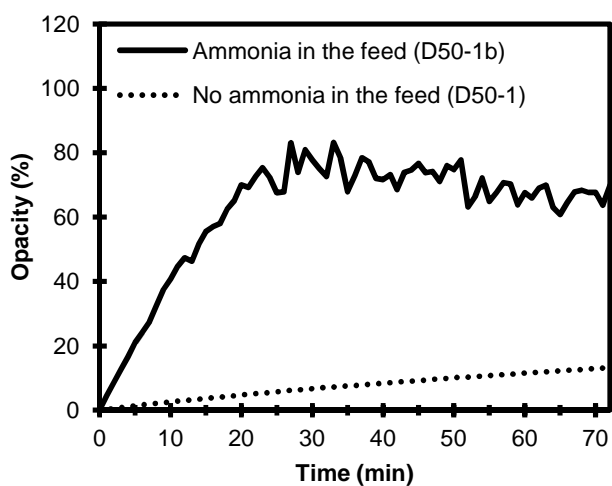


Figure 7.15. Comparison of the opacity of films cast from latexes produced at different pH during the polymerization process. The acidic latex (D50-1) was neutralized with ammonia to the same pH of D50-1b.

As it can be observed in Figure 7.15, the opacity of D50-1 film was much lower. In Chapter 6 it has been concluded that, by using low pH during the reaction, the formation of

water-soluble oligomers was reduced. As a consequence, the water whitening resistance was considerably improved for latex D50-1.

It is postulated that²⁷, during film formation, water-soluble species become trapped in the interstitial areas of the film. These species are hydrophilic and, hence, become the driving force for the diffusion of water into the interstitial areas causing the water whitening phenomena. It is, therefore, likely that water-soluble species have a detrimental effect on water whitening resistance of the films, and, hence, care should be taken with process conditions that favor the formation of water-soluble material.

It is worth to mention that it was not possible to obtain a high quality film on the oriented polypropylene sheet from D50-1 latex at the pH obtained after the reaction (pH=1.8) due to de-wetting predominantly caused by the lower viscosity of the carboxylated latex at this pH²⁸. Therefore, the final pH of D50-1 latex was adjusted to different values using ammonia and the effect of the final pH on the water whitening resistance was studied. Figure 7.16 displays the results of water whitening resistance test for the films made from D50-1 dispersion at different pHs. As it can be observed, the higher was the pH, the better was the water whitening resistance (lower opacity).

It is known that copolymers containing carboxylic acid groups, such as acrylic acid, are pH-responsive¹⁹. When the $\text{pH} < \text{pK}_a$, the carboxylic acid is not dissociated. At higher pH values, when they are negatively charged, carboxylic acid groups provide colloidal stability in the wet latex due to the electrosteric stabilization. During the film formation, while the water continues evaporating, the concentration of electrolyte in the remaining aqueous phase will

increase and, as a consequence, loss of particle stability could be expected⁶. If the loss of stability occurs early during the drying process, bulk aggregates could be formed, hindering uniform film formation. As a consequence, at lower pH, a less uniform film would be obtained due to poorer electrosteric stabilization. Hence, more defects would be present in the final film structure where water-soluble species can be trapped, increasing the opacity when the film is immersed in water. Arnold et al.²⁹ observed a similar effect on the surfactant distribution during film formation of carboxylated latexes at different pHs. They partially attributed the heterogeneity of the surfactant distribution to the surface charge density effect on the particle packing; namely, as discussed in this work, a more stable formulation leads to a better polymer particle packing (better film structure) and, hence, a better distribution of the surfactant in the film.

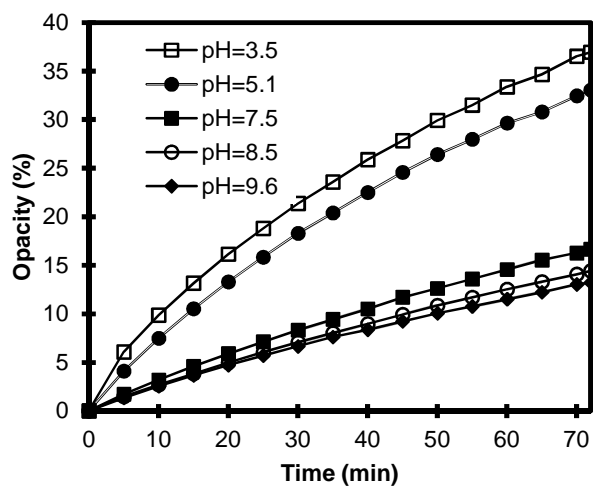


Figure 7.16. Effect of the pH of the final dispersion in the opacity of the films.

A support for the mentioned hypothesis is provided by AFM images of the cross-section of the films. The obtained phase images are shown in Figure 7.17 for the films made from D50-1 dispersion at two final pHs, 3.5 and 8.5, respectively. The packing efficiency of the particles in the film (as a measure of the stability during film formation) was evaluated by quantifying the number of neighbors of the particles. In the film made with the dispersion at pH 8.5, 80% of the particles had six neighbours in the plain, meaning that the majority of the particles present hexagonal close-packing, whereas in the film made at pH 3.5, only 49% of the particles had six neighbours presenting greater disorder. Therefore, AFM images also confirm the hypothesis that the higher the stability of the latex, the better the regularity of the film (less defects and hence less room for accumulation of water-soluble species), and, hence, the lower the opacity.

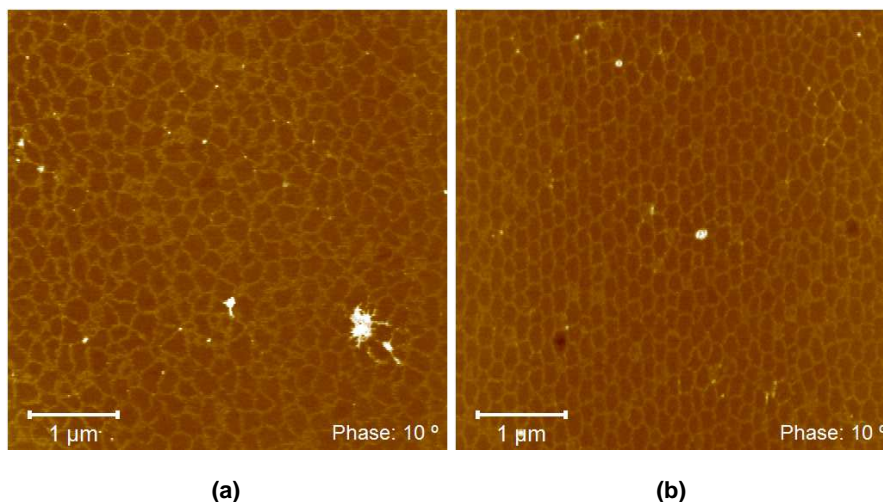


Figure 7.17. AFM cross-section phase images of the films made from D50-1 latex at different final pH. (a) pH 3.5 and (b) pH 8.5.

Furthermore, the effect of the final pH on the drying kinetics and water evaporation of the D50-1 dispersion was also studied. As it can be observed in Figure 7.18, up to water fractions of 30 wt% (close to the maximum volume fraction for random close-packing of monodisperse hard spheres; 64%), the evaporation was not affected by the pH of the dispersion, but upon reaching such water content, the evaporation rates clearly deviated for each pH; namely, the latex at higher pH lost water much faster than the latex at acidic pH. This result is in good agreement with the data reported by Wang et al.¹⁹ that also found that the time needed to evaporate most of the water in latexes was substantially higher at acidic pH (the time required for evaporation, for a latex at pH 3.5 was almost double than for the latex at pH 9.5). Figure 7.18 and Table 7.2 reports the Speckle rate and the characteristic times at the end of the three stages of the drying kinetics according to the criteria reported in Figure 7.2, respectively. The comparison of the data shows that the time needed to evaporate most of the water during the film formation and the end of stage III of the Speckle rate were somewhat correlated. Although the times needed to fully evaporate the water and to reach the end of stage III did not perfectly match, they were in reasonable agreement as well as the difference between the two latexes.

A possible explanation for this different behavior could be that, at lower pH value, the carboxylic acid is not dissociated and, hence, there are hydrogen bonding interactions between COOH and water³⁰. As a consequence, water molecules are restricted and evaporate more slowly, and the film, therefore, takes longer time to reach the dry stage¹⁹. A direct consequence of this could be that, if the drying takes longer time at lower pH, water-soluble species, such as

surfactants, will have more time to aggregate within the film, and hence water whitening resistance will be negatively affected (Figure 7.16).

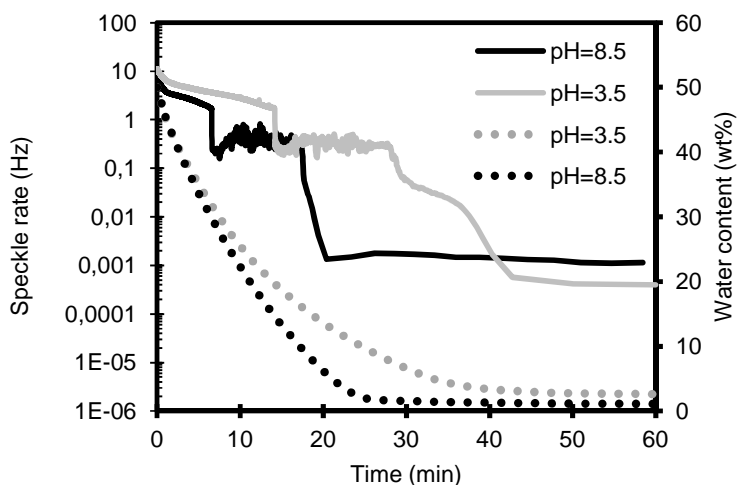


Figure 7.18. Gravimetric water content as a function of time (dashed lines) and drying kinetic profiles obtained from the Horus (solid lines) of D50-1 latex at different pH.

Table 7.2. Characteristic times of the drying kinetics of D50-1 latex at different pH.

pH	End of stage I (min)	End of stage II (min)	End of stage III (min)
3.5	14.1	28	42.5
8.5	6.5	17.3	20.5

7.3.3.2. Effect of the conventional anionic surfactant concentration

Figure 7.19 presents the results of water whitening resistance test for the films obtained from D50-1 – D50-5 latexes. The difference between the dispersions was the surfactant concentration (Dowfax[®]2A1) used in the synthesis (Table 7.1). For comparison purposes, the final pH of all the dispersions was increased to 8.5. Figure 7.19b presents the opacity (%) value of each film at the end of the measurement (at 120 min) versus surfactant concentration. Clearly, a minimum around 10 mM was observed on the opacity value probably due to two counteracting mechanisms: latex stability and excess of surfactant in the aqueous phase.

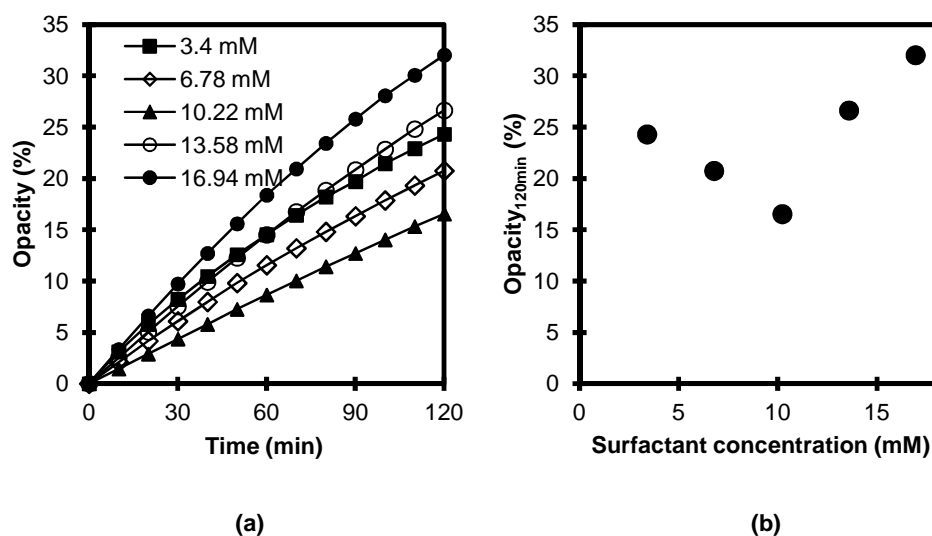


Figure 7.19. Opacity of the films formed from latexes produced using Dowfax[®]2A1: (a) evolution of the opacity during the experiment and (b) opacity values at the end of experiment (120 min) versus surfactant concentration.

The mechanism by which a better film structure is obtained could be that the ordering of the particles during water evaporation is affected by the electrostatic repulsive interaction between particles³¹. These interactions are directly related to the amount of surfactant adsorbed on the particle surface. Juhué and Lang³¹ found that ensuring maximum colloidal stability of the latex by post-adding surfactant to a latex until full coverage of the particles leads to an optimum packing of the particles. Poorer colloidal stability resulted in the settling of the particle flocs.

If the amount of surfactant is insufficient at the particle surface, the repulsive interactions should be weak and flocculation can occur during water evaporation. As a consequence, more defect or voids could be formed in the films and, hence, poorer water whitening resistance is expected. Increasing the surfactant concentration from 3.4 to 10.11 mM, the repulsive interaction would be stronger yielding a better film structure, and hence improving water whitening resistance of the films up to 10.22 mM of surfactant concentration. This hypothesis is supported by AFM images of the cross-section of the films (Figure 7.20). Increasing the surfactant amount from 3.40 to 10.22 mM (Figure 7.20a-c), a more homogeneous film structure was obtained; higher particle orientation could be observed within the film.

However, further increasing the surfactant concentration (from 10.22 to 16.94mM), although higher coverage of the particles would be expected, led to a poorer water whitening resistance of the final films. From these results, it can be concluded that other aspects besides the structure of the film also do play a role in the water whitening resistance, and upon achieving certain degree of stability, further addition of surfactant has a deleterious effect due

to an excess of surfactant present in the aqueous phase. As it can be observed in the AFM images of the cross-section of the films (Figure 7.20), increasing the surfactant concentration from 10.22 mM (Figure 7.20c) to 16.94 mM (Figure 7.20d), the excess of surfactant aggregated within particle interstices, lowering water whitening performance of the films.

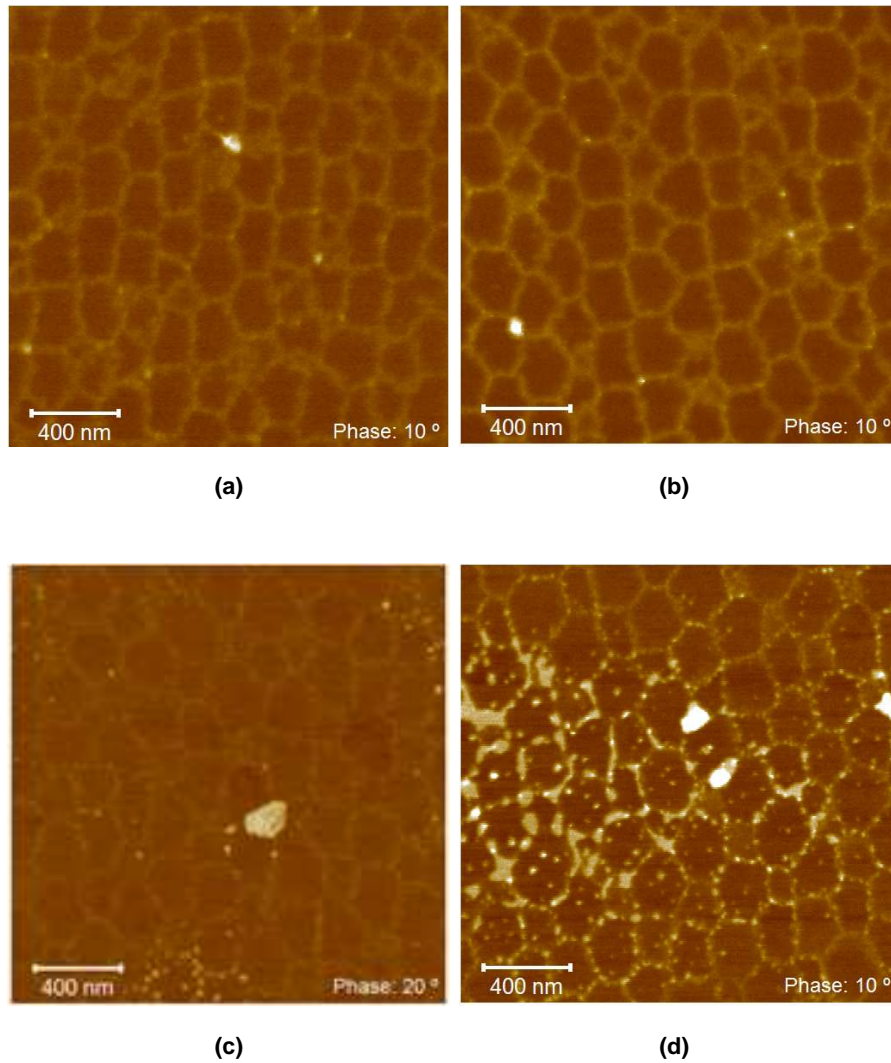


Figure 7.20. AFM images of the cross-section of films made from latexes synthesized using different Dowfax[®]2A1 concentrations (pH 8.5). (a) 3.40 mM, (b) 6.78 mM, (c) 10.22 mM, and (d) 16.94 mM.

7.3.3.3. Improving water whitening resistance using polymerizable surfactants/Stabilizer

Figure 7.21 presents the final opacity (%) values (after 120 min immersed in water) for the films made from latexes synthesized using different concentration of polymerizable surfactants (Latemul[®]PD-104 and Sipomer[®]Pam-200) and polymerizable stabilizer (Sipomer[®]Cops-1). For comparison purposes, the final pH of the dispersion was adjusted to 8.5. Values for Dowfax[®]2A1 have been also included in Figure 7.21 for the sake of comparison. Contrary to what was observed for the conventional surfactant Dowfax[®]2A1, when polymerizable surfactants or stabilizer were used, water whitening resistance improved with increasing surfactant concentration even at surfactant concentrations that showed a deleterious effect for Dowfax[®]2A1 (from 10 to 17 mM). When polymerizable surfactants or stabilizer were used, high concentration of surfactant did not have any negative effect on the water whitening resistance likely, due to the incorporation of the surfactant/stabilizer in the polymer backbone and reduction of surfactant migration within the film, and hence avoiding aggregation between particle interstices. AFM images of the cross-section of the films (Figure 7.6) clearly showed that, when high surfactant concentration was used (around 17 mM), surfactant aggregation occurred within the film only when the conventional surfactant Dowfax[®]2A1 was used (Figure 7.6e).

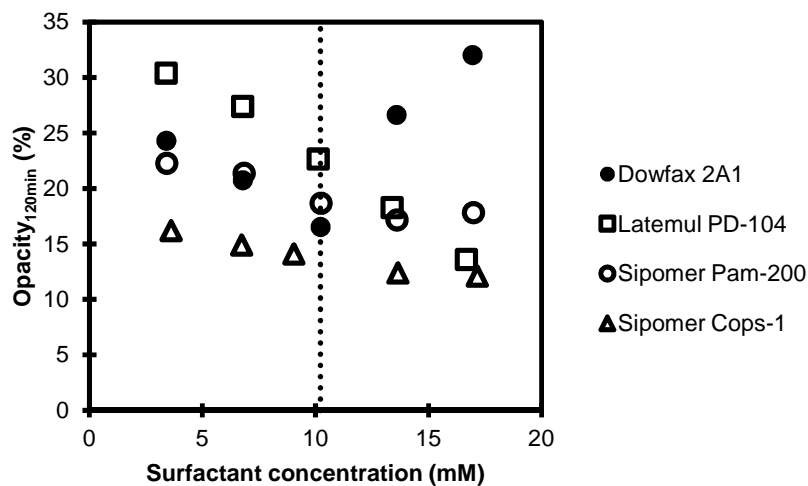


Figure 7.21. Effect of the surfactant concentration and type on the final opacity of the films.

When surfactant concentration was below 10 mM, the same trend was observed for all the surfactants; increasing the surfactant concentration water whitening resistance was improved. As it was discussed above, increasing the surfactant concentration leads to a more homogeneous structure due to a stronger repulsive interaction, and hence, improved water whitening resistance. AFM images revealed that increasing the surfactant amount from 3.4 mM (Figure 7.6a-d) to 17 mM (Figure 7.6e-h) better film structure was obtained.

The differences in opacity values for the different surfactants at the same concentration can be due to several factors that are not straightforward. Although the same molar concentrations were used and, hence, the same concentration of charges could be expected (e.g., similar surface charge density), the parking area is not the same for all the surfactants,

and hence, the amount of surfactant adsorbed in the particle surface might be different and the stability provided by different surfactants at the same concentrations too. Also, it should be noted that the amount by weight of each surfactant was different because the molar masses differed substantially (see Chapter 2), and hence for the same concentration, those with higher molar mass will be proportionally more abundant in the film (e.g., Latemul[®]PD-104).

In order to shed more light on these results, the kinetics of film formation was studied. Figure 7.22 presents the characteristic values of the end of stage III of film formation for latexes synthesized using different surfactant concentration. As it can be observed, the water evaporation (which is related with the end of stage III of film formation) was affected by the surfactant system as well as by the surfactant concentration.

The addition of surfactant has been correlated with slower evaporation rates^{32,33}. However, other studies showed that surfactant accelerates the evaporation of water^{34,35}. Winnik and Feng³⁵ found that, adding extra SDS to acrylic latex, the drying rate increased. They suggest that surfactant creates a hydrophilic membrane that aids water evaporation. In this study, both trends could be observed. On the one hand, when the conventional surfactant Dowfax[®]2A1 was used, the increase of the surfactant concentration lowered the water evaporation at high surfactant concentrations, probably due to the migration of surfactant to the surface of the films (Figure 7.4), forming a barrier at the interface that retards water evaporation. On the other hand, when polymerizable surfactants or stabilizer were used, the increase in the surfactant/stabilizer concentration led to shorter times for water evaporation (except for Sipomer[®]Pam-200, where the time to reach the stage III remained almost constant). When polymerizable surfactants/stabilizer was used, surfactant migration to the air-film

interface was reduced or impeded (Figure 7.5); therefore, faster water evaporation was observed probably due to the hydrophilic membrane created by the surfactant that favored water evaporation.

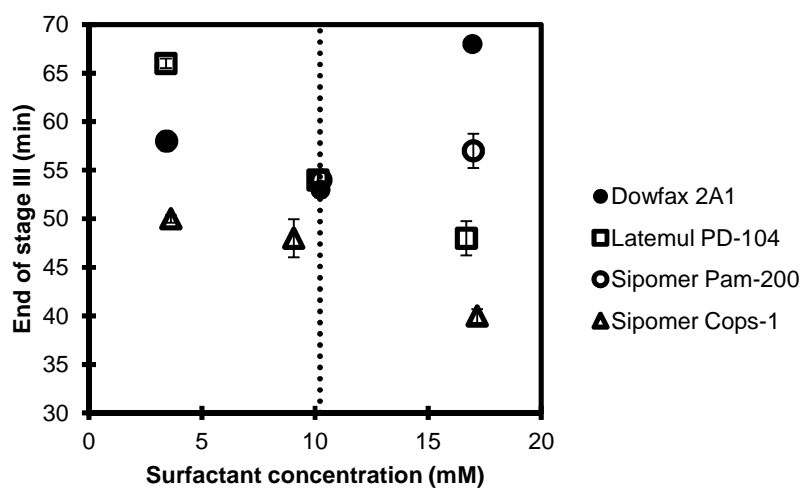


Figure 7.22. Characteristic values of the end of stage III of the film formation obtained from drying kinetics measurements.

Interestingly, the results obtained from the drying kinetics followed the same trend found in the opacity values. When the lowest amount of surfactant concentration was used (3.4 mM), the film reaching faster the end of stage III was the film containing Sipomer[®]Cops-1. Films containing Dowfax[®]2A1 and Sipomer[®]Pam-200 behaved similar, whereas the one with Latemul[®]PD-104 took longer time to reach the end of stage III.

7.4. Conclusions

In this chapter the adhesive performance and water whitening resistance of pressure-sensitive adhesives synthesized using polymerizable surfactants/stabilizer were studied.

In Chapter 6 it was found that the pH used during the polymerization process had a strong influence on the microstructure and therefore, on the final adhesive properties. When the polymerization was carried out under basic pH gel was not formed and hence, the SAFT, the work of adhesion and the peel strength of the final film were considerably reduced.

It was observed that latexes synthesized under acidic pH presented a substantial amount of gel polymer, the higher the surfactant concentration, the higher the gel content (Chapter 6). Therefore, the final adhesive properties were mostly dominated by the gel content.

SAFT and the work of adhesion of the films made of latexes with different surfactants and concentrations were not affected by the surfactant migration. However, it was found that the molecular weight of the surfactant was playing a role in the adhesive properties, e.g. the lower the molecular weight of the surfactant, the higher the SAFT. Films made of Sipomer[®]Pam-200 showed an excellent work of adhesion, most likely due to favourable interaction of the phosphate groups with the stainless steel probe employed.

The peel strength was affected by the surfactant migration to the air-film interface. When polymerizable surfactants (Latemul[®]PD-104 and Sipomer[®]Pam-200) and the polymerizable stabilizer (Sipomer[®]Cops-1) were used, films with superior peel strength were

obtained due to the incorporation of these surfactants into the polymer backbone and hence, reduced surfactant migration to the air-film interface.

It was demonstrated that the pH also had a strong influence on the water whitening resistance of the films. On the one hand, the pH used during the polymerization process affected the amount of water-soluble species produced (Chapter 6); the higher the pH, the greater the amount of water-soluble species and the poorer the water whitening resistance. On the other hand, the pH at which the final dispersion was adjusted before making the film also had a substantial effect on the water whitening resistance. The best performance was obtained when the latex was neutralized to a pH around 8.5-10 before the film formation due to a better electrosteric stabilization, leading to a more homogeneous film structure. Furthermore, the final pH of the latex affects the drying kinetics of the film formation, i.e., the lower the pH of the latex, the longer the time to form a film.

The water whitening phenomena was affected by the surfactant concentration as well as by the surfactant system. When a conventional surfactant was used, to obtain a film with superior water whitening resistance, a sufficient amount of surfactant was needed to enable stabilization during film formation, but not too much to prevent hydrophilic pathways in the film. However, this behavior was not observed when either polymerizable surfactants or polymerizable stabilizer were used. For these systems, increasing the amount of surfactant improves the water whitening resistance and hence, increasing the surfactant amount lower opacity values were obtained.

Part of this work was carried out in BASF SE (Ludwigshafen, Germany) during the internship and part of it has been published or will be published soon:

- Aguirreurreta, Z.; Dimmer, J.-A.; Willerich, I.; de la Cal, J. C.; Leiza, J. R. Water Whitening Reduction in Waterborne Pressure-Sensitive Adhesives Produced with Polymerizable Surfactants. *Macromol. Mater. Eng.* **2015**, *300*, 925–936.
- Aguirreurreta, Z.; Dimmer, J.-A.; Willerich, I.; Leiza, J. R.; de la Cal, J. C. Improving the Properties of Water-Borne Pressure Sensitive Adhesives by Using Non-Migratory Surfactants. *Accepted in International Journal of Adhesion and Adhesives*, **2016**.

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Chapter 8. Conclusions

The main objective of this thesis was to synthesize high solids content water-borne acrylic latexes using polymerizable surfactants in order to overcome the negative effects caused by the migration of conventional surfactants and hence, to improve the performance of the final products.

Due to the wide variety of commercially available polymerizable surfactants, in this work, those with different double bond reactivity and different head group type were chosen to be used in the emulsion polymerization of model acrylic latexes. On the one hand, the anionic polymerizable surfactant Sipomer[®]Pam-200 with a methacrylate double bond and a phosphate anionic group and the anionic polymerizable surfactant Latemul[®]PD-104 with a less reactive vinyl double bond and sulfate anionic group, and on the other hand, the anionic polymerizable stabilizer Sipomer[®]Cops-1.

60 wt% solids content acrylic water-borne coatings with particle sizes below 350 nm were synthesized by seeded semi-batch emulsion polymerization using polymerizable surfactants and polymerizable stabilizer. It was found that it was possible to obtain stable high solids content latexes using relatively low amount of polymerizable surfactant/stabilizer (3.6 mM) when the reactions were carried out under basic conditions due to electrosteric

stabilization provided by the methacrylic acid. However, when the polymerizations were carried out under acidic conditions, the system was mostly stabilized by electrostatic stabilization provided by the ionic surfactant and hence, higher surfactant amount was needed to obtain stable latexes. The polymerizable surfactant Latemul[®]PD-104 provided the best stabilization during the synthesis of high solids content latexes under acidic conditions because when Latemul[®]PD-104 was used, the minimum amount of surfactant needed to obtain a stable latex was 4.95 mmol (21.5 mM) whereas with Dowfax[®]2A1 and Sipomer[®]Cops-1 was 6.2 mmol (26 mM). It was not possible to obtain a stable latex when the polymerizable surfactant Sipomer[®]Pam-200 was used probably due to surfactant burial or surfactant lost in the aqueous phase that did not contribute in particle stabilization. When the polymerizable stabilizer Sipomer[®]Cops-1 was used the polymerization strategy was change (all the stabilizer added into the initial charge) in order to obtain 60 wt% stable latexes with less stabilizer amount. However, when this stabilizer was fully added to the initial charge, the target particle size (320 nm) was not obtained and latexes with larger particle sizes were obtained due to the increase of the ionic strength of the medium at the beginning of the reaction which led to coagulation or flocculation of seed latex particles.

Unexpectedly and contrary to what was observed in another works carried out in our research group, gel was formed in the seeded semi-batch emulsion copolymerization of MMA/BA/MAA (at weight composition of 49.5/49.5/1 wt%) that was attributed to the differences found in the polymerization process conditions (i.e. larger particle sizes) that favored higher average number of radicals per particle and hence the gel formation. Furthermore, when Latemul[®]PD-104 and Sipomer[®]Cops-1 were used in the polymerizations carried out under

acidic conditions, the measured gel content was even higher, probably due to the ionic association of sulfate/sulfonate ionic head groups of the surfactant/stabilizer incorporated into the polymer backbone.

The performance of high solids content acrylic water-borne latex films containing polymerizable surfactants/stabilizer was compared to that of the latexes stabilized with conventional surfactant Dowfax[®]2A1. The kinetics of water absorption was different depending on the pH used to synthesize the latex. It was observed that the films formed from latexes synthesized under acidic conditions absorbed less water at the beginning of the water uptake experiments due to the lower amount of water-soluble species present in the final films. However, independently of the pH used to synthesize the latex, the water uptake of the films was proportional to the surfactant amount used during the polymerization. For the films containing the same weight percent of surfactant, the ones containing the conventional surfactant Dowfax[®]2A1 absorbed more water due to surfactant aggregation within particle interstices. The aggregation of Dowfax[®]2A1 within particle interstices was confirmed by Atomic Force Microscopy (AFM). When polymerizable surfactant Latemul[®]PD-104 and polymerizable stabilizer Sipomer[®]Cops-1 were used, the water absorption of the films was substantially reduced. The mechanical properties were considerably affected by the surfactant used during the polymerization, because depending on the surfactant type employed the gel content of the final latexes was different.

The synthesis of 50 wt% of solids content acrylic water-borne pressure-sensitive adhesives using polymerizable surfactants was also studied in this thesis. It was found that the pH used during the polymerization process had a strong influence on the kinetics and

microstructure of the polymer produced. When basic pH was used during the polymerization process, more water-soluble species were formed and as a consequence lower monomer conversion was obtained. Furthermore, the polymer microstructure was also affected by the high pH leading to a polymer with negligible gel content. The surfactant concentration also had an effect on the polymer microstructure. It was observed that increasing the surfactant amount (independently of the surfactant type used but more pronounced for Latemul[®]PD-104) a new population of polymer particles was produced increasing the total number of polymer particles which led to an increase of gel content that was attributed to an enhanced incorporation of the acidic monomer (AA) into the polymer backbone. Thus, all the latexes synthesized at acidic pH presented a substantial amount of gel polymer, the higher the surfactant concentration, the higher the gel content. The adhesive properties were mostly dominated by the gel content.

SAFT and the work of adhesion of the films made of latexes with different surfactants and concentrations were not affected by surfactant migration. However, it was found that the molecular weight of the surfactant was playing a role in the adhesive properties, e.g. the lower the molecular weight of the surfactant, the higher the SAFT. Films made of Sipomer[®]Pam-200 showed an excellent work of adhesion, most likely due to favourable interaction of the phosphate groups with the stainless steel probe. The peel strength was affected by the surfactant migration to the air-film interface. Due to the incorporation of polymerizable surfactants and polymerizable stabilizer to the polymer backbone and hence reduced surfactant migration, films with superior peel strength were obtained.

The water whitening resistance of pressure-sensitive adhesives was strongly affected by the pH. On the one hand, the use of high pH during the polymerization process led to films

with poor water whitening resistance due to the presence of water-soluble species in the final films. On the other hand, the pH at which the final dispersion was adjusted before making the film also had a substantial effect on the water whitening resistance. The best performance was obtained when the latex was neutralized to a pH around 8.5-10 before the film formation due to a better electrosteric stabilization, leading to a more homogeneous film structure. The water whitening phenomena was also affected by the surfactant concentration as well as by the surfactant system. When a conventional surfactant was used (Dowfax[®]2A1), to obtain a film with superior water whitening resistance, a sufficient amount of surfactant was needed to enable stabilization during film formation, but not too much to prevent hydrophilic pathways in the film. However, this behavior was not observed when either polymerizable surfactants or polymerizable stabilizer were used. For these systems, increasing the amount of surfactant the water whitening resistance was improved.

Overall, it can be concluded saying that the use of polymerizable surfactants or polymerizable stabilizer allowed synthesizing high solids content water-borne polymeric dispersions (~ 60 wt% solids content) and improved the performance of the films produced with these dispersions in coatings and pressure-sensitive adhesives applications.

List of publications and conference presentations

Parts of this Thesis have been published or will be published soon. The list of papers that would be issued from this work is as follows (variation in the paper title might be possible):

“Water whitening reduction in waterborne pressure-sensitive adhesives produced with polymerizable surfactants” Ziortza Aguirreureta, Jörg-Alexander Dimmer, Immanuel Willerich, José C. de la Cal, Jose R. Leiza, *Macromolecular Materials and Engineering*, 2015, 300, 925-936.

“Improving the properties of water-borne pressure sensitive adhesives by using non-migratory surfactants” Ziortza Aguirreureta, Jörg-Alexander Dimmer, Immanuel Willerich, Jose R. Leiza, José C. de la Cal. Accepted in *International Journal of Adhesion and Adhesives*.

“Assessing the performance of polymerizable surfactants in emulsion polymerization” Ziortza Aguirreureta, José C. de la Cal, Jose R. Leiza. To be submitted.

“Water sensitivity and mechanical properties of water-borne coatings produced with polymerizable surfactants” Ziortza Aguirreureta, Jose R. Leiza, José C. de la Cal. To be submitted.

Parts of this work have been presented in international and national conferences.

Oral presentations

“Improving the performance of high solids content acrylic latexes using polymerizable surfactants” Z. Aguirreurreta, J.C. de la Cal, J. R. Leiza. Career in Polymers VI, Prague, Czech Republic, July 2014.

“Emulsionatzaile polimerizagarrien erabilera emultsio polimerizazioan” Z. Aguirreurreta, J.C. de la Cal, J. R. Leiza. Materialen Zientzia eta teknologia II. Kongresua, Donostia, Spain, June 2014.

“High solids content latexes with migratory-free surfactants” Z. Aguirreurreta, J.C. de la Cal, J. R. Leiza. Graduate Research Seminar in Polymer Colloids, Shanghai, China, June 2013.

Poster presentations

“Improving the performance of high solids content acrylic latexes using polymerizable surfactants” Z. Aguirreurreta, J.C. de la Cal, J. R. Leiza. Frontiers in Polymer Colloids: From Synthesis to Macro-Scale and Nano-Scale Applications, Prague, Czech Republic, July 2014.

“High solids content latexes with migratory-free surfactants” Z. Aguirreurreta, J.C. de la Cal, J. R. Leiza. IPCG Research Conference 2013, Shanghai, China, June 2013.

Award for **“Outstanding poster presentation”** during IPCG Research Conference 2013.

Laburpena eta ondorioak

Emulsio-polimerizazioan emulsionatzaileak oso garrantzitsuak dira, bai prozesu guztian zehar (gehien bat polimero partikulen nukleazioan eta partikula dispertsioaren egonkortasunean), bai azken produktuaren kontserbatze-denboran (izozte-urtze egonkortasunean adibidez). Osterantzean, emulsionatzaile konbentzionalek kalteak eragin ditzakete azken produktuen propietateetan, emulsionatzaile horiek polimero partikulan adsorbatuta baitaude eta handik desorbatu baitaitezke. Latexari ebakidura altuak aplikatuz gero, latexak egonkortasun mekanikoa gal dezake. Honetaz gainera, latexak estaldura gisa aplikatzen direnean, emulsionatzailearen migrazioaren ondorioz estaldura-geruzaren urarekiko sentikortasuna kaltetu daiteke, geruzaren barrenean agregatu hidrofilikoa eratu baitaitezke. Emulsionatzaileak estaldura-geruzaren goi edota beheko gainazalera migratuz gero, geruzaren itsaskortasuna kaltetu daiteke.

Emulsionatzaile konbentzionalek eragin ditzaketen kalteak gainditzeko, emulsionatzaile polimerizagarriak erabil daitezke. Emulsionatzaile polimerizagarriek konbentzionalen egitura anfifiliko berdintsua mantentzen dute. Desberdintasun nagusia ondorengoa da: emulsionatzaile polimerizagarriek C=C lotura bikoitz bat dute beraien egituran eta ondorioz, monomeroekin kopolimerizatu dezakete. Beraz emulsionatzailea partikulara

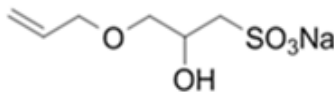
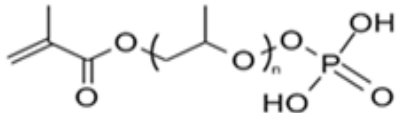
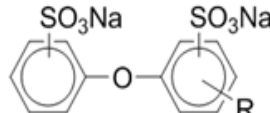
kobalenteki lotuta baldin badago, migrazioa ekidi daiteke eta ondorioz, azken produktuen propietateak hobetu daitezke.

Solido eduki altuko latexak (zeintzuetan polimero edukia %50 edo gehiagokoa den) interes handikoak bilakatu dira industrian, hala nola, ohi baino geruza gutxiagoz baliatuta estaltzen baitute produktua, ur gutxiago izatean azkarrago lehortzen baitira eta biltegiratze edota garraioan aurrezteko aukera ematen baitutelako. Ondorioz, solido eduki altuko latexak zenbait aplikaziotan erabiltzeko egokiak dira, adibidez, itsasgarri edota estaldura gisa. Solido eduki altuko latexen egonkortasuna bermatzeko, emulsionatzaile kantitate handiak behar izaten dira eta hori ez da onuragarria aplikazioaren ikuspuntutik.

Tesi honen helburu nagusia emulsionatzaile polimerizagarriak erabiliaz solido eduki altuko (%50-60) ur-oinarriko estaldura eta itsasgarri akrilikoak sintetizatzean datza, azken produktuaren propietateak hobetu ahal izateko.

Emulsionatzaile polimerizagarri ugari aurki daitezkeenez merkatuan, erreaktibitate eta buru hidrofiliako desberdinak zutenak aukeratu ziren latex akrilikoaren emulsio-polimerizazioan erabiltzeko. Tesi honetan zehar 2 emulsionatzaile polimerizagarri anioniko (Latemul[®]PD-104 eta Sipomer[®]Pam-200) eta egonkortzaile anioniko polimerizagarri bat (Sipomer[®]Cops-1) erabili dira. 1. Irudian, emulsionatzaile eta egonkortzailearen egiturak azaltzen dira.

1.Irudia. Emulsionatzaile eta egonkortzaile komertzial polimerizagarrien egitura.

Emulsionatzailea/ Egonkortzailea	Egitura	Pisu molekularra (g/mol)
Sipomer®Cops-1		218
Sipomer®Pam-200		~500
Latemul®PD-104	$\text{H}_2\text{C}=\underset{\text{CH}_3}{\text{C}}-\text{CH}_2\text{CH}_2\text{O}-(\text{CH}_2\text{CH}_2\text{O})_n(\text{CH}_2\underset{\text{CH}_3}{\text{CHO}})_m\text{O}-\text{S}(=\text{O})_2\text{O}^-$	1674
Dowfax®2A1		575

%60-ko solido edukia zuten estaldura akriliko egonkorak sintetizatu ziren ereinadun polimerizazio erdi-jarrai bidez emulsionatzaile eta egonkortzaile polimerizagarriak erabiliz. Frogatu zen, emulsionatzaile edota egonkortzaile polimerizagarrien kontzentrazio baxuak erabiliz (3.6 mM) solido eduki altuko eta tamaina txikiko (partikula tamaina 320 nm inguru) latex akriliko egonkorak sintetizatzea posible zela beti ere ereinadun polimerizazio erdi-jarriak ingurune basikoan burutzen baziren, azido metakrilikoari esker, sistema elektroesterikoki egonkortuta baitzegoen. Ordea, polimerizazioak ingurune azidoan burutu zirenean (ez zen amoniarik gehitu) emulsionatzaile edota egonkortzaile kantitate handiagoak behar izan ziren

latex egonkorak lortu ahal izateko (21-26 mM), sistema soilik elkarrekintza elektrostatikoz egonkortuta baitzegoen. Aipatzekoa da, polimerizazioak ingurune azidoan burutu zirenean ez zela latex egonkorrik lortu Sipomer[®]Pam-200 emulSIONatzaile polimerizagarria erabili zenean, seguraski ehorztutako edo/eta ur-fasean polimerizatutako Sipomer[®]Pam-200-ak ez zuelako sistema egonkortzen.

EmulSIONatzaile/egonkortzaile polimerizagarriekin sintetizatutako solido eduki altuko (%60) latexen propietateak emulSIONatzaile konbentzionalekin sintetizatutako latexen propietateekin alderatu ziren. EmulSIONatzaile edota egonkortzaile polimerizagarriak erabiliz, latexen izozte-urtze egonkortasuna hobetu zen. Geruzen urarekiko sentikortasunari dagokionez, edozein zela ere erabilitako emulSIONatzaile mota (polimerizagarria edo konbentzionala) geruzek xurgatutako ura sintesian erabilitako emulSIONatzailearen kantitatearen proportzionala zela ikusi zen. EmulSIONatzaile kantitate bera zuten geruzak alderatuz, ur gehien xurgatu zuten geruzak emulSIONatzaile konbentzionala (Dowfax[®]2A1) zutenak izan ziren, emulSIONatzaile molekulez osatutako agregatu hidrofiliakoak baitzeuden geruzen barnealdean. Agregatu hidrofiliakoen presentzia Indar Atomikoen Mikroskopia (AFM) bidez froatu zen. EmulSIONatzaile edota egonkortzaile polimerizagarriak erabili zirenean, Latemul[®]PD-104 eta Sipomer[®]Cops-1 hain zuzen ere, geruzen urarekiko sentikortasuna nabarmenki hobetu zen, emulSIONatzailearen migrazioa ekidin zelako.

%50-eko solido edukia zuten itsasgarri akrilikoak ere sintetizatu ziren emulSIONatzaile edota egonkortzaile polimerizagarriak erabiliz. Itsasgarrien sintesian pH-ak eragin nabarmena izan zuen, bai polimerizazio zinetikan bai polimeroen mikroegituran ere. Adibidez, ereinadun polimerizazio erdi-jarraia pH basikoan burutu zenean ez zen monomeroaren konbertsio totala

lortu eta gelik gabeko polimeroa lortu zen. Ondorioz, emulsionatzaileen eragina aztertzeko polimerizazioak ingurune azidoan burutu ziren.

Erabilitako emulsionatzaile kontzentrazioak eragina izan zuen itsasgarrien sintesian; zenbat eta emulsionatzaile gehiago erabili polimerizazioan, orduan eta polimero partikula gehiago sortu ziren nukleazio sekundarioen ondorioz, batik bat Latemul[®]PD-104 emulsionatzaile polimerizagarria erabili zenean. Partikula gehiago sortzeak polimeroaren mikroegituran eragina izan zuen, hau da, sisteman gero eta polimero partikula gehiago, orduan eta gel kantitatea handiagoa azido akrilikoaren inkorporazioa handiagoa izan zelako. Ingurune azidoan sintetizatuko latex guztietan gela neurtu zen; gero eta emulsionatzaile gehiago erabili latexaren sintesian, orduan eta gel gehiago.

Aztertutako itsasgarrien propietateen artean (SAFT, tack eta peel) soilik peel-a izan zen emulsionatzailearen migrazioarekin kaltetua izan zen bakarra. Ondorioz, Latemul[®]PD-104, Sipomer[®]Pam-200 eta Sipomer[®]Cops-1 erabili zirenean itsasgarrien peel-a nabarmenki hobetu zen.

Itsasgarrien urarekiko sentikortasuna ere aztertu zen, hain zuzen, txuritze fenomenoan. Alde batetik, ikusi zen pH-ak izugarriko eragina zuela itsasgarrien txuritzean. Bestetik, emulsio-polimerizazioan erabilitako emulsionatzaileak ere eragina zuela frogatu zen. Emulsionatzaile konbentzionala erabili zenean (Dowfax[®]2A1), txuritzearekiko erresistentzia hobetu ahal izateko nahikoa emulsionatzaile behar izan zen filmaren eraketan egonkortasuna bermatzeko baina ez soberan, agregatu hidrofilikoen sorrera ekiditzeko. Aldiz, emulsionatzaile edota egonkortzaile polimerizagarriekin ez zen portaera hori ikusi. Emulsionatzaile edota

Laburpena eta ondorioak

egonkortzaile polimerizagarriak erabili zirenean itsasgarrien txuritzea hobetu zen nahiz eta kantitate handiak erabili.

Appendix I. Characterization methods and techniques

I.1. Solids content and conversion

Approximately 1mL of latex was withdrawn from the reactor during the polymerization process, put in a pre-weight aluminium pan and immediately thereafter 0.1 mL of a 1% hydroquinone solution was added. The pan was dried in the oven at 60°C until constant weight was achieved. The solids content (SC) was obtained gravimetrically and is given by:

$$SC = \frac{\text{weight of the solid material}}{\text{weight of latex}} \quad (1.1)$$

The instantaneous and cumulative conversion, X_i and X_c , were determined by the following equations:

$$X_i(t) = \frac{SC_i - SW_i}{MW_i} \quad (1.2)$$

$$X_c = \frac{SC_i - SW_i}{MW_{tf}} \quad (1.3)$$

where SC_i the solids content, SW_i is the fraction of initiator plus surfactant in the reactor, MW_i is the fraction of monomer plus polymer in the reactor at the sample time and MW_{tf} is the fraction of monomer plus polymer at the end of the feed.

I.2. Coagulum amount

The amount of coagulum was measured by filtering the latex through a 85 μm nylon mesh and drying the retained amount. The results are presented as the weight of the coagulum with respect to the total weight of monomer in the formulation.

I.3. Particle size and particle size distribution (PDS)

I.3.1. Dynamic Light Scattering (DLS)

Particle size was measured by Dynamic Light Scattering (DLS) using a Malvern Zetasizer Nano ZS. The equipment determines the particle size by measuring the rate of fluctuations in light intensity scattered by particles as they diffuse through a fluid.

Samples were prepared by diluting a fraction of the latex with deionized water. The analyses were carried out at 25°C and each run consists in 1 minute of temperature equilibration followed by 3 size measurements per sample. An average is given as a final value.

I.3.2. Capillary Hydrodynamic Fractionation chromatography (CHDF)

To determine the particle size distribution of the latexes (PSD) Capillary Hydrodynamic Fractionation chromatography technique was used (CHDF-2000 from Matec Applied Science).

It was operating at a flow rate of 1.4 mL/min and at 35°C. The detector wavelength and the carrier fluid used were different depending on the particle size of the latex to be analyzed, as it is shown in Table I.1. The samples were diluted to 0.5 wt% using the carrier fluid and they were analyzed using Matec software v.2.3.

Table I.1. Experimental conditions to measure the particle size distribution of the latexes.

Parameters	dp < 300 nm	dp >300 nm
Detector Wavelength (nm)	200	220
Carrier fluid	1/4X-GR500	1X-GR500

I.4. Gel content and swelling capability

The gel content by definition is the fraction of polymer that is not soluble in a good common solvent such as tetrahydrofuran (THF). The swelling capability is referred to the ability of the insoluble polymer fraction to swell with the same solvent. The gel fraction and the swelling capability were measured by Soxhlet extraction.

To measure the gel content glass fiber square pads (CEM) were used as backing. A few drops (0.1 g approximately) of latex were placed on the filter (filter weight = W_1) and dried in the oven at 60°C overnight. The filter together with the dried polymer was weighed (W_2) and a continuous extraction with THF under reflux in the Soxhlet for 24 hours was done afterwards (Figure I.1). After this period of time, the wet filter was dried in the oven and the weight of the

dry sample was taken (W_3). Gel content was calculated as the ratio between the weight of the insoluble polymer fraction and that of the initial sample, as Equation I.4 shows.

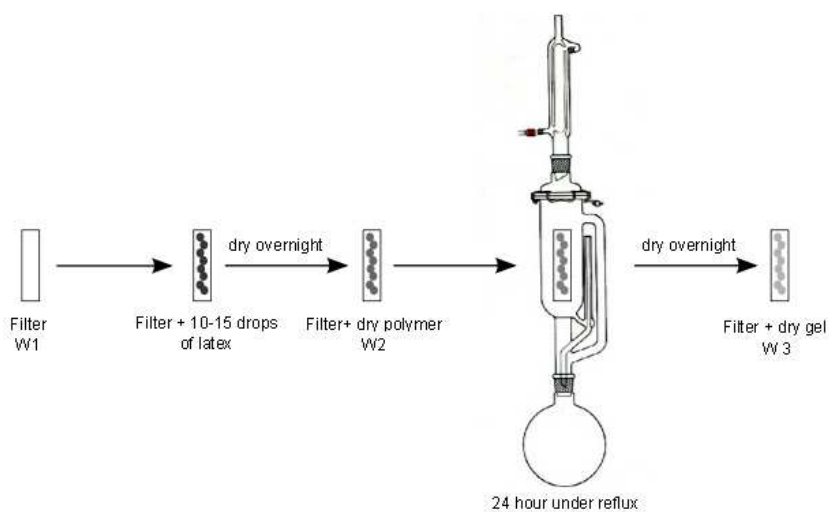


Figure I.1. Scheme of Soxhlet extraction method for gel content measurements.

$$\text{Gel content (\%)} = \frac{W_3 - W_1}{W_2 - W_1} \times 100 \quad (I.4)$$

The schematic representation of the swelling capability measurement is shown in Figure I.2. To measure the swelling capability, first of all, latexes were dried in the oven. Then, a glass fiber tube was weighed (W_1) and placed in a Soxhlet system under THF reflux for 1 h. The humidified tube was then weighed (W_2) and dried in a ventilated oven at 60 °C for 2 h. About 0.25-0.30 g of dried polymer was then placed on the glass fiber tube and a Soxhlet

extraction with THF under reflux was carried out for 24 h. It was checked that the extraction time was long enough to have a constant gel value and the values obtained were in all the cases comparable to those obtained using the square sample pads as backing. In other words, the sol fraction extracted in both experiments was the maximum that could be extracted under the conditions used. The humidified tube and the swollen gel were then weighed (W_4), and dried in a ventilated oven at 60 °C overnight. Finally, the dried glass fiber tube containing the gel polymer was weighed (W_5). The swelling capability was calculated by means of Equation I.5. It was checked that the extraction time was long enough to have a constant gel value and the values obtained were in all the cases comparable to those obtained using the square sample pads as backing. In other words, the sol fraction extracted in both experiments was the maximum that could be extracted under the conditions used.

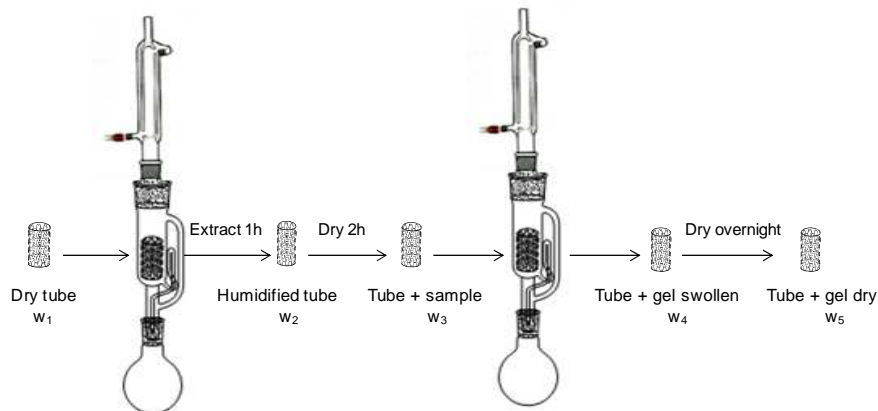


Figure I.2. Scheme of Soxhlet extraction method for swelling capability measurements.

$$\text{Swelling capability} = \frac{W_4 - W_2}{W_5 - W_1} \quad (1.5)$$

I.5. Molecular weight and molecular weight distribution (MWD)

The molecular weight of the soluble fraction (obtained by Soxhlet extraction) was determined by Size Exclusion Chromatography/ Gel Permeation Chromatography (SEC/GPC). The samples taken out from the Soxhlet were first dried, redissolved in THF to achieve a concentration of about 0.1 % (g/ml) and filtered (polyamide $\Phi=45 \mu\text{m}$) before injection into the SEC instrument. The set up consisted of a pump (LC-20A, Shimadzu), an autosampler (Waters 717), a differential refractometer (Waters 2410) and three columns in series (Styragel HR2, HR4 and HR6, with pore sizes ranging from 10^2 to 10^6 \AA). Chromatograms were obtained at 35°C using THF flow rate of 1 ml/min. The equipment was calibrated using polystyrene standards (5th order universal calibration) and therefore, the molecular weight was referred to PS.

The absolute molecular weight of the soluble fraction presented in Chapter 6 and Chapter 7, was analyzed by Size Exclusion Chromatography (SEC) using Multi Angle Light Scattering (MALS) and Refractive Index (RI) detectors. This equipment was composed of a LC20 pump (Shimadzu) coupled to a miniDAWN Treos multiangle (3angles) light scattering laser photometer equipped with a He-Ne laser ($\lambda=658 \text{ nm}$) and an Optilab Rex differential refractometer ($\lambda=658 \text{ nm}$) (all from Wyatt Technology Corp., USA). Separation was carried out using three columns in series (Styragel HR2, HR4 and HR6; with pore sized from 102 to 106 \AA). Calibration and normalization of the MALS as well as band broadening correction was done as described elsewhere¹. The dried soluble fraction (sol) of the polymer obtained after Soxhlet

extraction in THF was diluted in HPLC grade THF at 3 mg/mL, filtered with a nylon syringe filter of 0.45 μm (Scharlau Chromatography), and injected in the equipment (100 μL). Analyses were performed at 35°C and THF was used as mobile phase at a flow rate of 1 mL/min. The dn/dc used was calculated by averaging the dn/dc of the polybutylacrylate (0.064 mL/g) and polymethylmethacrylate (0.084 mL/g). The calculated dn/dc was 0.066 mL/g. The SEC/MALS data were analyzed by using the ASTRA software version 6.0.3. The absolute molar masses were calculated from the MALS/RI data using the Debye plot (with the 1st order Zimm formalism).

I.6. References

- (1) A. Agirre, A.; Santos, J. I.; Etxeberria, A.; Sauerland, V.; Leiza, J. R. Polymerization of n-Butyl Acrylate with High Concentration of a Chain Transfer Agent (CBr_4): Detailed Characterization and Impact on Branching. *Polym. Chem.* 2013, 4, 2062–2079.

Appendix II. Film properties and characterization methods

II.1. Water static contact angle

For the measurements of the water static contact angle, 120 μm wet thick films were cast onto glass substrate, at 22°C and 55% relative humidity during one day. In order to remove hydrophilic material present in the air-film interface, films were rinsed with water and later allowed to dry at room temperature. The measurements were carried out in a Contact Angle System OCA (Dataphysics) equipment, taking an average value from 20 measurements. The contact angles were measured at the air-film interface Figure II.1 before and after rinsing the films with water.

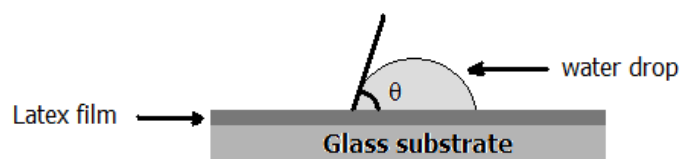


Figure II.1. Scheme describing the method used to measure the contact angle with water.

II.2. Water uptake

In order to measure the amount of absorbed water by the films, the films were formed by casting the latexes onto round silicon moulds and drying them at 22°C and 55% relative humidity during 3 days until a constant weight was achieved. All the resulting films had the same weight (0.34 g). The obtained films were weight (m^0) and they were placed into different flasks full of distilled water. Then, they were removed from the flask at given times, they were dried with paper and weighted (m^t). After weighting the films, they were placed again in their respective flask. The amount of absorbed water was defined as follows:

$$\mathbf{Water\ uptake} = \frac{m_t - m_0}{m_0} \times 100 \quad (\text{II.1})$$

After the end of the experiment the wet films were dried in the oven at 60°C (until a constant weight of the films was obtained) to check if they had lost any weight from the original dried films.

The reproducibility of the measurements was very good (see Figure II.2).

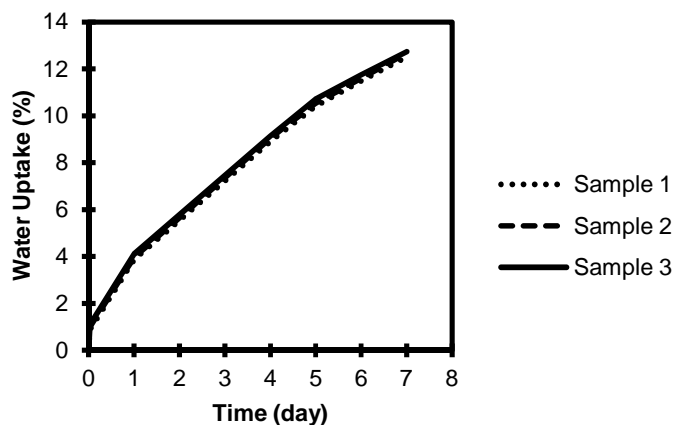


Figure II.2. Reproducibility of the water uptake measurement for the latex synthesized using 1 wbm% of Dowfax[®]2A1 (D50-5A latex, see Chapter 5).

II.3. Mechanical properties: tensile test

In order to assess the effect of the surfactant on the mechanical properties of the films, tensile test were carried out. The films were first dried in Teflon moulds during one week under controlled conditions (22°C and 55% of humidity). Afterwards, films were cut in the dimensions given in Figure II.3. Measurements were carried out in a universal testing machine, TA HD Plus Texture Analyzer at 22°C and 55% of relative humidity applying a crosshead speed of 25 mm/min to an approximately 0.5 mm thick latex film. At least five specimens per sample were tested and the average values are reported.

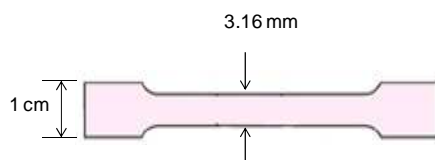


Figure II.3. Dimensions for the probe employed for the tensile test measurements.

II.4. Atomic Force Microscopy (AFM)

Topography and phase images of the latex films presented in Chapter 5 were analyzed using Atomic Force Microscopy. AFM measurements were performed in tapping mode using a Nanoscope IIIa (Multimode from Veeco) equipped with an integrates silicon tip/cantilever (TESP) having a resonance frequency of ~ 340 KHz. Films were formed by casting the latex onto a round silicon mould and dried at 22°C and 55% relative humidity during 1 week and their surface was analyzed. The films were cut using a diamond knife by cryosection in order to analyze the cross-section of the films.

II.5. UV/VIS spectroscopy

A representative example of the normalized raw data obtained from UV/VIS spectroscopy is shown in Figure II.4. As it can be observed in Figure II.4 the absorbance between 300 and 650 nm was registered at different time.

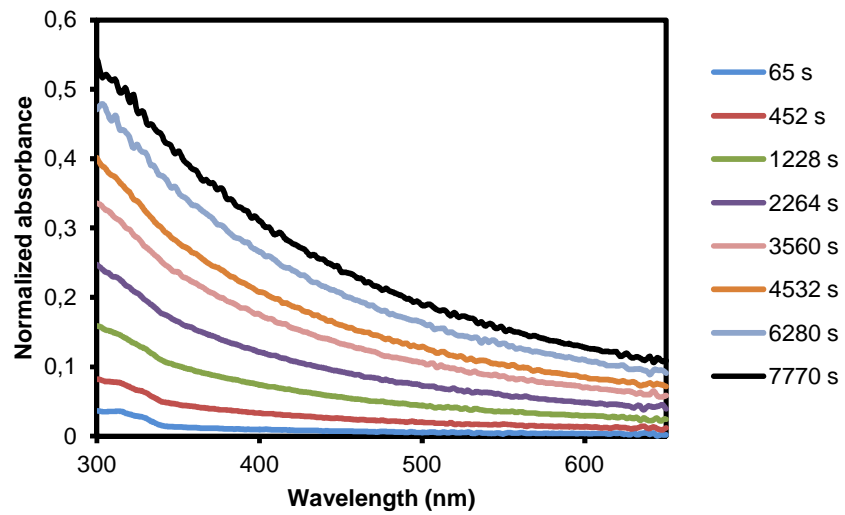


Figure II.4. Normalized raw data obtained from the UV/VIS spectroscopy for a representative film made with the conventional surfactant Dowfax[®]2A1.

Appendix III. Some aspects to consider for the successful synthesis of high solids content (HSC) latexes with controlled particle size

III.1. Introduction

As it was mentioned in Chapter 4, one of the most efficient routes to synthesize high solids content latexes with unimodal particle size distribution and controlled particle size is to enlarge the particle size of a seed during a semi-batch polymerization process¹.

The amount of the seed latex in the initial reactor charge is an important parameter for controlling the evolution of the particle size during the seeded semi-batch polymerization and to achieve a target particle size at the end of the process. The amount of the seed required in seeded semi-batch polymerizations to produce a latex with a certain solids content and with a certain particle size can be estimated assuming that the number of polymer particles remains constant during the polymerization by means of the following equation²:

$$m_{seed} = \frac{m_{latex} SC_{target} \bar{d}_{p,seed}^3}{SC_{seed} \bar{d}_{p,target}^3} \quad (III.1)$$

where m_{seed} (g) is the amount of the seed latex, SC_{seed} (wt%) is the polymer content of the seed, m_{latex} (g) is the amount of the latex desired at the end of the polymerization process, SC_{target} (wt%) is the target polymer content, $\bar{d}_{p,seed}$ (nm) is the diameter of the seed particles and $\bar{d}_{p,target}$ (nm) is the target particle diameter.

As it can be observed in Equation III.1 the amount of the seed required strongly depends on the seed latex particle size. Furthermore, for a given amount of seed, the target particle size ($\bar{d}_{p,target}$) strongly depends on the seed latex particle size ($\bar{d}_{p,seed}$) as it can be observed in Equation III.2 which has been extracted from Equation III.1. Therefore, in order to achieve the target particle size in the synthesis of high solids content latexes an accurate determination of the seed latex particle size is vital because a small difference in the particle size of the seed latex can have a huge influence on the final particle size of the latex as it will be shown below.

$$\bar{d}_{p,target} = \sqrt[3]{\frac{m_{latex}SC_{target}\bar{d}_{p,seed}^3}{SC_{seed}m_{seed}}} \quad (III.2)$$

For example, in a given seeded semi-batch polymerization, assuming that the particle size of the seed is $\bar{d}_{p,seed} = 50$ nm and that $SC_{seed} = 15$ %, in order to achieve a latex with $SC_{target} = 60$ % and $\bar{d}_{p,target} = 300$ nm (considering $m_{latex} = 600$ g), according to Equation III.1, 11.11 g of seed latex (m_{seed}) are needed. However, as it can be observed in Figure III.1, for this amount of seed latex, if the particle size of the seed is 40 nm or 60 nm instead of 50 nm the final particle size of the latex will be 240 nm or 360 nm, respectively. Therefore, small

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differences in the measured particle size of the seed latex can have a huge influence in the control of the particle size during the synthesis of high solids content latexes, which in turn might influence the stability during polymerization as well as the viscosity of the final latex.

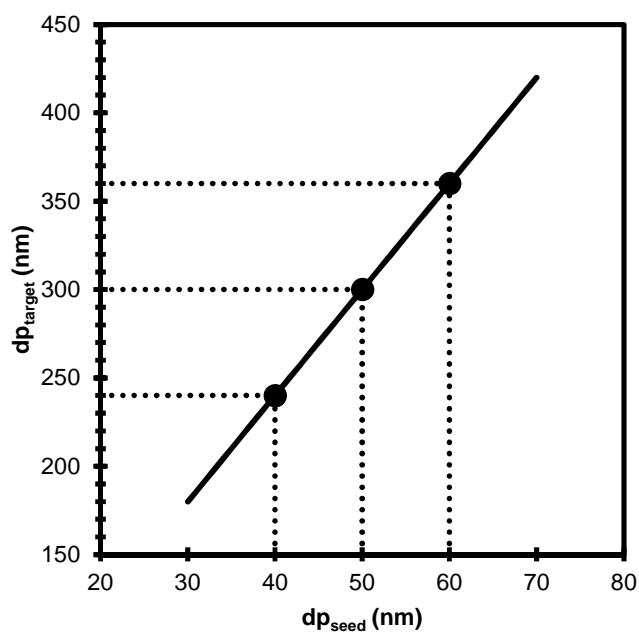


Figure III.1. Effect of the seed particle size on the target particle size.

III.2. Effect of the particle size of the seed latex in the synthesis of high solids content latexes

III.2.1. Synthesis of seed latexes

15 wt% solids content polymethyl methacrylate-co-butyl acrylate-co-methacrylic acid (MMA/BA/MAA at weight composition of 49.5/49.5/1) seed latexes were synthesized by semi-batch emulsion polymerization as described in Chapter 4. Four seed latexes were synthesized using different surfactants and the final characteristics of the seed latexes are shown in Table III.1. Note that the polymerizable stabilizer Sipomer®Cops-1 was not used in the synthesis of the seed latexes because as it was shown in Chapter 3, this stabilizer is not able to nucleate.

Table III.1. Final characteristics of the seed latexes.

Seed latex	Surfactant	Surfactant		SC (wt%)	$d_{p, Z-AVE}$ (nm)	$d_{p,v}$ (nm)	Surface coverage (%)
		(g)	(mM)		DLS	CHDF	
D15	Dowfax®2A1	0.9	3.07	14.8	75	66	13
SLS15	Sodium lauryl sulphate	0.9	6.14	15.0	68	63	19
L15	Latemul®PD-104	0.9	1.06	14.9	63	66	6
S15	Sipomer®Pam-200	0.9	3.54	14.9	63	70	--

In all polymerizations stable seed latexes with small particle sizes were obtained using relatively low surfactant concentration. Although all latexes were synthesized using the same amount of surfactant (0.9 g), the surfactant molar concentration used was not the same

because the molecular weight of the surfactants differs from one to another. As the surfactant concentration used was not equivalent and the parking area (a_s) of each surfactant was different (See Chapter 2 for details) the surface coverage of the seed latexes was also different. Therefore, although all seed latexes were stable (no coagulum was measured after filtration), different stability of the seed latexes upon salt or electrolyte addition could be expected. Note that the surface coverage of S15 seed latex was not determined due to the lack of a_s data for the polymerizable surfactant Sipomer[®]Pam-200 (see Chapter 2 for details). However, in S15 seed latex low surface coverage could be also expected because as it was previously discussed in Chapter 3, part of the polymerizable surfactant Sipomer[®]Pam-200 used during the synthesis could be lost due to the formation of water-soluble oligomers or burying of the surfactant in the polymer particles that do not participate in the stabilization of polymer particles. In order to determine the surface coverage of SLS15 seed latex, the a_s value for SLS was taken from literature³.

As shown in Table III.1, all the seed latexes were very similar on size. It is worth mentioning that the techniques used to measure the particle size of the seed latexes, Dynamic Light Scattering (DLS) and Capillary Hydrodynamic Fractionation chromatography (CHDF), provided almost the same average particle size. This is in agreement with the work done by Elizalde et al.⁴ that they found that for monodispersed polystyrene standard latexes DLS and CHDF techniques provided reasonably accurate particle sizes. As it can be observed in Figure III.2, in this work monodispersed seed latexes were obtained.

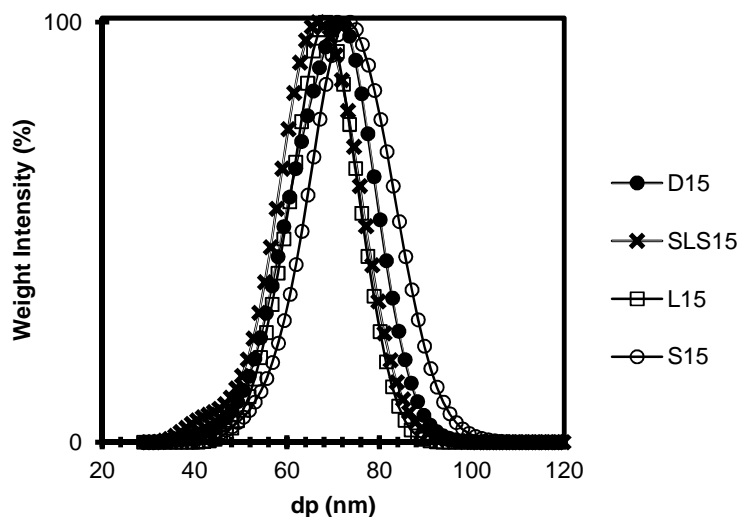


Figure III.2. Particle size distribution of the seed latexes measured by CHDF.

III.2.2. Synthesis of high solids content latexes

Five latexes of MMA/BA/MAA (at weight composition of 49.5/49.5/1) with a target solids content of 60 wt% and target particle size of around 320 nm were synthesized by using different surfactants, growing the respective seed latexes. The general formulation used and the polymerization process employed are described in Chapter 4. Table III.2 summarizes the main characteristics of the latexes. The same recipe was used in all polymerizations being only different the amount of the seed used, because as it was shown before the amount of the seed required to achieve a certain solids content and particle size depends on the solids content and particle size of the seed latex (see Equation III.1). It is worth mentioning that in order to

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estimate the amount of the seed required, the value of the seed particle size obtained by DLS technique was considered because this technique is nowadays probably the fastest and easiest one for particle size analysis.

Note that in all polymerizations the surfactant amount used was equivalent in moles and that in the synthesis of C60-B latex D15 seed latex was used (Table III.2).

In all polymerizations stable latexes without coagulum were obtained and the pH of all the latexes was between 7.0 and 7.5 because ammonia was added to the preemulsion. However, in none of the reactions the target particle size (320 nm) was achieved, namely, in D60-B, SLS60-B and C60-B reactions latexes with smaller particle sizes were obtained whereas in L60-B and S60-B reactions latexes with larger particle sizes were obtained (Table III.2).

Table III.2. Main characteristics of high solids content latexes synthesized by seeded semi-batch emulsion polymerization.

Latex	Seed latex	Amount of seed (g)	Surfactant	Surfactant amount (mmol)	SC (wt%)	dp (nm)
D60-B	D15	31.91	Dowfax [®] 2A1	0.85	60.6	271
SLS60-B	SLS15	24.95	Sodium Lauryl Sulfate	0.85	60.4	247
L60-B	L15	18.85	Latemul [®] PD-104	0.85	60.3	343
S60-B	S15	18.69	Sipomer [®] Pam-200	0.85	60.3	400
C60-B	D15	31.91	Sipomer [®] Cops-1	0.85	60.3	283

Figure III.3 shows the predicted and experimental particle size evolution (measured by DLS) during the polymerization time for the five latexes. It is worth mentioning that to calculate the predicted particle size evolution it was assumed that the number of particles of the seed remained constant during the polymerization and that instantaneous conversion was 1. Therefore, it could be expected that in D60-B, SLS60-B and C60-B reactions, where the evolution of the particle size was below the predicted one (Figure III.3a, Figure III.3b and Figure III.3e, respectively), secondary nucleation occurred during the polymerization whereas in L60-B and S60-B reactions, where the evolution of the particle size was above the predicted one (Figure III.3c and Figure III.3d, respectively), some coagulation or flocculation occurred. However, particle size distributions (PSDs) obtained from CHDF analysis (Figure III.4) revealed that in all cases latexes with unimodal PSDs were obtained. Consequently, it could be said that secondary nucleation did not occur during D60-B, SLS60-B and C60-B reactions and that no flocculation or coagulation occurred during L60-B and S60-B reactions. Therefore, the fact that the predicted particle size was not achieved in none of the reactions should be related to some aspect of the seed latex rather than to the ability that the surfactants had to stabilize the growing polymer particles.

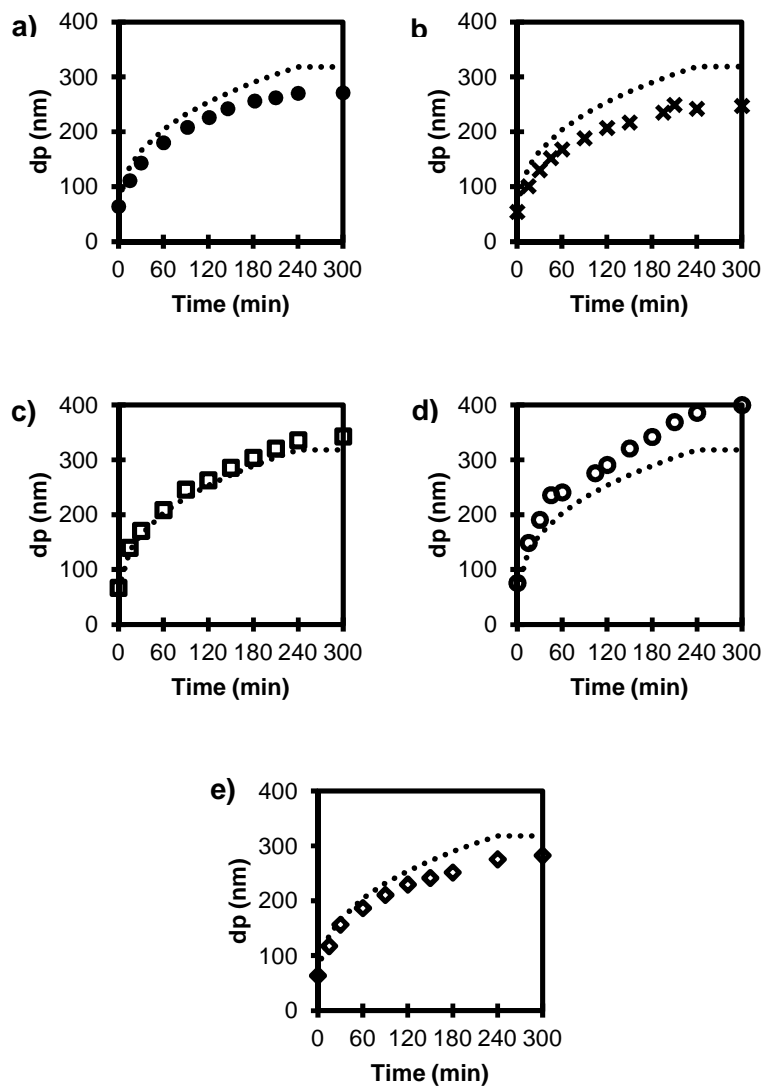


Figure III.3. Evolution of the experimental (symbols) and predicted (dashed lines) particle diameter during the polymerization process for latexes synthesized using different surfactants: a) D60-B, b) SLS60-B, c) L60-B, d) S60-B and e) C60-B.

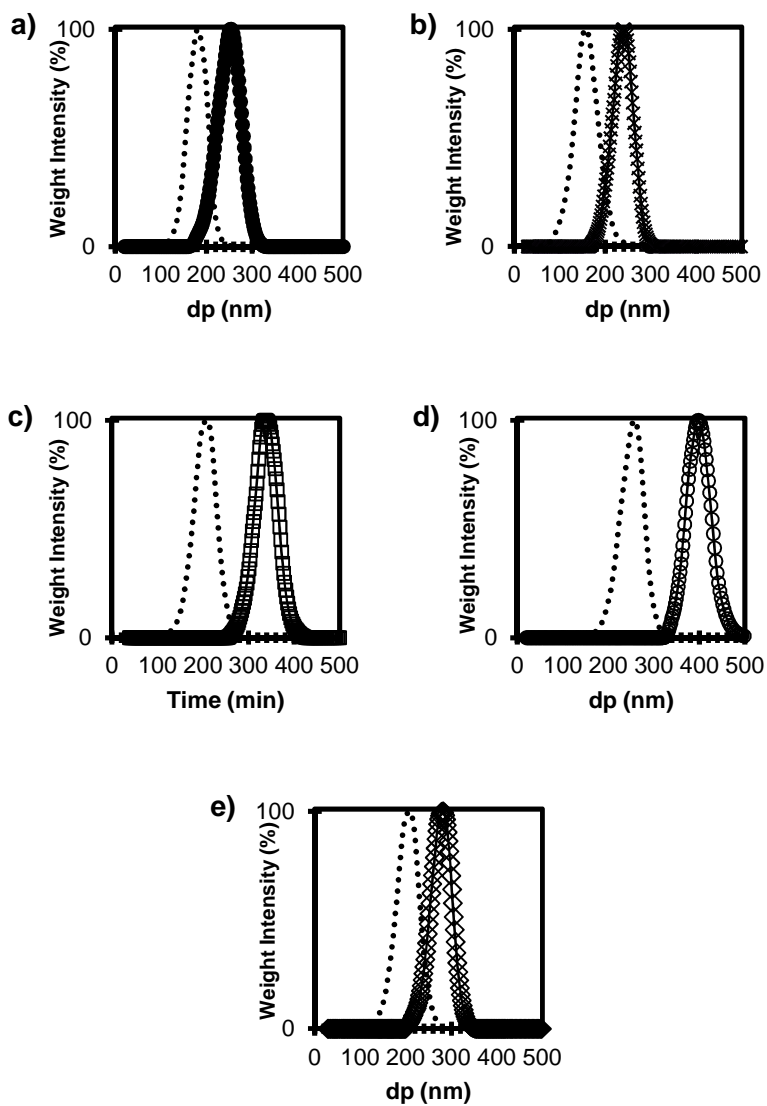


Figure III.4. Particle size distribution at 60 minutes of reaction (dashed lines) and final latexes (symbols). a) D60-B, b) SLS60-B, c) L60-B, d) S60-B and e) C60-B.

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At this point it is interesting to remind that in the seeded semi-batch reactions the ionic initiator KPS was fully loaded in the initial charge and hence likely the ionic strength of the seed latex substantially increased. It was previously shown that the surface coverage of the seed polymer particles was different depending on the surfactant used during the synthesis of the seed latexes, but in all cases the surface coverage was low (Table III.1). As a consequence, it could be expected that the addition of KPS may affect the stability of the initial charge and hence, special attention was paid to the beginning of the reaction. Table III.3 summarizes the seed latex used, the final particle size of the seed and the particle size at the beginning of the reaction (0 minutes) of the seeded semi-batch emulsion polymerizations. It is worth mentioning that the data of $d_{p,t=0min}$ that appears in Table III.3 corresponds to the sample withdrawn from the reactor after the shot of KPS was added.

Table III.3. Summary of the seed latex used, final particle size of the seed ($d_{p,seed}$) and particle size at the beginning of the reaction ($d_{p,t=0min}$) of the seeded semi-batch emulsion polymerizations.

Latex	Seed latex	$d_{p,seed}$	$d_{p,t=0min}$
		(nm) DLS	(nm) DLS
D60-B	D15	75	64
SLS60-B	SLS15	68	54
L60-B	L15	63	67
S60-B	S15	63	76
C60-B	D15	75	64

As it can be observed in Table III.3 in all cases the measured particle size at the beginning of the reaction ($d_{p,t=0\text{min}}$) differed from the measured seed latex particle size ($d_{p,\text{seed}}$). In reactions where seed latexes synthesized using conventional surfactant Dowfax[®]2A1 and SLS were used (D60-B, SLS60-B and C60-B reactions) the measured particle size at the beginning of the reaction was smaller than the particle size of the seed. On the contrary, in reactions where seed latexes synthesized using polymerizable surfactants Latemul[®]PD-104 and Sipomer[®]Pam-200 were used (L60-B and S60-B reactions) the measured particle size at the beginning of the reaction was larger in comparison to the seed latex particle size. Therefore, it can be said that the differences found between the seed latex particle size and particle size at the beginning of the reaction ($t=0$ min) seemed to be related with the addition of KPS into the initial charge.

When the shot of KPS was added to the initial charge the ionic strength of the medium increased and as a consequence, the electric double layer thickness around the seed polymer particles decreased. As the surface coverage of the seed latex particles was different (Table III.1), the decrease in the electrical double layer led to different situations. On the one hand, in L60-B reaction, where a seed latex (L15) with the lowest surface coverage was used (Table III.1), the decrease in the electric double layer led to a increase in the particle size of the seed latex at the beginning of the reaction (Table III.3) due to coagulation or coalescence of polymer particles with increasing the ionic strength. Same behaviour could be expected in S60-B reaction. On the other hand, in D60-B, SLS60-B and C60-B, where D15, SLS15 and D15 seed latexes were used, respectively, the increase of the ionic strength at the beginning of the reaction did not lead to coagulation of polymer particles most likely due to the higher surface

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coverage of the seed latexes used in these reactions (Table III.1). Therefore, smaller particle sizes were measured at the beginning of D60-B, SLS60-B and C60-B reactions (Table III.3) due to the decrease in the electrical double layer. Note that in D60-B and C60-B reactions the same seed latex was used (D15) and therefore, the observed reduction in the particle size at the beginning of the experiment was the same (Table III.3).

Consequently, the target particle size was not achieved in these experiments because the particle size used to calculate the amount of seed needed (number of particles) was different to actual one used in the experiment and hence, the particle growth led to a different particle size. Taking into account the particle size measured at the beginning of the reaction ($d_{p,t=0min}$, Table III.3) the predicted particle size evolution was calculated again, and as it can be observed in Figure III.5, in all cases the experimental particle size evolution fitted perfectly with the predicted particle size evolution.

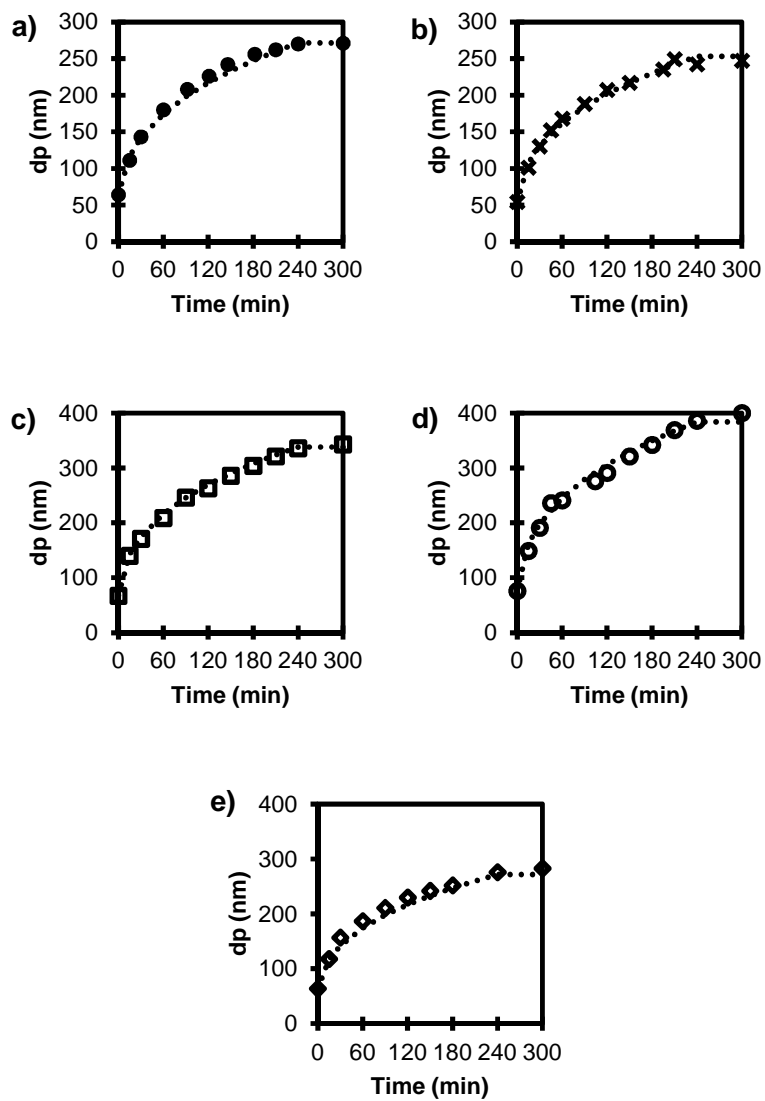


Figure III.5. Evolution of the experimental (symbols) and predicted (dashed lines) particle diameter (calculated using $d_{p,t=0 \text{ min}}$) for latexes synthesized using different surfactants: a) D60-B, b) SLS60-B, c) L60-B, d) S60-B and e) C60-B.

III.3. Effect of the particle size on the viscosity of the latexes

It is well known that the solids content, particle size distribution (PSD) and viscosity of the latex are closely related⁵⁻⁷. In the case of unimodal PSD latexes, for the same solids content, smaller particle size latexes will present higher viscosities due to the lower distance between particles which lead to the increase of the particle-particle interaction potential leading to an excessive increase on the viscosity of the latex^{2,6,8}. Therefore, if the evolution of the particle size is not controlled during the polymerization, latexes with different viscosities will be obtained.

Figure III.6 presents the viscosity vs. shear rate of the latexes (the details of the viscosity measurements are given in Appendix II). As it can be seen, the viscosity of all the latexes show shear thinning (pseudoplastic) behavior, characterized by the decrease of the viscosity as the shear rate increases. This behaviour is typical for most suspensions of solids in liquids, including latexes⁶. The viscosity, at low shear rate range, was found to be at least two orders of magnitude higher than for the high shear rate range. It is in the high shear rate range (10 to $>10^6$ s^{-1}) that most of the industrial applications take place⁹.

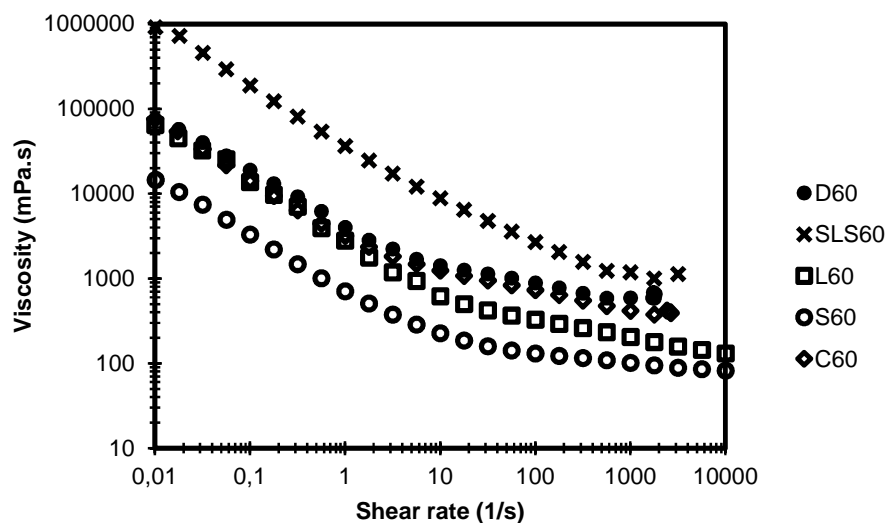


Figure III.6. Viscosity vs. shear rate for latexes at 60 wt% of solids content synthesized using different surfactants.

As expected, although all latexes presented shear thinning behavior, the viscosity was significantly affected by the particle size of the final latex. For the sake of comparison the viscosity values at 100 s^{-1} were taken and are summarized in Table III.4. Note that in Table III.4 the viscosity values of the latexes synthesized in Chapter 4 are also shown. In those latexes the evolution of the particle size during the polymerization was perfectly controlled. It is worth to mention that in this work viscosity values between 100 and 500 mPa.s at 100 s^{-1} of shear rate are considered as acceptable or relatively low viscosities, because this range is also considered in the industry.

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Table III.4. Viscosity (at 100s^{-1}) of the latexes synthesized using different surfactants.

Particle size not controlled			Controlled particle size ^{a)}		
Latex	dp (nm)	Viscosity at 100 s^{-1} (mPa.s)	Latex	dp (nm)	Viscosity at 100 s^{-1} (mPa.s)
D60-B	271	886	D60-1B	323	211
SLS60-B	247	2685	SLS60-1B	328	218
L60-B	343	326	L60-1B	324	386
S60-B	400	130	S60-1B	318	345
C60-B	283	731	C60-1B	319	205

^{a)} The synthesis of these latexes is presented in Chapter 4.

As it can be observed in Table III.4, all the latexes synthesized under controlled conditions presented relatively low viscosities. In the reactions where the evolution of the particle size was not controlled, only latexes synthesized using the polymerizable surfactants Latemul[®]PD-104 and Sipomer[®]Pam-200 (L60-B and S60-B latexes, respectively) presented relatively low viscosities, which in turn were the ones with the highest particle sizes. Latexes having smaller particle sizes (D60-B, SLS60-B and C60-B) were the ones with the highest viscosity and the viscosity values were far from being acceptable for industrial applications.

III.4. Conclusions

It has been demonstrated that the particle size of the seed latex is a key factor to control the evolution of the particle size and hence to obtain a target particle size during the polymerization of high solids content latexes when seed latexes with low surface coverage are employed.

It was observed that when the shot of KPS was added to the initial charge the particle size of the seed latexes changed due to the increase of ionic strength of the medium. Therefore, as the real particle size of the seed latex at the beginning of the reaction differed from that used to make the calculations, the target particle size was not obtained.

It has been also observed that the particle size of the latex had a huge influence on the viscosity of the latex. When the evolution of the particle size was controlled latexes with relatively low viscosities were obtained. However, latexes with particle sizes smaller than the predicted one presented high viscosities, which is not desired from the industrial and application point of view.

It can be concluded that to growth seed particles to high solids (likely to any solids), stable seed latexes against ionic strength are needed if the initiator is fully loaded in the initial charge or that the addition of the whole amount of anionic initiator to the initial charge should be avoided.

III.5. References

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