

Synthesis, Microstructure, Morphology and Properties of ABS polymers: rosin soap vs polymerizable surfactants

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Aita, Ama, Lorea, Eneko, Borja eta Gorka

Zuek gabe ez litzateke posible izango. Maite zaituztet.

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Chapter 1. Motivation and Outline of the thesis

1.1. Motivation and main objective of the thesis

Rubber-toughened plastics are an important commercial class of polymers, and Acrylonitrile-Butadiene-Styrene (ABS) represents one of the most important two-phase polymer systems with amorphous structure ^{1,2}. ABS polymers are elastomeric and thermoplastic compounds with a complex microstructure that allows the compatibility between the two polymeric phases (polybutadiene and styrene-acrylonitrile copolymer) and consequently, the combination of elastomeric and thermoplastic properties in a single polymer. ABS includes a large family of resins with excellent chemical and mechanical properties, for instance, good toughness and dimensional stability, high chemical resistance, and other special features, such as transparency, high heat performance and flame retardant properties. The compositional flexibility offered by the use of a three-monomer system combined with the option to alter structural and compositional parameters during the synthesis of the polymer, allow the polymer to be customize to meet specific requirements of the product ¹⁻⁴.

ABS polymer is considered an engineering plastic due to its broad balance of properties between the elastic behaviour and durability of polybutadiene (PB), the rigidity and good processability of polystyrene (PS) and the excellent thermal and chemical resistance of polyacrylonitrile (PAN). Due to its versatile properties, ABS polymer has been used in a wide range of applications, such as, automotive, transportation, healthcare and household appliances, electric and electronic devices, among others ¹⁻⁴. The main global market for ABS is the automotive industry, specifically in 2021, about 40 % of global ABS was used in the construction

of numerous car parts, such as bumpers, couches, panels, etc ⁵. ABS polymer can also be used to replace metallic materials in structural parts due to its good strength and mechanical properties.

ABS polymer was for the first time patented in 1948 and commercialized in the early 1950s ⁶. In 2020, around 11.4 million metric tons of compounded ABS were produced and the production has been slightly increased in the last years ⁷.

ABS polymer is composed by a multiphase structure that consists of a dispersion of PB particles in a styrene-acrylonitrile (SAN) matrix. At the same time, these PB particles are grafted with SAN chains and this grafting of the SAN onto the PB is critical to achieve effective dispersion and compatibility of both phases. Therefore, the grafting of acrylonitrile (AN) and styrene (S) monomers onto a PB substrate is the essence of the ABS process. There are several polymerization methods that are employed in the synthesis of grafted-ABS, including mass or bulk polymerization, solution polymerization and emulsion polymerization processes.

Industrially, the choice of one type of process or another is governed by a variety of technical and economic factors, such as, the final properties that are needed for the material and the cost of the process. Emulsion polymerization process for the manufacturing of ABS has been practiced for more than 60 years and is considered as the standard method for the synthesis of grafted-ABS since about 85 % of the grafted polymer is produced by this method ^{1,8,9}. Although emulsion polymerization is more complex than the mass process, it is widely used because a wide range of polymers with different properties can be obtained, particularly, polymers with high rubber content and specific particle sizes that cannot be obtained with other polymerization methods. Furthermore, since the aqueous medium acts as a heat sink, even at high monomer

conversions, the viscosity of the resulting latex is not highly increased and heat removal problems are substantially reduced. However, the emulsion process has some drawbacks, for example, the use of additional compounds, such as emulsifiers and buffers that can somehow contaminate the final material. In addition to this, coagulation or precipitation stage is needed to separate the polymer from the aqueous phase and the wastewater treatments are economically expensive increasing production costs ^{2,3,9}.

As mentioned above, industrial manufacturing processes for ABS usually comprise polymerization, where the grafted-ABS latex (raw material) is yield by emulsion polymerization, followed by coagulation and compounding, which is mainly necessary for preparing the final ABS product ⁸. Specifically, the manufacturing process to produce ABS polymer is composed by four different steps (Figure 1.1).

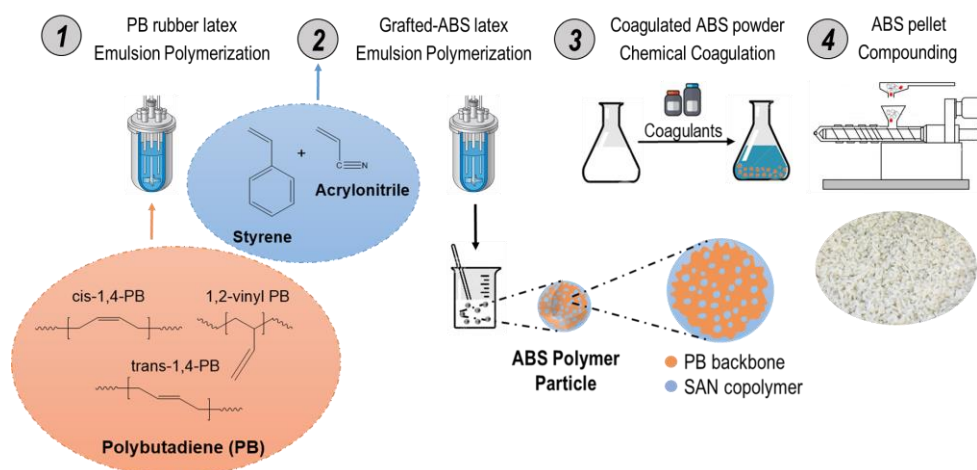


Figure 1.1. ABS manufacturing process summarized in four steps.

In the first stage, the PB rubber substrate is typically produced by free radical emulsion polymerization of butadiene, and it is subsequently used in the next step as seed latex. The

second stage of the process consists in the grafting reaction of styrene and acrylonitrile monomers in presence of the polybutadiene seed latex by a free radical process to obtain the grafted-ABS latex. As ABS polymer is generally sold as pellets, a chemical coagulation process is carried out to separate the grafted-ABS latex from the aqueous phase. Finally, it is blended along with more SAN copolymer that has been polymerized separately, and also with additional additives to obtain the final ABS pellet, which is then moulded by the customer into its end-use application¹⁻⁴.

In this work, the grafting reaction of styrene and acrylonitrile monomers onto the PB matrix has been extensively analyzed. A seeded semi-batch emulsion polymerization initiated by a water-soluble thermal initiator and stabilized by a rosin soap emulsifier has been used as reference ABS process.

So far, rosin soaps and fatty acid soaps have been the most widely used emulsifiers in the synthesis of ABS compared to other anionic surfactants, such as alkali metal or ammonium soaps, alkyl sulphate and sulphonates, among others¹⁰⁻¹⁷. Rosin soaps are composed of rosin acids, which undergo a chemical reaction with a hydroxide base to form the corresponding rosin salt or rosin soap¹⁸. As the word acid indicates, it contains a carboxylic group in the hydrophilic segment of the molecule, and therefore, in order to maintain the anionic form of the surfactant during the reaction, the synthesis must be carried out at basic medium. Therefore, rosin soaps are pH dependent surfactants and it is necessary to use a buffer solution along with the surfactant in order to guarantee the electrostatic stabilization of the polymer particles. This might be a challenge in the synthesis of grafted-ABS latexes, as the AN monomer can undergo secondary reactions at pH above 9, resulting in the formation of toxic organic compounds^{19,20}. In this work, a commercial rosin soap was used to synthesize the grafted-ABS latexes that were used as

reference latexes throughout the thesis. Usually, the amount of rosin soap needed is larger than other conventional anionic surfactants, since the CMC value for the mentioned surfactant (42.7 mM) is much higher than the cmc values of Dowfax™ 2A1 (0.45 mM) and sodium dodecyl sulphate (SDS) (8.3 mM) surfactants for instance^{21,22}. Also, as mentioned above, the rosin soaps come from the rosin acids, which are originally yellowish in colour, so both the use of higher amounts of surfactants and the use of buffer solutions contribute to the yellowness of the final ABS polymer and hence, it is necessary to use higher amount of pigments during the processing stage. In addition, it is worth mentioning that when high amount of conventional surfactants are used, a small residual amount of surfactant may be deposited in the injection molds, resulting in the formation of gases that negatively affect production and hindering the subsequent cleaning of the molds. Apart from the disadvantages mentioned so far, mainly during the synthesis of grafted-ABS latex, there are other drawbacks with respect to the coagulation process. Usually, the precipitation of the ABS polymer is carried out by means of a chemical coagulation process, which consists in the use of some acid and salts as coagulants. These acids and salts will remain in the wastewater after coagulation and will contribute to the increase in the Total Organic Carbon (TOC) of the water phase. Consequently, complex and expensive wastewater treatment is needed to decrease the TOC from the water before discarding it.

In order to find an alternative to the problems mentioned above related to the use of rosin soaps in the production of ABS, a large part of this thesis has been devoted to study the possibility of replacing the rosin soaps by polymerizable surfactants in the grafting reaction of the ABS. Polymerizable or reactive surfactants have the ability to bond covalently to the polymer particle due to the presence of a double bond in its molecular structure^{23,24}. There are different types of reactive surfactants, but in this work only surfmers (surface active monomers) were studied²³⁻²⁷, which act mainly as a conventional surfactant, but in addition to being adsorbed to

the surface of the particle, they can react and consequently are chemically bonded to the polymer.

The main goal of this thesis was to implement the use of polymerizable surfactants in the grafting reaction of ABS latex in order to overcome the negative effects caused by the use of conventional rosin soap surfactants. Specifically for the ABS system, the use of non-pH dependent surfactants could help to limit the production of toxic organic compounds since the reactions could be run at lower pH values and thus limit acrylonitrile secondary reactions. In addition, the replacement of rosin soap by other surfactants may reduce the yellowness of the final polymer and therefore less amount of pigments would be used during the processing stage. Furthermore, when polymerizable surfactants are used, a smaller amount of them is desorbed into the aqueous phase during the coagulation since they are bonded to the particle. This reduction in free surfactant could help as well to decrease the amount of residual surfactant in the injection molds, slightly reducing the economic cost and time consumed during the posterior cleaning stage.

1.2. Outline of the thesis

The content of the thesis has been divided in eight chapters. The first includes a brief introduction to the subject and explains the motivation and outline of the work.

Chapter 2 is based on a detailed introduction of the ABS polymer and its manufacturing process, especially, the grafting reaction through the emulsion process is explained, since it is the most important part of the ABS manufacturing process of this work. In addition, an

introduction based on the fundamentals of polymerizable surfactants and their use in ABS polymer is included.

In **Chapter 3**, the synthesis of ABS latexes using the conventional rosin soap and water-soluble thermal initiator (reference latexes) is described along with the characterization of the main properties of the latexes. In addition, the synthesis and properties of ABS latexes using thermal and redox oil-soluble initiator systems was addressed and compared with the ones obtained for the reference latexes.

In **Chapter 4**, the grafting emulsion polymerization of ABS latexes using four selected commercial polymerizable surfactants is presented. A comparison between these latexes and the reference latexes regarding the reaction kinetics and the main properties of the latexes are included. In addition, the characterization of the surfactant incorporation is addressed.

In **Chapter 5**, the macroscopic characterization of grafting properties of ABS latex (i.e. grafting degree and grafting efficiency) is optimized using ATR-FTIR and NMR spectroscopy. Furthermore, a comparison between the reference latexes and the latexes synthesized using polymerizable surfactants and on the other hand, oil-soluble initiators was carried out and discussed.

In **Chapter 6**, the microscopic characterization of the particle morphology and internal grafting properties of ABS latex is performed using advanced microscopic techniques. Notably, the internal grafting of the ABS particles was for the first time analyzed in the ABS latex state by HAADF-STEM tomography analysis coupled with 3D morphology reconstruction. The effect on internal grafting properties and particle morphology of two of the ABS latexes synthesized in Chapter 4 are addressed and compared with the properties and morphologies attained with the

reference latexes (Chapter 3). In addition to this, the morphology of the ABS particles synthesized using oil-soluble initiators were analyzed by STEM and discussed.

In **Chapter 7**, the relationship between the microstructure and the final properties of the ABS materials was evaluated. For that purpose, chemical coagulation and compounding of the ABS polymer was carried out. Subsequently, the characterization of the impact and mechanical properties and the distribution and morphology of the particles in the final materials were analysed.

Finally, **Chapter 8** summarizes the most relevant conclusions of the thesis.

Appendix I contains a summary of the materials used to synthesize and characterize the ABS latexes, and a detailed description of the latex characterization methods and techniques. **Appendix II** includes a preliminary study based on the use of polymerizable surfactants in the batch emulsion polymerization of SAN copolymer. Also, additional characterization results of the ABS latexes synthesized in Chapter 3 and Chapter 4 are included. In **Appendix III**, additional information obtained from the literature and experimental results regarding the characterization of the grafting properties of ABS polymer are summarized along with a description of the 3D-electron tomography technique used to characterize the particle morphology. **Appendix IV** contains a detailed description of the compounded material's characterization methods and techniques. Finally, **Appendix V** describes a preliminary study of the synthesis of polybutadiene latex in a pressure reactor by emulsion polymerization process that was carried out during the internship at CP2P of the University Claude Bernard at Lyon.

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Chapter 2. Introduction

2.1. Acrylonitrile-Butadiene-Styrene (ABS) polymer system

As it has been mentioned in the previous chapter, ABS polymer is composed of three different monomers: acrylonitrile (AN), butadiene (B) and styrene (S). Acrylonitrile provides thermal and chemical resistance, butadiene contributes to the elasticity and good mechanical properties of the material, and styrene gives rigidity and processability to the polymer. The use of these three monomers provides a unique combination of properties (see Figure 2.1).

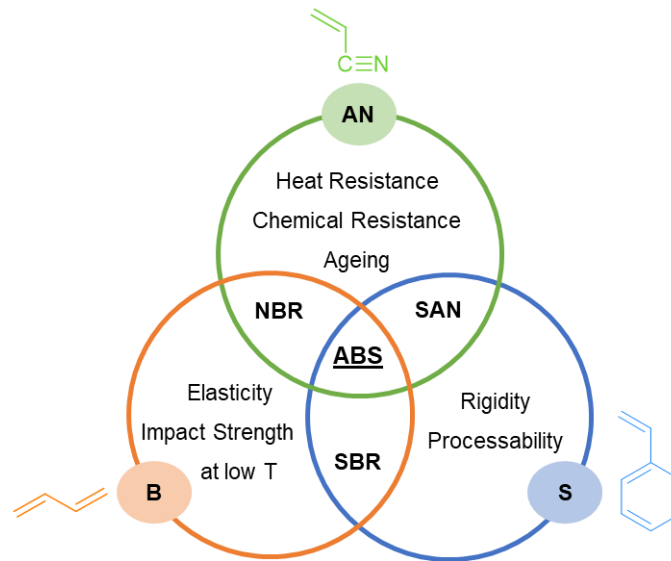


Figure 2.1. Combination of Acrylonitrile (AN), Butadiene (B) and Styrene (S) properties to form ABS polymer.

In addition, during the production process of ABS, structural and compositional parameters can be varied to tune the polymer properties. ABS polymer has been positioned as an engineering plastic that contains improved properties compared to other widely used polymers, such as nitrile-butadiene rubber (NBR), styrene-acrylonitrile polymers (SAN) or styrene-butadiene rubber (SBR)¹ (see Figure 2.1), since it contains a combination of the properties given by all the polymeric systems mentioned previously.

Historically, the earliest method to produce ABS was mechanically blending SAN copolymer with modified PB rubber (SBR or NBR)²⁻⁴. In this case, grafting did not take place and the dispersion depended on the degree of mixing, so the final properties of the material were poor due to the low compatibility between the two polymeric phases. Although it was the easiest and fastest method to produce ABS, nowadays, this type of ABS is hardly produced. On the other hand, grafted-ABS polymer is the one that governs the market since it allows to obtain a combination of properties between the different polymeric phases, which are compatible due to the grafting⁴. The nature of these polymers is complex since it is composed by a multiphase structure in which a soft elastomeric phase, that is, polybutadiene (PB) particles are grafted with SAN copolymer chains, and simultaneously these particles are dispersed in a hard SAN matrix, as it is shown in Figure 2.2. The grafting reaction will be explained in detail in Section 2.2.1.2, but summarizing it can be said that during the reaction, which is generally carried out by emulsion polymerization process, the SAN chains are grafted onto the PB backbone chains, but free SAN chains are also formed. More specifically, the microstructure of ABS can be varied depending on the type of initiator used in the grafting reaction (it will be further discussed in Chapter 3 and Chapter 5). For instance, when water-soluble initiators are used, the SAN chains can be grafted both inside the particle forming occlusions or clusters that are dispersed in the PB core (internal grafting) and on the surface of the particle (external grafting) forming a shell that surrounds the

particle along with the free SAN chains that have been polymerized but not covalently attached to the polymer particle⁵⁻⁷. The typical microstructure of grafted-ABS polymer particles synthesized using water-soluble initiators is shown in Figure 2.2.

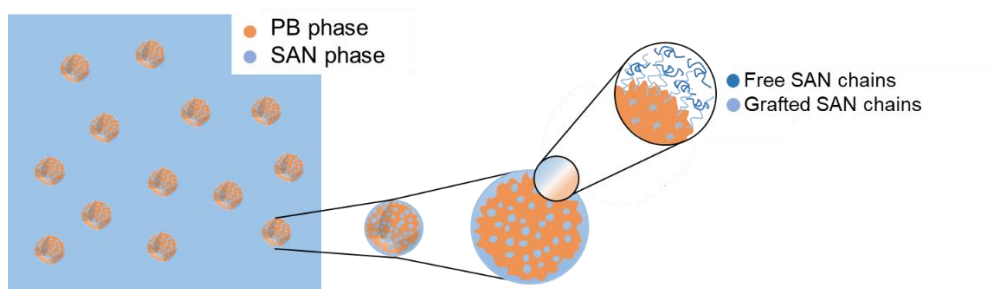


Figure 2.2. Multiphase structure of grafted-ABS polymer containing grafted PB particles dispersed in a SAN matrix.

2.2. Manufacturing process

During the initial stage of the ABS development, the manufacturing process was based on the direct physical blending of ungrafted PB rubber with a copolymer of SAN. Nowadays, the grafting polymerization followed by mechanical blending is the main production process, since only the mechanical blending of PB and SAN was giving low compatibility between the phases and, consequently, ABS materials with poor mechanical and optical properties were obtained. Therefore, this work has mainly focused on investigating the grafting emulsion polymerization process varying parameters, such as the surfactant type and concentration, followed by coagulation and mechanical blending to obtain the final compounded ABS material. So for now on, the grafted-ABS will be referred as simply ABS for simplification.

Three main polymerization types are used for the synthesis of ABS polymer: mass or bulk polymerization, suspension polymerization and emulsion polymerization. The choice of a process is generally governed by a variety of technical and economic factors. The three polymerization types will be briefly explained in the following lines, and emulsion process will be explained in detail in section 2.2.1.

The mass polymerization process is conducted in absence of solvent in a monomer medium, so previously polymerized PB (uncrosslinked) by solution polymerization, is dissolved in an azeotropic mixture of S and AN monomers (76:24 wt% S:AN) ⁸⁻¹¹. The polymer is usually produced in two or more continuous stirred tank reactors (CSTR), therefore, the material is more homogeneous in comparison to polymers made in batch processes ¹². The reaction mixture contains additional reagents, such as initiator and CTA, which are necessary to carry out the polymerization and obtained the proper microstructure. Sometimes diluents are additionally used to reduce the viscosity of the reaction medium and to improve the processing at high conversions ^{8-10,12}. Initially, the uncrosslinked PB rubber is dissolved in the monomers (styrene and acrylonitrile), obtaining a homogeneous phase. When the polymerization starts, the monomers are copolymerized to produce both free SAN and grafted SAN chains, and two polymeric phases can be distinguished; SAN copolymer chains dissolved in the monomers and the grafted and non-grafted PB chains dissolved in the monomers. At this point, the smaller phase (SAN copolymer in monomer) is dispersed in the larger phase (grafted and non-grafted PB in monomer). However, as the polymerization proceeds, the phase corresponding to the SAN copolymer dissolved in monomer becomes bigger in volume and a phase inversion occurs resulting in a dispersion of grafted-PB particles in a continuous SAN phase ^{10,13}. Finally, the product is devolatilized to remove the unreacted monomer, which is recovered and recycled back to the reactor to improve the process yield ^{11,12}.

The suspension process of ABS is a two-stage process in which initially a mass reaction, containing PB chains and SAN copolymer chains dissolved in the monomers (styrene and acrylonitrile), is stopped at a monomer conversion around 15 – 30 %, and then, the mixture of polymer and unreacted monomer is transferred and suspended in water using a suspending agent and the polymerization is continued until the desired conversion is reached ^{11,14–18}. Finally, the unreacted monomers are removed before the suspension is centrifuged and dried, directly obtaining the ABS polymer particles.

As mentioned in the previous chapter, the ABS manufacturing process involving emulsion polymerization process is mainly divided into four different steps that includes the synthesis of PB rubber latex, which is used in the next step as seed, the grafting of S and AN monomers in presence of PB seed to obtain the ABS latex. Then, the coagulation process to isolate the grafted polymer is carried out and finally mechanical blending of the coagulated ABS polymer (dispersed phase) along with more SAN copolymer (continuous phase), which will act as matrix in the final material, together with other additives to obtain the final ABS compound.

One of the main differences between the mass, suspension and emulsion ABS products is the microstructure of the polymer, involving the shape, size and internal morphology of the particles ^{13,3}. For instance, the volume fraction of the rubber phase for a given rubber content can be much higher for ABS products manufactured by mass polymerization due to the higher SAN chains occluded within the particle compared to the emulsion-ABS particles, as shown in Figure 2.3. ^{19,3}.

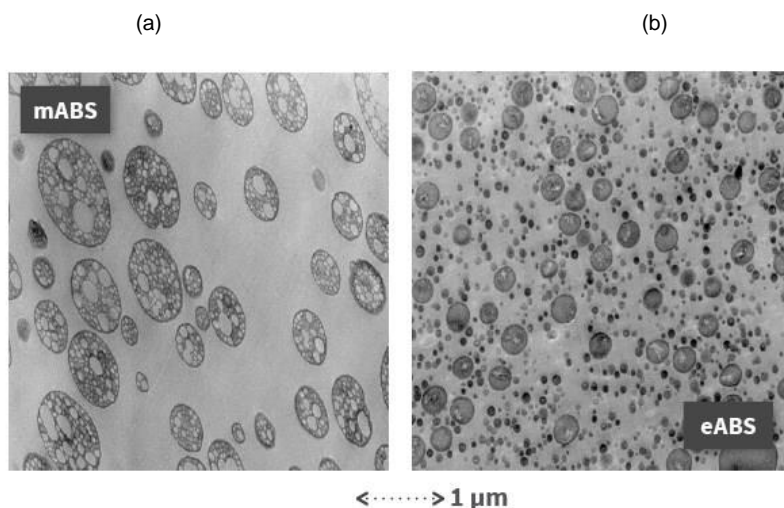


Figure 2.3. Electron microscopy images of ABS polymer particles produced by (a) mass and (b) emulsion polymerization processes ²⁰.

As mentioned, the particle size is also affected by the polymerization process, resulting in average sizes around 1000 – 2000 nm and 100 – 500 nm for ABS produced by mass and emulsion polymerizations, respectively. Nevertheless, the control of the particle size is better in emulsion than in mass as it can be exactly defined by the type and amount of surfactant, whereas in mass polymerization the only way to control the particle size is varying the shear rate of the reaction ¹. The smaller particle sizes in emulsion-ABS lead to higher gloss materials, while the high particle sizes in mass-ABS have less gloss and surface quality, but more translucent and good unpigmented colour materials are obtained, which can reduce the amount of pigments required during the processing stage. In addition, in mass-ABS materials the extent of rubber content is limited to around 20 % because of viscosity limitations, however, the rubber efficiency is higher due to the higher occlusions per amount of rubber, which means that less amount of rubber is needed to achieve a great impact strength in comparison to emulsion-ABS ¹.

On the other hand, the suspension process has some advantages, which are similar to those of emulsion process, compared to the mass process, such as good heat removal and low dispersion viscosity, but on the other hand, the production capacity is lower for the same reactor volume. In comparison to emulsion process, it has lower level of impurities in the final product and the process of separating the polymer from the aqueous phase is less costly than for emulsion ABS latexes. However, it has the same waste water problems and in terms of the process, only batch suspension polymerization are used industrially and continuous processes are not operating yet, which can lead to ABS polymer with non-homogenous copolymer compositions, among others ^{11,20}. Moreover, there are several characteristics and properties of the polymer that can only be obtained by emulsion polymerization, as it will be explained in the following section.

2.2.1. Emulsion polymerization in ABS manufacturing process

Emulsion polymerization is the most relevant process to obtain waterborne polymer dispersions. It is a heterogeneous free-radical polymerization in which colloidal polymer particles are produced in a continuous medium, typically water. This technique offers several advantages over mass and suspension polymerization. From an environmental point of view, the use of water as dispersion medium or continuous phase is a great advantage since the heat generated during the reaction is easily dissipated and it is much easier to control temperature due to the lower viscosity of the medium and the high specific heat capacity of water. This advantage is especially important in industrial scale operations, nevertheless, it is important to mention that free radical polymerizations are highly exothermic reactions and an efficient heat removal system is essential for the safety and control of the process. A very important feature of emulsion polymerization is compartmentalization, which is a unique feature of this technique that allows to obtain high molar

masses and high polymerization rates at the same time. Unlike other homogeneous systems, in emulsion polymerization the viscosity of the medium does not depend on the molar mass of the polymer, so this technique is ideal to obtain polymer particles with very high molar masses, above 10^3 kDa^{21–25}.

The understanding of emulsion polymerization is important, so in the following lines the process of a batch emulsion polymerization is briefly explained²³. Although batch emulsion process is not frequently used industrially, it is easier to understand as the fundamentals occur in a sequential way, whereas in the semi-batch and continuous modes the processes occur simultaneously.

The main components in an emulsion polymerization are the monomer(s), the dispersing medium (water), the initiator (usually water-soluble, but oil-soluble can also be used) and the surfactant. The monomers are dispersed in water in the presence of surfactants. The surfactants adsorb on the surface of the monomer droplets, stabilizing them. In most formulations, the amount of surfactant exceeds the one needed to completely cover the monomer droplets and saturate the aqueous phase. The excess of surfactant forms micelles that are swollen with monomer. Most initiators are water-soluble, therefore the radicals are formed in the aqueous phase. These radicals are often too hydrophilic to directly enter into the organic phases (monomer droplets and micelles). Therefore, they react with the monomer dissolved in the aqueous phase, forming oligoradicals that grow slowly because of the low concentration of monomer in the aqueous phase. After adding some monomer units, the oligoradicals become hydrophobic enough to be able to enter into the organic phases of the system. Because the total area of the micelles is about three orders of magnitude greater than that of the droplets, entry of radicals into the micelles is more likely. The entering oligoradicals find a monomer-rich

environment within the micelle, and hence they grow fast forming a polymer chain. The new species formed upon entry of a radical into a micelle is considered a polymer particle. The process of formation of polymer particles by entry of radicals into micelles is called heterogeneous nucleation^{23,26}. Polymer particles can also be formed when the oligoradicals grow in the aqueous phase beyond the length at which they are soluble in water and precipitate. The precipitated polymer chain is stabilized by the emulsifier present in the aqueous phase, and monomer diffuses into the new organic phase, which allows a fast growth of the polymer chain. The process of formation of polymer particles by precipitation of oligoradicals is called homogeneous nucleation^{23,27}. Both homogeneous and heterogeneous nucleation may be operative in a given system.

During nucleation, monomer droplets, monomer swollen micelles and monomer swollen polymer particles coexist in the batch reactor. Polymer particles efficiently compete for radicals and as their number increases, they become the main polymerization loci. The monomer that is consumed by free-radical polymerization in the polymer particles is replaced by monomer that diffuses from the monomer droplets through the aqueous phase. Therefore, the size of the particles increases and that of the monomer droplets decreases. The number of micelles decreases because they become polymer particles upon entry of a radical, and also because they are destroyed to provide surfactant to stabilize both the polymer chains that precipitate in the aqueous phase and the increasing surface area of the growing polymer particles. After some time, all micelles disappear. This is considered to be the end of the nucleation and only limited formation of new particles may occur after this point because heterogeneous nucleation is not possible and there is no free surfactant available in the system to stabilize the particles formed by homogeneous nucleation. The stage of the batch emulsion polymerization in which particle nucleation occurs is called **Interval I**^{23,26,28}.

In **Interval II**, the system is composed of monomer droplets and polymer particles. The monomer consumed by polymerization in the polymer particles is replaced by monomer that diffuses from the monomer droplets through the aqueous phase and hence, the monomer partitions between the different phases of the system according to a thermodynamic equilibrium. In the presence of monomer droplets, the concentration of the monomer in the polymer particles reaches a maximum value that is roughly constant during Interval II.

Because of the polymerization and monomer transport, the polymer particles grow in size and after some time, the monomer droplets disappear, marking the end of Interval II. The monomer conversion at which Interval II ends depends on the extent in which the polymer particles are swollen by the monomer. In general, the more water-soluble the monomer, the higher the maximum swelling, and hence, the lower the monomer conversion at the end of Interval II. This means that for many systems the monomer polymerizes during **Interval III**. In this interval, the monomer concentration in the polymer particles decreases continuously ²³.

Emulsion polymerization for the synthesis of ABS was commercialized in the early 1950s, and it has been widely used since then due to several advantages ^{1,3,10,11}:

- In the grafting reaction, using the correct initiator system, low temperatures can be used running the reaction at atmospheric pressure, making the process relatively inexpensive.
- Mixing and transfer of the heat of reaction is achieved more easily than in mass polymerization process due to the low viscosity and good thermal properties of the water phase.

- Capability of producing ABS with a wide range of composition, for example, higher rubber content than with other processes can be obtained.
- Many changes can be made, such as, rubber particle size, rubber content, SAN ratio, molar mass (M_w) of the grafted SAN and of the free SAN, ratio of grafted SAN to free SAN, etc.
- Other monomers can be added to yield products with even better properties.

However, the process has also, some disadvantages:

- The energy requirements are generally higher than in other types of polymerization due to the energy used in the coagulation, washing and drying steps.
- Energy consumption remains high, even when the process is carried out under strict security measures.
- Large volume of hot air is required to heat the initial water where polymerization takes place, increasing the capital cost of the equipment.
- After the coagulation process, large volumes of waste water must be treated before being discarded.

Having all the advantages and disadvantages in mind, lets now study each of the steps needed to produce the ABS by emulsion polymerization in more detail.

2.2.1.1. Synthesis of polybutadiene (PB) rubber latex

The synthesis of the PB rubber is typically produced by free radical emulsion polymerization of butadiene^{3,10,19,29-31}. The radical source can be provided by water-soluble (e.g.

KPS), and oil-soluble (e.g. AIBN) thermal initiators or by redox (e.g. H_2O_2 as oxidant and Fe ion as a reductant) initiator systems. As the butadiene monomer has two double bonds in its structure, depending on monomer addition site, different polymer configurations can be obtained: 1,2-vinyl-PB, which contains a pendant vinyl group, and 1,4-PB, which has two isomers, cis-1,4-PB and trans-1,4-PB (Figure 2.4). The ratio of each isomer depends on various parameters, such as initiator and surfactant type and content, and polymerization temperature. For instance, it was reported that the 1,2-vinyl-PB content was not affected by the reaction temperature, however, when increasing polymerization temperatures, the cis-1,4-PB content increased, and when decreasing the temperature, the trans-1,4-PB content ^{29,32}. In addition, it was observed that PB synthesized at low temperatures, containing higher amount of trans-1,4-PB improved physical properties, whereas the one synthesized at high temperatures, contained random sequences of the three isomers, which could be the main reason for the weak physical properties of the polymer ²⁹.

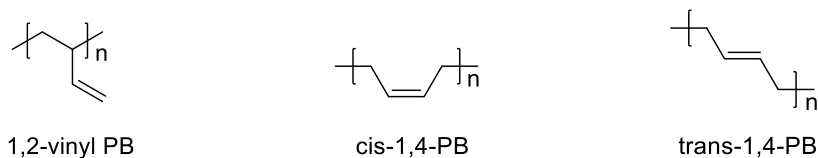


Figure 2.4. Different polybutadiene (PB) isomers that can be obtained during the synthesis of polybutadiene.

During the polymerization of butadiene, crosslinking can occur at high conversions (above 60 % ³³) through the abstraction of the allylic sites or by copolymerization with the pendent double bond (see Figure 2.5), especially in the more sterically accessible pendant vinyl group. However, crosslinking density can be controlled by the use of chain transfer agents (CTA), the type and concentration of initiator, reaction temperature, degree of conversion or by addition of

comonomers^{19,29–31,34}. Regarding the stabilization of the particles, different surfactant types can be employed, such conventional detergents^{35,36}, but fatty acid and rosin soaps have been the most used ones by far^{3,10,19,29,37}. In addition, the use of soap-free emulsion polymerization is also possible using reactive surfactant functional monomers or high level of potassium persulfate initiator^{30,31}.

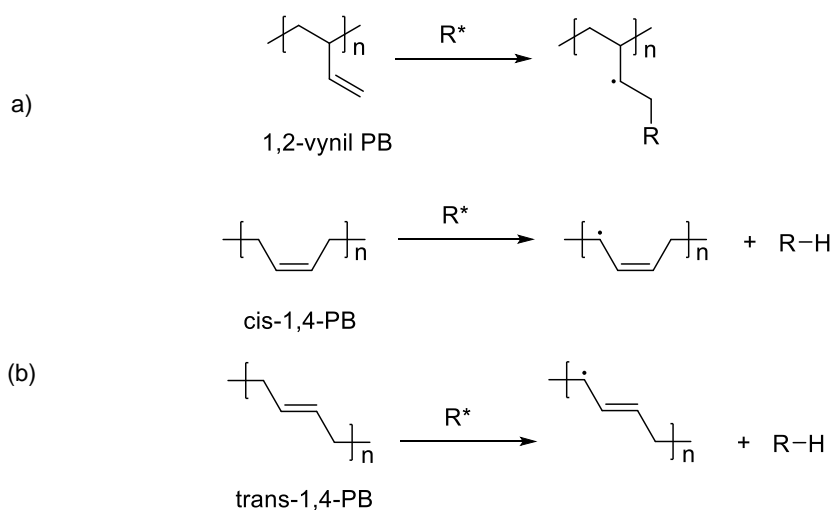


Figure 2.5. Crosslinking mechanism of polybutadiene (PB) isomers by (a) copolymerization with the pendant double bond and (b) H abstraction of the allylic site, where R^* is an active polymeric radical.

In the polymerization of butadiene, batch, semi-batch or continuous processes can be used. For instance, batch emulsion polymerization of butadiene is one of the most used emulsion polymerizations in industry due to the low polymerization rate of the monomer. Therefore, it is of high importance to improve the initiator efficiency in the particle nucleation and to increase somehow the polymerization rate in order to decrease the long polymerization times. In addition, due to the physical properties of the butadiene at room temperature that it is on vapour state, the reaction needs to be run under pressure and special safety equipment are required.

The desired particle size of the rubber latex can be obtained by direct growth during the nucleation, through agglomeration process subsequent to the polymerization by the controlled addition of acids to the latexes synthesized with carboxylate based surfactants (rosin and fatty acids) or by growing the already existing polymer particles in a secondary reaction by the addition of more monomer, initiator and surfactant^{10,29}. However, the latexes obtained by agglomeration of smaller particles typically have a broader particles distribution than those obtained by growing the particles during the polymerization, and that could be undesirable for some applications¹⁰. Finally, it has to be taken into account that the PB particle size, particle size distribution and the degree of crosslinking can have direct effect on the grafting, as well as in the mechanical properties of the final product, as it will be explained in Section 2.3.1.

2.2.1.2. Grafting reaction of styrene (S) and acrylonitrile (AN) onto PB rubber

Grafting of S and AN onto the PB backbone chains is the essence of the ABS process, since it is critical to achieve effective dispersion of the grafted-PB particles in the SAN matrix and thus, achieve good compatibility between both phases. The mechanism for grafting reaction is shown in Figure 2.6. It is a free radical process that can be initiated by the abstraction of hydrogen in the allylic sites (R1.a), by copolymerization with the pendant double bond (R1.b) or by radical addition to the PB chain (R2), where the radical (I*) could be both a new initiator radical fragment or a radical from a growing copolymer chain. In addition, the active radical (I*) can also react with a monomer unit of S or AN, and create a growing SAN copolymer radical chain (R3), which will be a competitive reaction with R1 and R2.

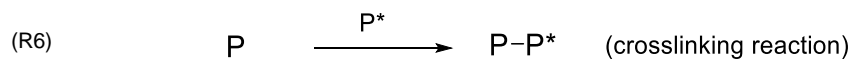
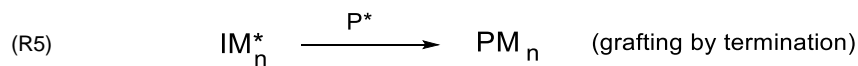
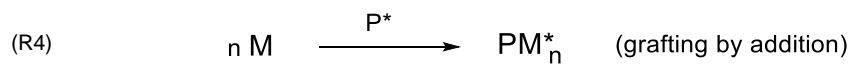
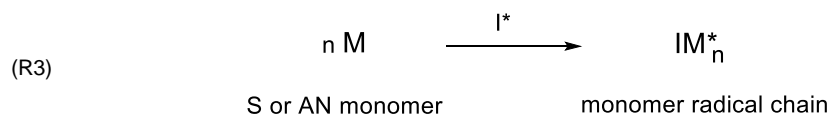
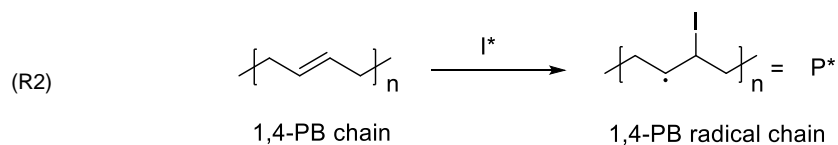
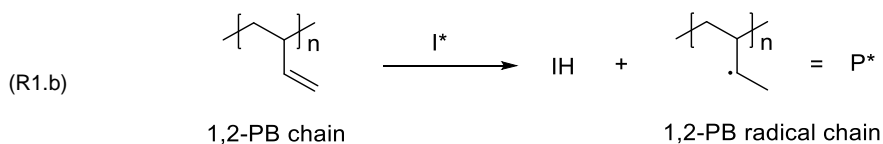
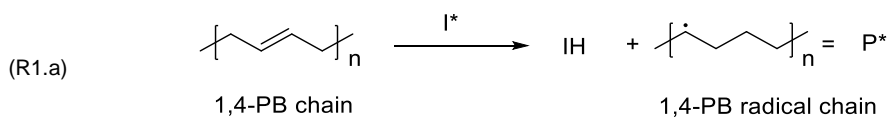


Figure 2.6. Mechanism of grafting reaction in free radical emulsion polymerization of ABS polymer, where I^* is a primary initiator radical or a growing copolymer SAN radical.

Moreover, the PB radical created in reaction R1 and R2 (P^*) can alternatively initiate polymerization by addition to a monomer unit (R4), terminate with a growing SAN copolymer radical chain (R5), induce crosslinking by combination with another PB chain (R6) or undergo

chain transfer reaction with a CTA (R7). It was reported that the resulting competition between creating growing polymer chains (R1 and R2) and free SAN copolymer chains (R3) was determined by the nature of the initiator. For instance, oxyradicals appear to yield higher degree of grafting than carbon centered radicals due to the higher rate of abstraction³⁸⁻⁴⁰, while the grafting level was attributed to be a function of the 1,2-vinyl PB content, monomer concentration, type and amount of initiator, reaction temperature and CTA concentration³⁸⁻⁴².

The grafting emulsion polymerization reaction can be carried out in batch, continuous or semi-batch processes¹⁰. In the batch process, all the reactants are charged in the reactor, the temperature is increased in order to start the polymerization and it is let polymerizing over a period of time. It is the less use process since does not offer control over the polymerization and moreover, care must be taken with heat release in the early stages of the polymerization since the polymerization is exothermic. In the continuous process, all the reactants are continuously added to the reactor and simultaneously the final product is removed from the reactor. A high amount of the industrial ABS is produced by continuous processes and CSTR are usually used. While the level of control and compositional drift can be maintained with various reactor designs (such additional reactors in series), the monomer concentrations remain relatively high at the end of the reactor train. Continuous process can also benefit from good process control and on-line process monitoring. However, the effects of corrections made during the polymerization reaction require three to four residence times before they are fully incorporated into the product¹⁰. The last option is the semi-batch emulsion polymerization process, where the PB seed latex along with the rest of reactants except the monomers are initially charged in the reactor and then the monomers, usually along with more initiator and surfactant, are fed over a period of time. In this case, as the feeding of initiator and monomers is controlled, the rate of polymerization can be also controlled and thus the heat released during the reaction. In addition, the temperature

can be also regulated during the reactions and this leads to more controlled structure and morphology of the polymer. Since the instantaneous S and AN concentration is controlled, it is very useful to produce a compositional change at one point in the reaction and also it provides the option for the addition of a functional monomer in the late stage of the polymerization. As in the batch process, the residual monomer can be lowered at the end of the reaction, which is an important environmental issue in industry ¹⁰. Therefore, it can be concluded that semi-batch emulsion polymerization is the most versatile process for the grafting reaction of ABS and it is usually used for the production of special grade ABS polymers.

A typical formulation recipe for the grafting reaction of ABS is shown in Table 2.1 ⁴³. As mentioned before, in semi-batch emulsion polymerization reaction, the PB seed latex, continuous phase, emulsifier, CTA and buffer if needed are first charged into the reactor. The temperature is raised and the initiator shot is added in order to start the polymerization. Then, both S and AN monomers are fed, along with more initiator and surfactant, over a period of time. Usually, the polymerization is performed in the range of 40 – 85 °C at atmospheric pressure and under nitrogen for between four and eight hours to reach high conversions at the end of the reaction. The solids content for ABS latexes are typically in the range of 25 – 50 %; above these values heat removal is challenging. The rubber content range is typically varied from 10 to 30 % and the feeding ratio for styrene and acrylonitrile follows the azeotropic composition (76:24 wt %). It is worth to mention that the difference in water solubility of S ($\delta = 0.3$ g/L at 25 °C) ⁴⁴ and AN ($\delta = 75$ g/L at 25 °C) ⁴⁴ can also perturb the concentration of each monomer at the reaction sites, which means that the concentration of S could be higher in the grafted SAN chains, while the AN concentration could be greater in the SAN free chains. However, this fact does usually not affect the compatibility between the two phases ^{3,45}.

Table 2.1. Typical formulation for the grafting emulsion polymerization of ABS ⁴³.

Components		wt (%) / * wbm (%)
Continuous phase	^a Water	75
Seed	^b Polybutadiene	7.4
Monomers	Styrene : Acrylonitrile	12.4 : 5
Initiator system	Potassium Persulphate	0.1 / * 0.7
Emulsifier	Sodium Oleate	0.1 / * 0.7
Chain Transfer Agent	Tert-dodecyl mercaptan	0.02

^a Amount coming from continuous phase and PB seed latex. ^b Amount regarding the PB polymer in the latex.

Since 1970, large amount of patents have been published regarding ABS manufacturing process, and especially the patent literature concerning the emulsion polymerization process was reviewed by Placek ⁴⁶. As said, the patent literature of ABS is very extensive, it could even be said that the number of patents related to ABS are quite similar to the number of articles in the literature. For that reason, some examples of different patents will be explained in order to identify the emulsifiers and initiator systems that have been most used in the grafting reaction of ABS. For instance, US438515732 ⁴⁷ presented an emulsion polymerization process for preparing a polybutadiene latex with bimodal particle size distribution followed by grafting of the polybutadiene latex in the presence of a monomer mixture. Different examples were presented and many different surfactants were employed in the process. Soap or fatty acid soaps based on sodium or potassium salts, such as alkali salts of saturated or unsaturated organic carboxylic acids with chain length between 12-18 carbons, were used as anionic surfactant. Another example of surfactants can be found in US350923830 ⁴⁸, where a method to produce two graft ABS copolymers with low and high degree of grafting, and thus obtain a bimodal composition ABS material, was explained. Fatty acid soaps, alkali metal or ammonium soaps, alkyl sulphates

and sulfonates, mineral acid salts of long chains aliphatic amines were the emulsifiers presented in this work. However, according to the author, the most successful surfactants were the sodium oleate, sodium palmitate and sodium stearate fatty acid soaps. On the other hand, various conventional water soluble initiators, such as alkali metal peroxides, persulfates, percarbonates or hydrogen peroxide, were used. In addition, they reported that the use of oil soluble initiators, such as diterbutyl peroxide, benzoyl peroxide and lauroyl peroxide may accelerate the polymerization process. US430126431 ² reports an emulsion polymerization process where the reduction of the residual monomer was assessed. A secondary initiator was employed and it could be a thermally decomposable free radical initiator or a redox initiation system in combination with a water soluble initiator. As thermal initiator, tertiary butyl peroctoate, benzoyl peroxide or tertiary butyl perpivalate were used. On the other hand, as oxidant component different hydroperoxides were used, and as reductant diethylene triamine (DET) and tetraethylene pentamine (TEP) amines were used.

2.2.2. Coagulation step in ABS manufacturing process

Many industrial polymers that are obtained by emulsion polymerization are neither used nor applied in latex form in their final applications (eg. SBR, EVA redispersable powders or ABS), but the polymer particles are separated from the aqueous phase prior their use. Therefore, recovery of the polymer particles is achieved by destabilizing the colloidal dispersion ⁴⁹. The destabilization of the latex is often industrially obtained by the addition of salts and acids or bases for anionically or cationically stabilized latexes, respectively, or by spray drying ^{50,51}.

ABS latex coagulation is a pre-processing stage in the manufacturing of ABS typically carried out through a continuous process, where the particles are precipitated from colloidal latex that has been synthesized previously by emulsion polymerization. There are several techniques

that have been used to destabilize the latexes, such as, chemical coagulation, evaporative precipitation, shear and freeze coagulations, among others ⁵²⁻⁵⁴. However, the most used one is the chemical coagulation process due to the rapid and controlled coagulation of the latex. In addition, the coagulation induced by chemical coagulants, mechanical shear and heat has been found to be the most effective process ⁵⁵.

2.2.2.1. Mechanism of destabilization of polymer particles

In emulsion polymerization, the polymer particles collide with each other due to Brownian motion and when agitation is applied also due to the fluctuating hydrodynamic force. When a colloidal particle is close to another one, they are attracted to each other by Van der Waals forces. If there is no counteracting force, the particles will irreversibly aggregate and the colloidal system will be destabilized. In emulsion polymerization, two colloidal stability mechanisms can take place according to the nature of the emulsifier: i) electrostatic stabilization with ionic emulsifiers and ii) steric stabilization with non-ionic emulsifiers ⁵⁶⁻⁵⁸. In this work, only the electrostatic repulsion force will be discussed since the surfactants used during the research are all of ionic nature.

Surface forces at the interface of the particle and the liquid are very important because of the nano-size of the colloids. One of the main surface effects is the electro-kinetic that consists in the electrical charge of each colloid, which produces an electrostatic repulsion between adjacent particles. If these charge is high enough, the colloids will remain separated and dispersed in the aqueous medium. If the opposite goal is wanted, reducing or eliminating the charge will result in the agglomeration of the colloids, changing the characteristics of the dispersion. Particle charge can be modify by changing the continuous phase pH, changing the

ionic species in solution or a more direct technique is to use surface active agents, which directly adsorb to the surface of the colloids changing its characteristics⁵⁷⁻⁵⁹.

The surface of the particles are usually negatively charged due to the presence of the anionic emulsifiers used in the polymerization process and the negative charges of the initiator fragments. The electrical double layer model is used to visualize the ionic environment of a charged colloid and explains how electrical repulsive forces occur (see Figure 2.7). Initially, attraction from the negative colloid causes some of the positive ions to form an attached layer around the surface of the colloid, this layer of counterions is known as the *Stern* layer. In addition, more positive ions are still attracted by the negative colloid, but at the same time are repelled by the Stern layer, as well as by other positive ions that are also trying to approach the colloid. This dynamic equilibrium results in the formation of a *diffusive* layer of counterions. Therefore, near the surface high concentration of charges are present and it gradually decreases with distance, until it reaches equilibrium with the counterion concentration in the solution medium. On the other hand, there is a lack of negative ions in the neighbourhood of the surface, because they are repelled by the negative colloid. These negative ions are called co-ions and their concentration will gradually increase with distance, until equilibrium is again reached. So the Diffuse layer, composed by counterions and co-ions can be visualized as a charged atmosphere surrounding the colloid. The charge density at any distance from the surface is equal to the difference in concentration of positive and negative ions at that point. So, the Stern layer and the Diffuse layer formed the electrical double layer, shown in Figure 2.7, and the thickness of this layer depends upon the valence and concentration of the ions in the solution and of the temperature⁵⁷⁻⁵⁹. The electrical double layer causes an electro-kinetic potential between the surface of the colloid and any point in the mass of the suspending liquid. This voltage difference (order of millivolts) is referred to as the surface potential. The magnitude of the surface potential is related to the

surface charge and the thickness of the electrical double layer. As the distance from the surface increases, the surface potential drops off in the Stern and diffuse layer, approaching zero at the imaginary boundary of the electrical double layer. As mentioned before, a charged particle will move with a fixed velocity and these mobility is related to the electrical potential at the boundary between the moving particle and the liquid, among others. This boundary is called the slip plane and is determined as the point where the Stern and diffuse layer meet and the potential at this point is called the zeta potential ^{57,58,60,61}.

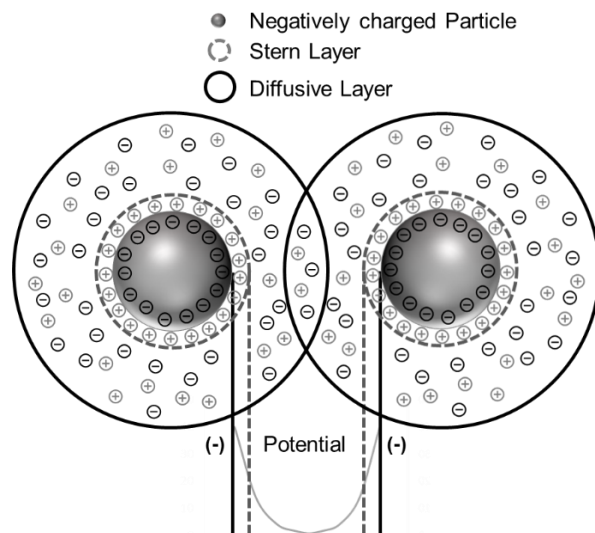


Figure 2.7. Diagram of the electrical double layers of two polymer particles separated by repulsion.

The DLVO theory (developed for dilute dispersions) explains the stability of the colloids in suspension and why some colloidal systems coagulate while other do not, based on the balance between two opposite forces; i) electrostatic repulsion and ii) Van der Waals attraction. This balance can be visualized in Figure 2.8. Electrostatic repulsion becomes significant when two colloids approach each other and their electrical double layers begin to interfere. An

electrostatic repulsion curve is represented as positive potential, as shown in Figure 2.8, and is used to indicate the energy that must be overcome if the particles are forced together. The energy has a maximum value when the particles are almost touching and decreases to zero outside the electrical double layer. This maximum energy is related to the surface potential and the zeta potential. On the other hand, Van der Waals attraction is the sum of forces between individual molecules in each colloid, with the molecules of the other colloid, and the variation of these forces with distance between particles is represented as negative potential, as shown in Figure 2.8. Assuming that the attractive and repulsive potentials are additive, the total interaction energy curve can be calculated as a function of the distance of two colloidal particles (Figure 2.8).

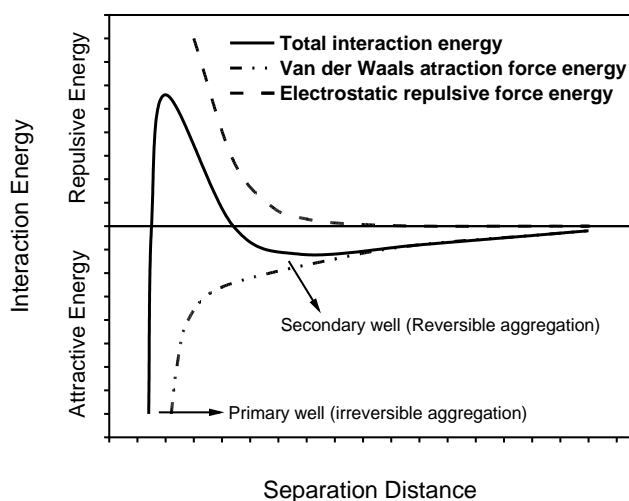


Figure 2.8. Van der Waals attraction, electrostatic repulsion and total Interaction energy curves.

In the repulsive section (Figure 2.8), the point of maximum repulsive energy is called the energy barrier. The height of the barrier indicates how stable the system is. In order for two particles to aggregate, the collision must have sufficient kinetic energy to jump over this barrier. If the barrier is passed, the net interaction is all attractive and as a result the particles irreversibly

aggregate. In many cases, the environment can be altered to increase or decrease the energy barrier by changing the ionic environment or pH of the medium, or by adding surface active agents that directly affect the charged colloid. For example, electronegative dispersions can be coagulated using cationic polymers, neutralizing simultaneously the colloid that is charged^{57,58,60,61}.

2.2.2.2. Chemical coagulation process

Before carrying out the coagulation process of the ABS latex, inorganic thermal stabilizers are added to the latex to prevent thermal degradation of the polymer during the drying stage after the coagulation. The chemical coagulation process is done by adding common coagulants, such as, diluted salts (aluminium or magnesium persulfate, calcium or sodium chloride) and acids (sulphuric and hydrochloric)^{19,62} to a colloidal dispersion. Depending on the nature of the surfactant, different coagulants are used. For example, strong and weak acids work well with fatty acid soaps, while metal salts are used with acid stable soaps⁶³. On the other hand, the use of non-ionic coagulants has also been reported⁶⁴. Moreover, acrylic lattices have been also used to control the coagulation process and obtain a narrow particle size distribution of the coagulated polymer⁶⁵.

It is worth to mention that the particle size, particle size distribution and powder structure of the resin depends on different factors of the coagulation process, such as pH, type and amount of coagulant, temperature, solids content of the latex, degree of agitation and residence time^{19,55,62,66,67}. The effect that all these parameters have in the coagulation process are listed in the following paragraphs:

- pH: when acid sensitive surfactants are used, such rosin or fatty acids, at high pH values the latex cannot completely coagulate because of the high electrostatic repulsion between particles^{55,68}. However, if the pH is very low, rapid coagulation will take place and particle aggregates with irregular shape will be obtained⁵⁵. Therefore, an equilibrium must be found in order to be able to coagulate the polymer particles, but without losing the original morphology.
- Concentration of acid coagulants: at high concentration of acid coagulant, e.g. sulphuric acid, the pH decreases at values less than 2 and due to the high electrolyte concentration, the particles exceed the energy barrier at the primary well, resulting in a rapid coagulation and consequently, particles with poor morphology and wide diameter distribution will be obtained. However, when lower concentrations of acid coagulants are used and the pH is maintained between 4.5 and 6, the energy barrier is large enough to inhibit particle aggregation at the primary well, and the system coagulates at the secondary well (see Figure 2.8). In addition, as the interaction energy at the equilibrium is not very low, the aggregates are easy to disperse and consequently, small size particles with good morphology properties will be obtained. Therefore, the concentration of coagulants can be used to control the size and shape of the aggregated polymer particles^{55,69}.
- Temperature: the effect of temperature is an important parameter of the process and the coagulation is usually carried out at 10 °C below the glass transition temperature (T_g) of the thermoplastic phase of the ABS polymer, that is the SAN copolymer ($T_g = 102 - 105$ °C)⁵⁵. The temperature, despite being a very important parameter in the coagulation process, it has not been widely studied in the literature. Chung et al.⁶⁶ reported that the use of high temperatures could promote

the entanglement of the grafted SAN chains, making easier the precipitation of the polymer particles. On the other hand, Li et al.⁶⁹ found that increasing the operation temperature, the particle size increased because more flocs appeared and the resulted particles were larger. This can be explained as follows; when precipitants are added, interfacial stress increases, Brownian motion speeds up, and consequently latex particles may be more susceptible to form with an irregular shape and loose structure ^{55,69}.

- Agitation speed: high agitation speed (above 450 rpm) provides more favourable conditions for breaking up the ABS particles than for coagulating them, but the size of the ABS particle aggregates becomes smaller when increasing the agitation speed. In conclusion, the size of the particle aggregates is governed by the equilibrium between the attractive forces among the latex particles and the shear stress provided by the agitator ^{55,69}.
- Latex to coagulant volume ratio: the volume ratio of latex to coagulant agent has one of the most important roles in the coagulation process. Reduction of this ratio leads to high particle size distribution in the desired size. Increase of the slurry content in the latex leads to the formation of more particles. In this condition, polymer content increases with low energy dissipation but increase the content of fine and smaller coagulated particles with a wide distribution in size ^{55,69}.
- Residence time: as it was mentioned above, during the coagulation process, the electrostatic forces are weak and the particles can be easily broken. Therefore, the higher the residence time, the higher will become the diameter of the particle.

It is worth to mention that in the emulsion process greater demand on wastewater treatment than other processes is created due to the high quantity of water used during the polymerization process. Moreover, the level of styrene, acrylonitrile, butadiene and other toxic organic compounds that can be emitted during the wastewater treatment must be controlled. A way to minimize the emission of these organic compounds is improving the conversion of the monomer and using installations to recover the unreacted monomer. Finally, when the latex is coagulated, the resulting particles can be filtered or centrifuged in order to recover the dry ABS powder ⁷⁰.

2.2.3. Processing step in ABS manufacturing process

Once the dry ABS polymer is obtained, the next step will be processing the dry polymer along with SAN copolymer, previously manufactured, and other additives, such as pigments, antioxidant or lubricants, depending on the final application of the material. For instance, the use of antioxidants have shown to help retention of physical properties during the processing stage ¹⁹. ABS polymer is known for its great versatility and variety of applications in which can be applied due to the ability to obtain materials with very different properties. For instance, the addition of SAN copolymer, as matrix in the final material, is one of the main combinations used in industry. As mentioned several times before, during grafting reaction, a fraction of SAN chains are grafted onto the PB backbone chains and this is a crucial parameter to enhance compatibility between the ABS dry polymer and the new SAN matrix, and at the same time, this compatibility provides better processability.

Industrially, the processing stage is simple and its main objective is to obtain a good mixture of the ABS and SAN copolymers in order to obtain homogeneous dispersion of the grafted rubber particles throughout the matrix, since the main properties such as the particle size,

particle size distribution, crosslinking, grafting degree, and other important structural parameters are previously determined during the polymerization of ABS latex ³. It is well known that processing can influence chemical and physical properties of the final material. Chemical changes may be induced by shear and high temperatures and thermal or oxidative degradation can also occur ⁷¹. For instance, agglomeration of dispersed particles during injection moulding at high temperatures (280 °C) could lead to morphological changes in the polymer particle ⁷¹. Therefore, the proper selection and control of process variables, such as temperature, pressure, residence time, etc., are important to maintain optimum performance. For example, the recommended processing temperature for ABS polymers ranges from 180 – 280 °C, depending on the ABS grade and which processing technique is going to be used. In addition, in many cases a temperature profile is designed from lower to higher temperatures to obtain an optimal processing of the material.

The most commonly employed technique for processing of ABS is the melt-blending using an extruder, which can be composed of a single or twin-screws ¹⁹. The homogeneity of the product will depend on the efficiency of the mixing equipment, therefore the device must provide sufficient dispersive and distributive mixing for a successful processing ^{3,19}. On the other hand, the selection of the compounding technique for a thermoplastics depends mainly on the processability of the material, which is determined by the properties of the polymer. As ABS is a very versatile polymer, these properties are varied to obtain different ABS grades and hence, ABS polymers are suitable for compounding by nearly all the common techniques used for thermoplastics, such as injection moulding, extrusion, blow moulding, among others.

ABS polymers exhibit viscoelastic behaviour and as other thermoplastics materials, it presents non-Newtonian behaviour, which means that an increase in shear rate or temperature

will result in a decrease on the viscosity of the material. For instance, increasing the shear rate one magnitude and the melting temperature 20 – 30 °C, reduces the viscosity of the ABS polymer by 75 % and 30 %, respectively ¹⁹. Before the processing, it is important to dry the material, since ABS polymers are slightly hygroscopic and surface defects may appear if the material is not completely dry. Typically, drying between 2 – 4 hours at 70 – 90 °C is enough, although it depends also on the ABS grade and which processing or compounding technique is used ².

2.3. Structure and property relationship

A knowledge about the principals of the structure of ABS and the parameters on which they depend is required in order to understand how they affect the properties of the final material. The complex nature of ABS makes the relationship between the structure and the final properties of the polymer challenging, as several structural parameters can affect a single property at the same time, and it is often difficult to vary one parameter independently or to analyse the effect of each separately. Despite this, a wide range of physical and chemical properties, such as mechanical and impact properties and chemical resistance can be obtained by varying different parameters during the emulsion polymerization process. For instance, the variation of the monomer to polymer (SAN to PB) ratio, rubber content, the degree of crosslinking of the PB, the particle size and particle size distribution, the grafting degree and grafting efficiency and the use of additives, among others can be used to obtain different properties and customize the final ABS polymer ^{3,4,11,19}.

2.3.1. Factors affecting the structure

The main factors affecting the structure and, consequently, the properties of the final polymer will be explained in flex's section. Obviously, there are other factors such as temperature or initiator system during the polymerization process or the use of additives during the processing stage that will affect the final properties of the polymer. However, in this section the main properties controlled by the emulsion polymerization process will be discussed.

- Volume fraction (X_v) of the rubber phase:

The X_v of the rubber phase (dispersed phase) in the final ABS material directly affects the mechanical properties of the polymer. Note that the X_v of the dispersed phase is higher than the X_v of the polybutadiene itself due to the inclusions of SAN chains within the particles and the shell surrounding the particle, so that in emulsion made ABS, generally, the X_v of the dispersed phase could be up to twice the X_v of the polybutadiene in the polymer ¹⁰. The mechanical properties of ABS polymer can be mainly divided into two groups: first the ones obtained under high strain rate conditions, such as toughness or impact strength, and the ones related with low strain rate behaviours, such as elastic properties, as for instance, high tensile and yield strength. On the one hand, the toughness determines the capability of a material to resist an impact force without breaking by absorbing and dissipating energy, however, the impact strength is the ability to resist high stress ^{72,73}. In the case of ABS, the impact resistance of the polymer is provided by polybutadiene, the higher the content the greater the impact resistance of the ABS. However, an excessive increase in butadiene can lead to a decrease in rigidity and dimensional stability, so a balance must be found between the proportion of PB and SAN matrix in order to obtain the best properties for each application ^{19,74}. On the other hand, the X_v of the rubber phase also affects the elastic modulus of the polymer, which can be defined as the resistance of the material to

deformed elastically, and this has been explained on the basis that the modulus of a two phase copolymer containing spherical dispersed particles, depends only on the X_v of the dispersed phase and the matrix phase ^{10,19,75}. As in the case of ABS, the modulus of SAN matrix is 1000 times greater than the modulus of the PB, in order to maintain low modulus values, the X_v is the most important parameter to control ^{10,19}. In addition, the tensile and yield stress are also strongly affected by the X_v of rubber phase. The tensile strength can be defined as the maximum stress that a material can withstand before breaking when subjected to a stretching or pulling force, while the yield strength is the maximum stress level at which a material begins to exhibit permanent deformation and is unable to return to its original dimensions, also known as plastic deformation ⁷⁶⁻⁷⁸. The increase of rubber phase generally lead to a decrease in the tensile strength due to the fact that the dispersed PB particles act as defects in the polymer matrix, creating stress concentrated point, which can lead to a decrease in the overall strength of the material ⁷⁹⁻⁸². In the same line, the yield strength decreases with increasing the rubber content because the PB particles are soft domains that reduce the stiffness of the material and therefore it requires lower stress to initiate plastic deformation ⁷⁹⁻⁸². In summary, higher rubber contents generally lead to an increase in the toughness and impact resistance, but decreases the tensile and yield strength of the ABS. However, it is worth to mention that the relationship between rubber content and mechanical properties is not linear and other factors, such as rubber-matrix adhesion, rubber particle dispersion and the presence of additives can influence the final properties of the polymer ⁷⁹⁻⁸¹.

- Rubber particle size and particle size distribution:

Both particle size and particle size distribution of the final ABS polymer are mainly determined by the conditions under which the PB is polymerized, since the subsequent grafting

reaction also increases the particle size due to the internal grafting but this is a relatively minor effect. Therefore, the particle size and particle size distribution of the ABS polymer can be controlled by the type and amount of surfactant used during the polymerization of butadiene³. In ABS materials, the size and distribution of PB particles has a great impact on the performance of the polymer. Usually, large size particles appear to enhance the impact strength, whereas smaller size particles favour the increase of tensile strength⁸³. In addition, it has been reported several times that empirically there is an optimum range of particle size that leads to optimal and improved impact properties for each toughened material^{3,19,84,85}. So far, it has not been clearly explained neither why there is an optimal particle size for this type of systems nor why this critical size varies from one polymer system to another. In the case of ABS, a range from 100 to 500 nm of particle size is considered for enhancing the toughness properties of the polymer, and specifically a maximum impact was reported at an average particle size of about 300 nm for a given ABS system^{19,84,86}. Nevertheless, it is worth mentioning that in ABS, the dependence of the particle size on the impact properties is conditioned by the internal morphology of the particles and by the compatibility between the two phases, which involves the adhesion between the dispersed phase and the matrix that will be explained in more detail later. On the other hand, the elastic modulus is independent of the particle size in ABS since it is a low strain elastic property¹⁹. Unlike modulus, the tensile and yield strength are not independent on the particle size, since an increased in the particle size at a given X_v of rubber, results in a decrease of the tensile yield stress. It is well known that in monomodal ABS polymers a relatively high amount of butadiene is necessary to achieve a high impact ABS, but on the other hand, the increase of butadiene will lead to a significant decrease on the tensile strength of the material. Therefore, it is a challenge to increase impact properties while maintaining tensile strength. However, it has been reported that a bimodal ABS system synthesized under the same rubber content as the reference

monomodal ABS and using two populations of PB particles, one with the same size as the reference system (320 nm) and the other one with a larger particle size (575 nm) showed a significant improvement in impact resistance, while the tensile strength decreased only slightly and hence, the rigidity was almost maintained⁸³. This was attributed to the contribution of the large size particles that can absorb more impact energy than the small ones and then dissipate the impact energy to the small particles. In conclusion, the synergetic effect of large and small rubber particles may be a key parameter to obtain higher performance ABS systems without the need to increase the rubber content⁸³. Finally, another important property of ABS polymer that is strongly related with the particle size is the gloss, as it decreases linearly as the particle size increases due to the higher interference of the particles with the incident light, e.g. small particles (100 nm) have high gloss properties, while large particles (500 nm) have low gloss properties. However, it must be taken into account that there are other factors during the processing stage, such as the temperature and pressure, which can also affect the gloss of the final material¹⁰.

- Crosslinking of the rubber phase:

The butadiene is a difunctional monomer, which at high monomer conversions during the polymerization can favour grafting and crosslinking reactions and hence production of crosslinked polymer³. As mentioned before, three different isomers can be obtained during the polymerization (see Figure 2.4) and the isomer ratio can be controlled by different parameters during the reaction, which plays an important role in the toughness of the polymers due to different properties of each isomer. For instance, rubber latexes with high vinyl content have higher branching and grafting ability due to higher reactivity of the vinylic group⁸⁵. The crosslinking and grafting of PB are related, since a slightly crosslinked rubber particle will have greater tendency to swell; namely higher monomer concentration, and consequently the

probability of grafting will be also increased ¹⁰. In addition, crosslinking has a strong effect on the impact properties of the polymer because the higher the crosslinking density, the stronger the connection among the interfaces of the PB particles and therefore higher crosslinking density of the PB itself, which would result in a higher modulus of ABS and a decrease in the effectiveness of the impact properties ^{72,85}.

- Grafting of SAN onto the PB:

Grafting is a critical parameter to have compatibility and therefore good adhesion between the rubber and the matrix phase due to the reduction of the interfacial tension between the two phases ^{72,85}. At low grafting levels, the surface of the particles cannot be perfectly covered and due to the Van der Waals attraction forces, particle aggregation can occur, which results in non-homogeneous dispersion of the PB particles in the SAN matrix, affecting both toughness and optical properties, such as gloss ^{10,19,87}. On the other hand, an increase in grafting could lead to an increase in the internal grafting of the particles, which leads to PB particles with more SAN occluded within the particle ¹⁰. The increase in grafting also contributes to the complete formation of the shell around the particles resulting in a better dispersion and therefore improving the mechanical properties of the polymer ³. However, it has been shown that a too high grafting density could lead to a worse dispersion of the particles, a fact that has been explained on the basis that highly grafted polymer particles can cause attraction and therefore form some aggregates ^{85,87,88}. For bimodal ABS systems it was reported that low levels of grafting in large particles combining with high levels of grafting in small particles resulted in optimum toughening ^{89,90}. In general terms, an increase in grafting leads to a better dispersion of the particles with a concomitant increase in yield stress and strain to failure ^{10,91}. The grafting properties of ABS polymer will be further explained in Chapter 5.

- Composition and molar mass of SAN matrix:

At a given rubber content, particle size and particle size distribution, the mechanical properties of ABS are strongly related with the properties of the SAN matrix (continuous phase)^{10,19}. The first thing to take into account when choosing the SAN matrix is the similarity in properties with the grafted SAN copolymer, mainly regarding the molar mass and the AN content. For instance, increasing the molar mass of the matrix leads to an increase in toughness, but this increase is not noticeable above 60 kDa, and conversely, below 25 kDa no effect can be seen on the toughness of the material¹⁹. Regarding other mechanical properties, above 25 kDa, the modulus and yield stress values of ABS appear to be independent of the molar mass¹⁹. On the other hand, if the difference between AN levels is higher than 5 %, partial phase separation can take place due to the immiscibility between both SAN copolymers¹⁹. Similarly, surface properties can also be decreased when the AN content of the matrix and grafted SAN copolymers are different because the copolymer with lower AN content will tend to segregate to the surface of the polymer during the processing stage^{19,92}. Due to the chemical resistance of AN, its content in the SAN copolymer has a significant effect on the environmental cracking resistance of the ABS, since the increase on AN content results in an increase on the cracking resistance of the material. Typically, the azeotropic composition (76:24 wt% S:AN) is used in the synthesis of SAN copolymer, but this does not necessarily mean a low AN content on the final polymer, since the final amount of AN can be controlled by adding more or less SAN matrix depending on the application. Standard grade ABS materials typically contain between 20 – 30 wt% of AN, whereas when improved chemical properties are sought the AN content would be increased up to 35 wt%¹⁹. In conclusion, it can be said that the greater the similarity between both SAN copolymers, the better the compatibility between the phases and consequently, better properties of the final material will be obtained.

2.4. Polymerizable surfactants in emulsion polymerization

In Chapter 1, it was explained that much of this work has focused on implementing the use of polymerizable surfactants in the grafting emulsion polymerization of ABS in order to replace the use of conventional rosin soap surfactants and thus, finding alternatives to the problems related to this surfactants, which were highlighted in the begging of the chapter.

Polymerizable surfactants, also called reactive surfactants, have the ability to covalently bond to the polymer particle due to the presence of a double bond in its structure, therefore they cannot be displaced from the interface as easily as conventional surfactants^{93,94}. This chemical bond can also be environmentally and economically beneficial regarding emulsion latexes because lower amount of surfactant needs to be used and therefore, the wastewater obtained after the coagulation step could be less contaminated^{94,95}. Furthermore, dispersions with greater stability can be obtained and it can also be used to functionalize the surface of the polymer particle^{96,97}.

There are three main groups of reactive surfactants, surfmers⁹⁸⁻¹⁰⁵ (surface active monomer), inisurfs¹⁰⁶⁻¹¹⁰ (surface active initiators) and transurfs¹⁰⁷⁻¹¹⁰ (surface active transfer agents)^{93,94}. The surfmers have been studied more deeply in literature, some of them are commercially available and their implementation in large scale processes has been demonstrated⁹⁴. In this work, only surfmers are reviewed and discussed.

2.4.1. Surfmers

Surfmers can be small molecules or macromolecules that are composed of three different parts; a hydrophobic segment, a hydrophilic segment and a polymerizable double bond, which

can be located in the hydrophobic or hydrophilic segment. At the same time, the hydrophilic segment can be anionic, cationic or non-ionic in nature ⁹⁴.

The main objective of the surfmer is to provide stabilization to the emulsion and to control the particle size ^{94,104}. But they also have the ability to copolymerize, and this is why desorption of the surfactant is substantially minimized ^{93,94,104,105}. Moreover, when the polymer dispersion is coagulated, the absence of surfactant in the water phase makes easier the treatment and purification of the wastewater ^{104,105}.

The reactivity of the surfmers is one of the most important parameter to consider. It needs to be well balanced with the monomers present in the polymerization medium, because in case of being too reactive, when incorporating into the polymer chain, its mobility will be limited and it could be buried inside the polymer particle during the feeding period, when the particle is growing. Consequently, the surfmer could not provide any stabilization to the colloidal dispersion. On the other hand, very low reactivity will result in low incorporation into the polymer particle and hence, at the end of the process an amount will still be free in the aqueous phase, which eventually may lead to the same drawbacks as conventional surfactants ^{93,94,105}.

An ideal reactive surfactant cannot be described because it directly depends on the monomer or comonomer system. Thus, guidelines about the optimal performance of surfmers in emulsion polymerization and processes have been reported and are briefly summarized below ^{93,94,111}.

- The surfmer must not react during the initial stage of the reaction, where the particle size can still increase to avoid being buried inside the particle. Nevertheless, to guarantee a high degree of polymerization, the surfmer must

react toward the final stages of the reactions, where the particle size will not increase significantly. So, an optimal behaviour will be to maintain low conversions of the surfmer at the beginning and to reach high conversions at the end of the polymerization. For that, the reactivity ratio of the surfmer (r_{surfmer}) with the comonomer should be zero or close to zero, however, the reactivity ratio of the comonomer ($r_{\text{comonomer}}$) with the surfmer should be between $0.5 < r_{\text{comonomer}} < 10$.

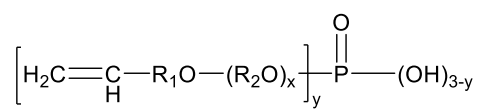
- The surfmer must be very efficient in stabilizing polymer particles.
- It should allow a certain degree of emulsification of the monomer mixture for minimizing the diffusional limitations, especially when water-soluble monomers and chain transfer agents are fed.
- In terms of concentration, the cmc of the surfmer must be low, so that polymerization in aqueous phase is limited. In addition, the formation of these polysoaps may lead to coagulation, so it must be avoided.
- At the end of the polymerization process, all the surfactant should have reacted and be chemically bounded to the polymer particle to ensure total stability of the system.
- Finally, the use of polymerizable surfactants should improve the performance of the final latex, or at least not affect it.

In conclusion, the right choice of the surfmer for a given monomer system, the amount of surfmer and the way of adding it to the system are crucial to obtain optimum stable latexes by emulsion polymerization.

2.4.2. Polymerizable surfactants in the emulsion polymerization of ABS

As far as the authors knowledge, in the open literature there are not publications of the emulsion polymerization process of ABS using reactive surfactants. However, two different patents using surfmers have been published, which will be described below.

In the EP3434732A1 ¹¹² patent a method to prepare ABS graft copolymer reducing the amount of residues in the wastewater and avoiding the addition of heat stabilizers was reported. In order to solve these issues, the use of a phosphate ester reactive emulsifier was proposed, the molecular structure of which is shown in Figure 2.9.



$$x = 1-4$$

$$y = 1-3$$

$$\text{R}_1 = \text{alkylene (1-10C)}$$

$$\text{R}_2 = \text{linear/branched alkylene (3-10C)}$$

Figure 2.9. Molecular structure of the phosphate ester reactive emulsifier used in the patent EP3434732A1 ¹¹².

The surfmer structure includes on the one hand a phosphate functional group, which was capable of acting as a metal ion deactivator and heat stabilizer, and on the other hand contains an allyl group capable of being copolymerized in the presence of comonomers. As the initiator system, peroxy compounds, persulfate compounds or a mixture thereof were used together with an oxidation-reduction catalyst. As the chain transfer agent, alkyl mercaptan compounds, preferably t-dodecylmercaptan, were used. The first part of the process consisted on the polymerization of polybutadiene or butadiene-styrene rubber latex with an average particle size

between 250-450 nm and 70-95 % of gel content. The second part consisted on preparing the ABS graft copolymer, starting from the previously synthesized rubber latex. This latter part, was composed by four steps. First, the conjugated diene rubber polymer, styrene and acrylonitrile monomers, a fatty acid salt as emulsifier and the initiator and catalyst were fed into the reactor and the reaction was performed for 10 – 30 minutes with a reaction temperature between 30 – 60 °C. Second, a continuous addition of styrene, acrylonitrile, CTA and initiator was done at a temperature of 5 – 15 °C higher than in the first step, to improve the efficiency of polymerization. In the third step, when the conversion reaches 75 – 90 %, the reactive emulsifier was added to functionalize the surface of the particle and hence, to serve as a heat stabilizer during thermoforming. Finally, when conversion rate reaches 90 – 95 %, an amount of initiator and catalyst was fed to improve polymerization conversion and the degree of grafting. Once the polymerization process was completed, the coagulation step was carried out. The process was performed between 80 – 100 °C. Acid coagulants, preferably metal salts coagulants, were used and they were fed in solution with a concentration of 5 – 15 %. As a results, an ABS product with better thermal stability, impact resistance and appearance was obtained. It is worth to mention that in this case the reactive surfactant was not added until the end of the polymerization and until that point a fatty acid salt was used as emulsifier in the nucleation of the PB particles and during the half first part of the grafting emulsion reaction.

Another patent in which reactive emulsifiers were used is US6753382B2 ¹¹³. Solids contents of around 46 wt%, were obtained by grafting styrene and acrylonitrile onto PB seed through emulsion polymerization. Different commercial reactive emulsifiers were used in the present invention; on the one hand, the anionic surfactants from the REASOAP SE serie (ADEKA), ELEMNOL RS serie (Sanyo Chemicals) and Hitenol BC serie (DKS) and on the other hand, the non-ionic surfactants from the REASOP NE serie (ADEKA) and RMA-560 serie

(Nippon Surfactants). However, the surfactant Hitenol BC-10 was the one used in the examples explained in the patent; the molecular structure is shown in Figure 2.10. A conventional rosin soap was also used as non-reactive emulsifier.

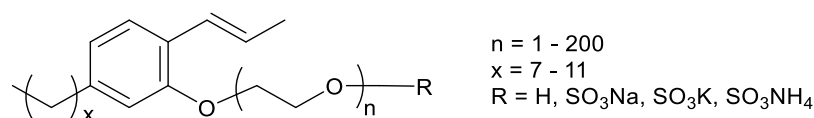


Figure 2.10. Molecular structure of the reactive emulsifier used in the patent US6753382B258 ¹¹³ (the molecular structure was reported from another patent ¹¹⁴).

The grafted ABS latex was prepared by adding t-dodecylmercaptane as CTA and a mixture of one or more peroxide and persulfate initiator systems. The emulsion polymerization was carried out at a temperature ranging from 40 – 80 °C for 2 to 7 hours. The process consisted on four steps. First, three different polybutadiene latexes were polymerized, one with high particle size and high gel content, another one with high particle size and low gel content and the last one with low particle size and low gel content using the reactive emulsifier. Second, the grafting reaction was performed by adding water, styrene and acrylonitrile monomers, a quantity of the reactive and/or conventional emulsifier, the CTA and the initiator system for 1 hour at 70 °C. Then, a second addition of both acrylonitrile and styrene monomers, CTA, initiator system and the reactive and/or conventional surfactant was done for 1 hour at 80 °C. Finally, the reaction was left during one hour to decrease the amount of residual monomer. According to the method, ABS latex having high solids content was prepared by decreasing the amount of residual surfactant during graft polymerization. For example, less amount of emulsifier was added and therefore, the amount of emulsifier present in the aqueous phase decreased. Furthermore, the use of reactive emulsifier prevents desorption of the surfactant from the surface of the polymer particle.

It is important to note that in all the examples of the patent a conventional surfactant and a reactive one were used in different stages of the reaction, but in none of the cases was the grafting reaction carried out using only the reactive surfactant.

Therefore, taking into account all the literature discussed in this chapter and the objectives established in Chapter 1, in this work the behaviour of four different polymerizable surfactants in the grafting emulsion polymerization of ABS were investigated, and both the kinetics of the reaction and the properties of the resulting latexes will be compared with those of the ABS reference latexes, which were synthesized using a conventional rosin soap as surfactant. Furthermore, as ABS polymer is not typically used in latex form, the effect of these polymerizable surfactants on the dry polymer, which was obtained after coagulation, and on the microstructure and mechanical properties of the compounded ABS polymer was also studied.

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Los capítulos 3, 4, 5, 6, 7, 8 y apéndices I, II, III, IV y V están sujetos a confidencialidad por la autora

List of publications and conference presentations

The work presented in Chapter 5 and Appendix III has been published:

“Characterization of grafting properties of ABS latexes: ATR-FTIR vs NMR spectroscopy”

Ainara Agirre, Miren Aguirre, Jose R. Leiza, *Polymer*, 2022, 253, 124997.

Part of this work has been presented in national and international conferences:

Oral presentations

“ABS Polimeroaren txertatzen propietateen determinazioa: EMN eta FTIR-ATR espektroskopien konparaketa”. A. Agirre, M. Aguirre, J. R. Leiza. *Materialen Zientzia eta teknologia V. Kongresua*, Bilbo, Spain, November 2021.

“Synthesis and Characterization of ABS polymers synthesized using polymerizable surfactants”. A. Agirre, M. Aguirre, J. R. Leiza. *Graduate Research Seminar in Polymer Colloids*, Kingston, Canada, June 2022.

Poster presentations

“Characterization of the grafting properties of ABS latexes: NMR vs ATR-FTIR spectroscopy”. A. Agirre, M. Aguirre, J. R. Leiza. *XVI Reunión del Grupo Especializado de Polímeros y XVII Simposio Latinoamericano de Polímeros*, Donostia, Spain, June 2022.

“Synthesis and Characterization of ABS polymers synthesized using polymerizable surfactants”. A. Agirre, M. Aguirre, J. R. Leiza. International Polymer Colloids Group (IPCG) Conference, Kingston, Canada, June 2022.

Laburpena eta ondorioak

Akrilonitrilo-Butadieno-Estireno (ABS) polimeroek, sendotasun bikaina, dimentsio egonkortasun ona eta erresistentzia kimiko, mekaniko zein beroarekiko erresistentzia duten erretxinen familia osatzen dute. Horrez gain, egitura eta konposizio parametroak aldatzean, produktuaren eskakizun zehatzak asetu daitezke propietate desberdinak lortuz. Propietate fisikoei dagokienez, talka eta propietate mekaniko ugari lor daitezke parametro desberdinak moldatuz, hala nola, monomeroen konposizioa, kautxuaren edukia, saretze maila, partikula tamaina eta tamaina banaketa, txertatze-propietateak, polimeroaren pisu molekularra eta partikularen morfologia, besteak beste.

Mikroegiturari dagokionez, Estireno-Akrilonitrilo (SAN) kopolimero kateak Polibutadieno (PB) bizkarrezurrean txertatzen dira. Aldi berean, txertatu gabeko kateak, hau da, libre geratzen direnak, PB matrizearen inguruan gainazal bat osatzen dute, "shell"-a deritzoguna. Partikularen fase desberdin hauek, morfologia konplexu bat osatzen dute. Horrela, PB kautxuaren eta SAN osagaiaren bateragarritasun hobea lortzen da. SAN kopolimeroa PBaren bizkarrezurrean txertatzea ABS polimeroaren lorpen prozesuaren funtsa da, eta ezinbestekoa den PB partikulen sakabanaketa eraginkorra lortzen da SAN matrizean.

Esan bezala, ABS erretxinak komertzialki garrantzitsuak dira propietateak aplikazio zehatzetara egokitzeko gaitasuna dutelako. Propietate horiek polimerizazio prozesuan eratutako egituren arabera zehazten dira. Industrialki, ABSa fabrikatzeko emulsio-polimerizazio prozesua

metodo arruntena da, txertatutako polimeroaren % 85a baino gehiago metodo honen bidez sintetizatzen baita. ABSaren emulsio fabrikazio prozesuan, ABS txertatua (lehengaia) emulsio polimerizazioaren bidez lortzen da, ondoren, koagulazio eta prozesaketa ematen da, ABS produktu final lehorra lortzeko.

Kolofonia eta gantz-azidoen xaboiak izan dira ABS-aren txertatze erreakzioetan gehien erabili diren emulsionatzaileak, beste tentsoaktibo anioniko batzuekin alderatuta. Hala ere, kolofonia-xaboiak erabiltzeak hainbat eragozpen eragin ditzake fabrikazio-prozesuan, eta baita ABS material finalean ere. Adibidez, egituran dagoen talde karboxilikoa dela eta, erreakzioan zehar surfaktantearen forma anionikoari eusteko erreakzioa ingurune basikoan gauzatu behar da. Hau lortzea erronka bat da ABS latexaren sintesian, izan ere, akrilonitrilo monomeroak 9 baino pH altuagoetan erreakzio sekundarioak izan ditzake, eta, ondorioz, konposatu organiko toxikoak sortu. Gainera, kolofonia-xaboiak kolofonia-azidoetatik datoz eta azido horiek horixkak dira, beraz, emulsifikatzaile hauek erabiltzeak ABS polimeroari kolore horixka ematen dio. Ondorioz, prozesatze-fasean pigmentu gehiago erabili behar izaten dira kolore horixka kendu ahal izateko. Aipatutako desabantailen gain, batez ere ABS latexaren sintesian, koagulazio-prozesuari lotutako beste eragozpen batzuk ere badaude. Eskuarki, ABS polimeroa koagulazio-prozesu kimiko baten bidez hauspeatzen da; prozesu horretan, zenbait azido eta gatz erabiltzen dira koagulatzaile gisa. Koagulazioaren ondoren, azido eta gatz horiek hondakin-uretan egongo dira, eta ur-faseko Karbono Organiko Totala (TOC) handitzen lagunduko dute. Ondorioz, hondakin-uren tratamendu konplexu eta garestia behar da uraren TOCa gutxitzeko.

ABSren ekoizpenean kolofonia xaboiak erabiltzeari buruz aipatu diren arazoei aurre egiteko, tesi honen helburu nagusia emulsifikatzaile polimerizagarrien erabilera ikertzea da ABSren latexaren sintesian, komertzialki erabiltzen den kolofonia xaboa ordezkatzeko.

Emultsifikatzaile polimerizagarriekin lortutako ABS latexak emultsio-polimerizazio prozesuan izandako portaera ikertu da (adb: errekzio zinetika, mikroegitura eta txertatze-propietateak, baita polimero-partikulen morfologia ere). Horretaz gain, ABS latexen koagulazio eta prozesaketa ikertu da, propietate mekanikoekin batera.

Horretarako, lau tentsoaktibo polimerizagarri anioniko aukeratu ziren ABS txertatze emultsio polimerizazioan erabiltzeko: Hitenol AR-10, Hitenol KH-10, Sipomer® PAM 200 eta Latemul PD-104. Erreferentzia tentsoaktibo gisa, Gresinox® 578 M (kolofonia xaboa) emultsifikatzaile anioniko konbentzionala erabili zen. Bestalde, bi ABS sistema desberdin sintetizatu ziren surfaktante bakoitzerako: sistema monomodal bat (R1), 130 nm inguruko partikula tamaina zuen polibutadieno erein bat erabiliz, eta sistema bimodal bat (R2), 300 nm eta 400 nm inguruko partikula tamaina zuten polibutadieno bi ereinen nahasketa erabiliz. Bestalde, uretan disolbagarria den KPS hastarazle termikoa erabili zen erreferentzia bezala. Horrez gain, erreferentzia surfaktante bera eta olioan disolbagarriak diren bi hastarazle desberdin erabiliz, AIBN hastarazle termikoa eta TBHP/FF6 redox hastarazle sistema, bi ABS sistemak (R1 eta R2) sintetizatu ziren.

R1 latexen kasuan ikusi zen koagulurik gabeko latex egonkorak lor zitezkeela emultsifikatzaile polimerizagarri gutxiago erabiliz (monomeroarekiko % 0,35 – 0,41 pisan Hitenol AR-10, Hitenol KH-10 eta Latemul® PD-104rentzat), % 1,5 erabili zuen erreferentzia-prozesuarekin konparatuta. Halaber, latex egonkorra lortu zen Sipomer® PAM 200 erabili zenean, baina, kasu horretan, surfaktante-kopuru handiagoa erabili behar izan zen (% 2,0) koagulurik gabeko latex egonkorra lortzeko. Horren ondorioz, uretan disolbagarriak ziren oligomeroak eratu ziren Sipomer® PAM 200aren homopolimerizazioaren ondorioz. Bestalde, R2 latexen Hitenol AR-10 eta Sipomer® PAM 200 sistemetan, latex egonkorak lortu ziren

erreferentzia surfaktante-kantitate bera erabiliz (%1,5). Hala ere, Hitenol KH-10ekin eta Latemul® PD-104rekin sintetizatutako latexetan emultsifikatzaile kantitate handiagoak erabili behar izan ziren (% 2,5).

Oro har, ez zen desberdintasun esanguratsurik ikusi surfaktante polimerizagarrien bidez sintetizatutako latex eta erreferentziako latexaren artean, erreakzio-zinetika, partikula tamaina eta partikula tamaina banaketari dagokienez, Sipomer® PAM 200 erabiliz sintetizatutako latexaren kasuan izan ezik, azken erreakzioaren batez besteko tamaina handiagoa izan baitzen. Ur-fasean eratutako oligomeroak polimeroaren partikulak ezegonkortu eta zenbait partikulen agregazio eragin zuten. Horrez gain, polimeroaren mikroegitura ere antzekoa izan zen, bai frakzio disolbagarriaren bai polimero totalaren gel eta masa molarrari dagokionez. Gainera, Hitenol AR-10 eta Sipomer® PAM 200 zuten latexetarako surfaktantearen inkorporazio-maila neurtu zen. Emaitzek erakutsi zuten surfmer-en % 50 eta % 85 baino gehiago kobalenteke lotu zirela polimero partikuletara, Hitenol AR-10 eta Sipomer® PAM 200 erabili zirenean, hurrenez hurren.

Latexen karakterizazioarekin jarraituz, txertatze-maila (GD) eta txertatze-efizientzia (GE) karakterizatu ziren txertatze propietateei dagokienez. Horretarako, lehenik eta behin, polimeroaren frakzio disolbagarri eta disolbaezinak makroskopikoki bereizi ziren, eta, ondoren, frakzio horien karakterizazioa FTIR-ATR eta EMN espektroskopia bidez burutu zen frakzio bakoitzean SAN eta PB-ren kontribuzioa lortzeko. Azpimarratu behar da EMN bidez emaitza zehatzagoak lortu zirela, EMN-an karakterizazioak ez duelako kalibratu baten beharrik, eta horrek berak FTIRen kasuan zati disolbagarriaren balioak balioetsi zituen. Horrez gain, EMNak aztertzean, lagin osoaren zati adierazgarri bat karakterizatu zen, eta horrek analisiari doitasuna eman zion. Beraz, ondorioztatu zen EMN zehatzagoa zela FTIR-ATR baino ABS polimeroaren

frakzio disolbaezinean SAN eta PB kuantifikatzeko orduan. ABS latexen zinetika eta mikroegituretan bezala, surfaktante polimerizagarriak erabiliz sintetizatutako latexen txertatze-propietateak erreferentziako latexen antzekoak izan ziren.

Bestalde, ABS latex-partikulen barne-morfologiari dagokionez, literaturan prozesatutako ABS laginetatik moztutako zeharkako sekzio meheen TEM irudiak analizatu dira batik bat, ABS latex polimero partikulen barne-morfologia ez da analizatu. Lan honetan, mikroskopia-teknika berriago eta aurreratuago bat erabili da partikulen morfologia eta ABS latexen barne-txertatze propietateak karakterizatzeko; HAADF-STEM tomografiaren hain zuzen ere. Horretarako, OsO_4 -rekin tindatutako latex lehorrak erabili ziren. Tomografia bidez lortutako mikroskopia irudiek erakutsi zuten uretan disolbagarria den hastarazlea erabili zenean, "core-shell" oreka-morfologia ez zela guztiz lortu, SAN kopolimeroa PB nukleoaren inguruko oskolaren artean eta PB partikulen barneko nano-domeinu txikien (klusterren) artean banatu baitzen surfaktantea edozein zela ere (kolofonia xaboi konbentzionala edo tentsoaktibo polimerizagarriak). Bestalde, barne-txertaturiko SAN kateak, txertatze totalaren frakzio oso txikia zela ikusi zen (% 10 baino gutxiago), eta horrek esan nahi du SAN kate gehienak kanpoan txertatu zirela, hau da, polimero partikulen inguruan. Gainera, erreferentzia-latexen barne-klusterren tamaina banaketa eta polimero fase desberdinen banaketa erradiala aztertu zen.

Fase organikoan disolbagarriak diren hastarazleak eta kolofonia xaboa erabiliz sintetizatutako bi ABS sistemak ere aztertu dira tesi honetan. Latex guztiak arrakastaz sintetizatu ziren, R2-AIBNa izan ezik, non erreakzioaren erdialdean koagulatu zuen. Latexaren egonkortasuna, zeta potentzialaren arabera, -30 mV inguruko balioarekin mugan zegoela ikusi zen, eta horrek polimero-partikulen agregazioa, eta ondorioz, latexaren koagulazioa ekar dezake. Gainerako latexek antzeko erreakzio-zinetika, partikula tamaina eta partikula

tamainaren banaketa erakutsi zuten erreferentziako latexaren emaitzekin alderatuta. Hala ere, desberdintasun nabarmenak aurkitu ziren txertatze-propietate eta partikulen morfologiari dagokienez. Alde batetik, txertatze handiagoa lortu zen olioan disolbagarriak diren hastarazleak erabili zirenean sortutako erradikalen izaera hidrofobikoagatik, hauek polimeroaren partikularen barruan sortu baitziren, eta, hala, txertatze-probabilitatea handitu egin zen. Bestalde, lortutako morfologia nabarmen aldatu zen erreferentziako latexarekin alderatuta, batez ere, polimeroaren partikula osoa estaltzen duen gainazal uniforme bat lortu beharrean, SAN kopolimeroaren lobulu gutxi eta handiak banatu zirelako partikularen gainazalean.

ABSaren prozesaketa beharrezkoa da polimeroa material erabilgarri bihurtzeko, normalean ez baita latex gisa erabiltzen. Horretarako, polimeroa ur-fasetik bereizi behar da lehenik, koagulazio kimikoaren bidez. Latex guztiak ondo koagulatu ziren, R2-KH-2.5 latexa izan ezik. Surfaktante-kantitate handiena R2 latexaren sintesian erabili zenez (R1 latexekin alderatuta), koagulatzaile kopuru handiagoa ere beharrezkoa izan zen sistema ezegonkortzeko, eta, ondorioz, koagulazioaren ondoren lortutako hondakin-uren TOC balioak zertxobait handiagoak izan ziren. Hala ere, R2-AR-1.5 eta R2-Sip-1.5 latexak hauspeatzeko, azido azetikoa gehitzea ekidin daitekeela frogatu zen, hondakin-uren TOC murriztuz. Gainera, koagulatutako R2 polimeroen hautsen kolorea nabarmen hobetu zen, eta hori oso preziatua da komertzialki; izan ere, kolofonia xaboiak surfaktante gisa erabiltzearen eragozpen handietako bat kolore horia baita.

Ondoren, ABS hauts koagulatuak estrusio bidez prozesatu ziren, eta injekzio bidez moldeatu, karakterizatzeko behar ziren probetak lortzeko. Alde batetik, tentsioaktibo polimerizagarriekin prestatutako R2 polimeroen kolore horia jaitsi egin zela ikusi zen erreferentzia-polimeroarekin alderatuta, indize horiaren testaren bidez. Bestalde, prozesatutako

ABS polimero OsO₄ tindatuen zeharkako sekzioak STEMen bidez aztertu ziren, polimero finalaren mikroegitura karakterizatzeko. Mikroskopia irudiek ABS partikulen sakabanatze homogeenak erakutsi zuten SAN matrizean zehar, partikulen agregazioen seinalerik gabe. Halaber, frogatu zen partikulen morfologia ezin hobeto mantendu zela koagulazio- eta konposizio-etapen ondoren. Azkenik, inpaktuari eta propietate mekanikoei dagokienez, prozesatutako ABS polimeroen portaera erreferentzia-polimeroen antzekoa izan zen. R2 eta R1 serieetan, hurrenez hurren, talka-propietate eta trakzio-propietate handiagoak neurtu ziren, ziurrenik R2 serieak formulazioan duen PB kantitate handiagoaren ondorioz.

Orain arte aipatutako guztia kontuan hartuta, ondoriozta daiteke ABS latexak sintetizatzeko tentsoaktibo polimerizagarriak erabiltzea aukera interesgarria dela kolofonia xaboa ordezkatzeko. Polimerizazio prozesu, mikroegitura eta partikulen morfologia ez ezik, prozesatutako ABSak ere antzeko portaera eta eragina izan duelako propietate mekanikoetan. Horrez gain, hain horiak ez diren materialak lortu ziren, eta koagulazio prozesuko hondakin uren TOCa murrizteko aukera ematen du, lortutako hautsaren ezaugarriei eragin gabe azido azetiko koagulatzailea ezabatzen denean.

Acronyms

ABS	Acrylonitrile-Butadiene-Styrene
AcO	Acetone
AcOH	Acetic acid
AF4/MALS/RI	Asymmetrical Flow Field Flow Fractionation/Multiple Angle Light Scattering/Refractive Index
AIBN	2,2'-Azobis(2-methylpropionitrile)
AN	Acrylonitrile
ATR-FTIR	Attenuated Total Reflectance-Fourier Transform Infrared
CDCl₃	Deuterated chloroform
CHDF	Capillary Hydrodynamic Fractionation Chromatography
CHP	Cumene hydroperoxide
CMC	Critical micelle concentration
CSTR	Continuous Stirred Tank Reactors
CTA	Chain Transfer Agent
DAD	Diode Array Detector
DLS	Dynamic Light Scattering
DMSO	Dimethyl sulfoxide
Dowfax™ 2A1	Dodecyl diphenyloxide disulfonate
dp	Average particle size (diameter)

Acronyms

dp_i	Intensity-average particle size (diameter)
dp_w	Weight-average particle size (diameter)
E	Young modulus
E_a	Activation energy
EA	Elemental Analysis
EM	Electron Microscopy
ET	Electron Tomography
EVA	Ethyl Vinyl Acetate
FF6	2-hydroxy-2-sulfonatoacetic acid disodium salt
FeSO₄	Ferrous sulphate
GC	Gel Content
GD	Grafting Degree
GD_c	Critical Grafting Degree
GD_{int}	Internal Grafting Degree
GE	Grafting Efficiency
GE_{int}	Internal Grafting Efficiency
HAADF-STEM	High Angle Annular Dark-Field Scanning Transmission Electron Microscopy
Hitenol AR-10	Polyoxyethylene styrenated phenyl ether ammonium sulfate
Hitenol KH-10	Polyoxyethylene-1-(allyloxymethyl) alkyl ether ammonium sulfate
HPLC	High Performance Liquid Chromatography
HPSP	High Pressure Syringe Pump
H₂O₂	Oxygen peroxide
a_k	Impact strength

K_p	Propagation rate coefficient
KPS	Potassium persulfate
Latemul® PD-104	Polyoxyethylene alkylether sulfate
$MgSO_4$	Magnesium sulphate
\bar{M}_w or M_w	Weight-average molar mass
$[M]_p$	Monomer concentration in the polymer particle
MVR	Melt Volume-Flow Rate
N_A	Avogadro's number
$NaHCO_3$	Sodium bicarbonate
NBR	Nitrile-Butadiene Rubber
NMR	Nuclear Magnetic Resonance
N_p	Number of particles
\bar{n}	Average number of radicals per particle
OsO_4	Osmium tetroxide
PAN	Polyacrylonitrile
PB	Polybutadiene
PDI	Polydispersity index
PS	Polystyrene
Re	Reynolds number
RI	Refractive Index
R_p	Polymerization rate
S	Styrene
SAN	Styrene-Acrylonitrile copolymer
SAN-g-PB	Styrene-Acrylonitrile grafted onto Polybutadiene (grafted-ABS)

Acronyms

SBR	Styrene-Butadiene Rubber
SC	Solids content
SDS	Sodium dodecyl sulphate
SEC	Size Exclusion Chromatography
SEM	Scanning Electron Microscopy
Sipomer® PAM 200	Polypropylene glycol mono methacrylate acrylic phosphate ester
SLS	Sodium Lauryl Sulphate
Sodium Gresinox® 578 M	Sodium soap of disproportionated rosin
STEM	Scanning Transmission Electron Microscopy
T	Temperature
TBHP	Tert-butyl hydroperoxide
t_c	Cooling time
t-DDM	tert-Dodecyl mercaptan
TEM	Transmission Electron Microscopy
T_g	Transition temperature
THF	Tetrahydrofuran
TN	Total Nitrogen
TOC	Total Organic Carbon
t_r	Retention time
UV	Ultraviolet
wbm	Weight based in monomer
wt	Total weight
XPS	X-ray Photoelectron Spectroscopy
Đ	Dispersity value

Z	Atomic number
ZP	Zeta Potential
δ	Solubility
γ	Interfacial tension
X	Conversion
Ø	Fraction
ρ	Density
σ	Tensile strength
ε	Elongation
2D	Two-dimension
3D	Three-dimension

