INTERACTION OF ACRYLIC LATEX WITH CALCIUM CARBONATE FILLERS

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Chapter 1. Introduction

1.1 Background and future perspectives of paints.

Cave paintings discovered in many locations around the world, indicate that prehistoric man developed the use of paint over 40.000 years ago¹. The paints used at that moment were a mix between earth pigments, like clays and chalks, with animal fats as binder and they were used to depict their hunts on cave walls. Around 2500BC, the Egyptians improved this technology considerably with the development of a clear blue pigment by grinding azurite, and instead of animal fats they used wax and eggs as binders and solvents for their paints². Over time, people improved much more techniques and materials and it was in the eighteenth century when the first paints factory opened in Europe and America. By the nineteenth century mass production brought prices down and paints started to be used in houses³. Nowadays, paints are everywhere and they are mainly used for decorating and protecting different surfaces.

Traditionally, solvent borne paints have been produced. In the early 1970s, more than 90% of the paints and coatings sold worldwide were solvent borne coatings with low solids content (5-20 % by weight)⁴, because during this period the only way to produce polymers was in solution. Solvent borne coatings, also called oil-based coatings, are paints synthesized and formulated based on organic solvents. However, at this time the market began to shift, due to the oil

embargo, which rose up the price of the raw materials, as well as concerned by the environmental contamination.

One of the mayor challenges associated with solvent borne paints and coatings is the high levels of volatile organic compounds (VOC)⁵, which involves compounds with low boiling points that can undergo chemical reactions in the atmosphere because of the interaction with ultraviolet radiation. VOC such as acetone, ethyl acetate, glycol ether and aliphatic hydrocarbons have been used over the past years as raw materials in paints and coatings formulations^{6,7}. Although health effects of VOCs depend on the concentration in the air and on how long and how often the person breathes the air, the effects can pass from headaches and nauseas to risk of certain types of cancer, liver and kidney damage⁸. Due to this, strict legislatures have been implemented in order to reduce or to eliminate completely volatile organic compounds (VOC), and maximum permissible emissions are set depending on the application and type of coatings (Solvent Emissions Directive 1999/13/EC and Decopaint Directive 2004/42/EC)^{9,10,11,12}.

Great efforts have been made in formulating alternatives paints which give very high performance while they contain low levels of VOC or no VOC. Research in the industry has generated four main alternatives: 1) high solids content coatings, 2) waterborne paints, 3) radiation curable coatings, and 4) powder coatings^{13,14}. In Figure 1.1, the global market estimation of paints and coatings can be observed, up to the 2025 year.

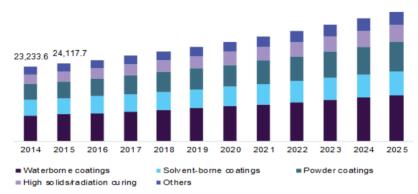


Figure 1.1. Global market estimation of paints and coatings market by products. Information taken from 15.

As it can be observed (Figure 1.1), the global market of paints and coatings is constantly increasing and it seems that the tendency is to move towards waterborne coatings. In Table 1.1 some of the advantages and disadvantages of waterborne coatings in comparison with solvent based coatings are reported¹⁶.

Table 1.1. Some of the advantages and disadvantages of waterborne coatings.

Advantages	Disadvantages
Non-flammable	More sensitive to temperature and humidity
Clean up with water	Lower gloss
Quick drying in good conditions	Problem to dry at low temperatures
Low odour	Can corrosion problems
Non-yellowing	

Waterborne technologies have many advantages and disadvantages when comparing with their counterpart. However, the biggest driver from switching to water base systems is that they fulfil VOC regulations.

A wide range of resins are available in waterborne coatings, including vinyls, two-component acrylics, epoxies, polyesters, styrene-butadiene, amine-solubilized, carboxyl-terminated alkyd and urethanes¹⁷. The development of latex based paints carried out the revolution in the market to use them as binder¹⁸. Latex consists of a colloidal system where polymer particles are dispersed in water. Waterborne coating technology also enables the production of paints with high solids content. This is because latexes can be prepared at low viscosities with high solids content (60 wt%)^{19,20,21}. Moreover, thanks to the development of the approach to synthesize bimodal particle size latexes, final solids content up to 70 wt% can be obtained, as reported in some publications^{22,23,24}.

The current importance of waterborne paints at coatings is indisputable, and their components will be described in the following sections.

1.2 Waterborne paints components

Waterborne paints are constituted by a large amount of raw of materials. Some of them are briefly introduced in Table 1.2.

Table 1.2. Typical components of water-based paints and their function.

	Components	Function	
Binder		Wetting of filler particles, film forming, paint adhesion on substrate	
	Medium (H ₂ O)	Particle dispersion	
	Functional filler	Whiteness, brightness and opacity	
Pigments	Extender	Space holding effect, low the price of the formulation	
	Dispersing agent	Wetting of filler particles, avoid sedimentation	
Additives	Defoarmer	Avoid foaming	
	Thickener	Paint stabilization and ease of handling	
	Biocide	Prevent the microbiological growth	

Depending on the final application, waterborne paint components and amounts will vary. For example, a typical matt paint consists of 20% water, 30% binder, 10% additives and 40% pigments²⁵. Taking into account these proportions, the binder and the pigments are the two mayor components in the formulation, that is why special attention will be given to these two components in the following sections.

1.2.1 Binder

The binder is the film-forming component of the paint and it imparts adhesion and has a great impact on properties such as gloss, flexibility and toughness²⁶. Thanks to the development of latex type binders, which contain water as principal liquid component^{27,18}, these paints could be applied in an environmental friendly way without the safety precautions required for paints based in organic solvents²⁸. Latex polymers are mainly prepared by a process called emulsion polymerization, which process has been widely discussed in the literature^{29,30,31}.

The first latex paints were introduced in the 1950's making use of the Styrene-Butadiene Rubber adhesives developed for use in the second world war. Afterwards, in the early 1950s appeared the first acrylic type latex paints, developed by Rohm and Hass³², which became available in North America around 1963 and about two years later in Europe. Since then, acrylic latexes have been widely used where exterior durability is required due to their high cost and carbon footprint. Acrylic latex paint have good durability because of their stability under excess of UV, heat and alkalinity and a good dirt pickup/crack resistance balance^{33,34,35,36}.

The choice of a particular acrylic polymer as a paint binder, determines the physical properties, in particular those that affect toughness and flexibility³⁷. These parameters depend on the glass-transition temperature (Tg) of the polymer, which is the temperature at which the polymer changes from a glassy to a rubbery state. At temperatures above its Tg the polymer is flexible; conversely at temperatures below its Tg it exists as a brittle material. The paint formulation requires a Tg value low enough to ensure latex particle coalescence during film formation and to avoid cracking due to the excessive brittleness, but high enough to present

desirable mechanical properties³⁸. A desirable Tg can be achieved by changing the composition of the copolymer in the latex synthesis. This is governed by the Fox equation³⁹:

$$\frac{1}{T_g} = \frac{W_x}{T_x} + \frac{W_y}{T_y} + \cdots$$
 1.1

where W_i is the weight fraction and Tg_i the glass transition temperature for each component. The most common acrylic monomers and their homopolymers Tg values can be seen in Table 1.3.

Table 1.3. Acrylic monomers and their homopolymers Tg values

Acrylates Tg (ºC)		Methacrylates Tg (⁰ C)	
Acrylic acid	110	Methacrylic acid	155
Methyl acrylate	8	Methyl methacrylate	105
Ethyl acrylate	-22	Ethyl methacrylate	65
Butyl acrylate	-54	Butyl methacrylate	20
Isobutyl acrylate	-53	Isobutyl methacrylate	48
2-ethylhexyl acrylate	-65		

Since the end of 1980s many of the acrylic resin formulations have used poly (butyl acrylate/methyl methacrylate) copolymers, due to the obtained paint films which tend to be slightly tougher and more hydrophobic than some of the ones used before as poly (MMA/EA)⁴⁰. Latexes for coatings contained approximately 62-64% BA, 1-2% acrylic acid (AA) and the remaining part was the hard MMA monomer, which composition gives a Tg value around 0 °C. The addition of the small amount of acrylic acid is very common in order to improve colloidal

stability of the latex particles, improve adhesion, or provide functionality for crosslinking or to increase their compatibility with other materials⁴¹.

1.2.2 Pigments

The pigment is the discontinuous phase giving additional or improved properties to the coatings⁴², these are solid particles insoluble in the application medium and although most pigments are natural minerals, some are synthesized. Pigments can be divided into two different categories: functional or extenders. Functional fillers, such as titanium dioxide and precipitated calcium carbonate, improve or provide film properties whereas extenders, such as clay, chalk and ground calcium carbonate (GCC) are cheaper and they are primarily used to increase the volume of a given coating and therefore to lower the formulation costs of the final product. Pigments have usually smaller particle dimensions than extenders and a much higher refractive index (RI). Some of the most commonly used are presented in Table 1.4^{43,44}.

Table 1.4. Some of the most commonly used pigments and fillers and their refractive index.

Pigments	RI	Filler	RI
Titanium dioxide (TiO ₂)	2.76	Calcium carbonate (CaCO ₃)	1.59
Zinc Oxide (ZnO)	2.0	Quartz sand (SiO ₂)	1.54
Zinc chromate (ZnCrO ₄)	1.9	Baryte (BaSO ₄)	1.6

In paint formulations, TiO₂ is the white pigment for excellence since it is the whitest and brightest due to its high refractive index^{45,46,47}. Because of the high cost of this pigment, research in coatings is trying to replace it with cheaper pigments, for example with calcium carbonate

(CaCO₃)^{48,49,50,51}. In 2014, Firat Karakas and coworkers studied the substitution of TiO₂ with CaCO₃, and they concluded that it was possible at least to reduce 4 wt% of TiO₂ with CaCO₃ without causing any adverse effect on the paint properties^{52,53}. Due to its cheap price and its availability, CaCO₃ is a widely used pigments in paint and coating industries in Europe⁵⁴.

Calcium carbonate (CaCO₃) comprises more than 4% of the earth's crust and is found throughout the world. Its most common natural forms are chalk, limestone, and marble, produced by the sedimentation of the shells of small fossilized snails, shellfish, and coral over millions of years. Although all three forms are identical in chemical terms, they differ in many other aspects, including purity, whiteness, thickness and homogeneity^{55,56,57}. The three major crystal types are calcite (rhombohedral), aragonite (orthorhombic) and vaterite (hexagonal) in mineralogy terms. Calcite is the most thermodynamically stable form at ambient temperatures. The aragonite is metastable and converts irreversibly to the calcite when heated above 400 °C⁵⁸. Lastly, vaterite is the less stable form and its hexagonal crystals are rarely seen in the natural occurring minerals⁵⁹. An example of the calcite and aragonite crystal morphology of CaCO₃ is shown in Figure 1.2.

Calcite (rhombohedral)

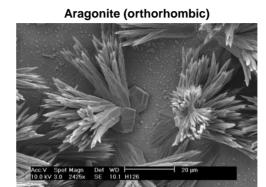


Figure 1.2. Images of CaCO₃ crystal types.

Calcium carbonate can be obtained as natural ground calcium carbonate (GCC) or synthesized as precipitated calcium carbonate (PCC). GCC is the naturally occurring form of calcium carbonate and is manufactured through mechanical processes from sedimentary rocks such as limestone or chalk, or from metamorphic marble rocks⁶⁰. By contrast, PCC is produced from natural limestone by a controlled chemical synthesis (bubbling carbon dioxide into a solution of calcium hydroxide), which is described below^{49,61,62}:

 $CaCO_3$ +Heat \rightarrow CaO + CO_2 ↑ (calcination)

 $CaO + H_2O \rightarrow Ca(OH)_2$ (hydration)

 $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 \downarrow + H_2O$ (precipitation)

In the first step, calcination of calcium carbonate occurs in a kiln at a very high temperature, to obtain calcium oxide and carbon dioxide. The carbon dioxide is cooled, and stored for reuse. Calcium oxide has a high affinity to water, and under controlled conditions, forms calcium hydroxide. At last, calcium hydroxide slurry reacts with carbon dioxide gas to precipitate an extremely pure calcium carbonate. Depending on carbonation conditions such as the temperature, pressure and CO₂ rate, precipitated calcium carbonates (PCCs) with different crystal shape, particle size and distribution can be tailored⁶³.

Both GCC and PCC can be used in a wide range of applications, such as in paper industry and paint formulations^{64,65,66,67}. It has to be mentioned that GCC is more available and cheaper to produce than PCC. However, PCC has a higher purity and smaller particle sizes can be obtained⁶⁸.

The price of raw materials is a very sensitive topic in industry, but in order to have a guidance, the approximate prices of TiO₂, GCC and PCC are shown in Table 1.5. It has to be pointed out that these prizes vary a lot depending on the grade, the supplier and the demand.

Table 1.5. The prices of the pigments.

Pigment	Prize (ε/kg)
TiO ₂	2.5-3
PCC	~1.5
GCC	0.06-0.2

As it can be observed in Table 1.5, there is roughly an order of magnitude of differences between TiO₂ and GCC.

1.2.3 Additives

A wide range of additives are available in the market, (wetting agents, deformers, thickeners, surfactants, biocides, dispersing agent etc). These components are added in low amounts, but have a major influence on the final paint properties^{69,70,71}. In this section, special attention will be paid to the rheology modifiers and to the dispersing agent, because of the important role that these components have on the final properties, as it will be explained.

-Rheology modifiers

Among the additives, the thickeners are very important in order to achieve the optimum rheology profile desirable for the final applications. If the rheology of the paint is not the proper one, it can affect the paint in terms of manufacturing, storage and application⁷². Paints based on binders that are dissolved in organic solvents exhibit a rheological profile that is very favourable with respect to application and film formation. However, when a water based binder dispersion is mixed with a pigment dispersion, a completely different rheological profile is obtained. For such systems the viscosity over the whole shear rate is usually too low⁷³. This disadvantage makes the use of rheology modifiers necessary for water based dispersion paints.

First thickeners were derived from starch and casein. However they produced poor films and presented undesirable flow properties⁷⁴. Therefore, they were soon replaced by cellulosic thickeners and clays. Cellulose ethers, such as hydroxyl ethyl cellulose (HEC), acrylic polymers (ASE) and specialty clays fall into the non-associative category. Among them, HEC is a common conventional thickener used for many years ^{75,76}. HECs are water-soluble polymers that dissolve and swell in water taking up space in the paint (Figure 1.3, left), therefore they increase the viscosity by polymer chain entanglement. Their ability to thicken is directly proportional to their molecular weight and concentration in the paint formulation. The greater the molecular weight, the more efficiently they thicken. However, they show also some drawbacks like no ideal viscosity during application and in drying and not good flow and levelling properties^{69,77}.

This carried out the development of associative thickeners in 1980 for latex based coatings. Associative thickeners present the ability to form uniform network, due to the interaction between the different particles of the medium, leading to the improvement of some physical properties like gloss or hiding power^{74,78}. Associative thickeners decrease low shear viscosity leading to better flow and levelling, and they increase high shear viscosity leading to higher film build and improved brush feel^{79,80}. The three most popular types of associative thickeners are styrene-maleic anhydride terpolymers (SMAT), hydrophobically modified alkali-swellable emulsions (HASE) and hydrophobically modified ethoxylated urethanes (HEUR)⁷⁴. Associative thickeners also employ water-soluble polymers, but they do not purely thicken through water absorption. Instead of this, these polymers contain hydrophobic groups that interact with each other and with the pigment and latex particles in the formulation to create a three dimensional network (Figure 1.3, right)⁸¹.

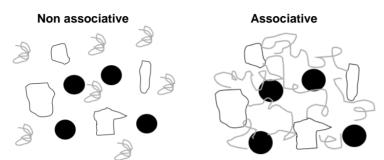


Figure 1.3. Representation of the non associative thickening mechanism on the left and the associative thickening mechanism on the right. (Irregular shapes represent the pigments, spheres the polymer particles and lines the thickener).

The interaction between different latexes and associative thickeners has been widely described in the literature, and they all conclude that thickening mechanism depends on the molecular architecture and molecular weight of the thickener, as well as the types and amounts of particles in the medium^{82,83,84,85}. Thickening mechanism does not depend on the water content like with non-associative thickeners.

-Dispersing agent

During the production of waterborne paints, pigments particles have to be dispersed in water at high speed. In this dispersing process, due to the high speed, pigments agglomerates are dispersed to primary particles. However, in the absence of a dispersing agent these primary particles can flocculate again⁸⁶. The flocculation is due to the Brownian motion of the particles⁸⁷. Small particles move randomly in a suspension, collide with each other and flocculate, reducing

their total surface energy. Therefore, when formulating a coating, the role of the dispersing agent is very important, to ensure well dispersed pigmented coatings with good final performances. If pigment particle aggregates are present, final properties such as gloss, opacity, strength, colour distribution and storage stability will be highly affected⁸⁸.

Stabilization of fillers can be achieved through many ways, such as pigments pretreatment, dispersing resins, resins in the system, and with the encapsulation of particles in a resin^{89,90,91}. However, the most commonly and effective way to handle the stabilization problem are the polymeric dispersing agents^{92,93,94}. These are composed of a long, usually linear, hydrocarbon backbone, along with ionisable groups, whose long chain can act as spatial steric stabilizer, and its surface electric charge as electrostatic stabilizer. Therefore, polymeric dispersants are able to well disperse pigment particles thanks to the combination of these principal mechanisms, called electrosteric stabilization⁹⁵;

- Electrostatic stabilization: This occurs when equally-charged sites of the pigment stabilizer surface came into contact and they repel each other. The resulting Coulomb-repulsion of the charged particles allow the system to remain stable.
- Steric stabilization: In this case, the surface of the pigment is covered by polymer,
 which makes impossible that two particles come into close contact.

The length of the polymeric chains is critical for the performance of polymeric dispersant. If the chains are too short (less than 2.000 g/mol), they do not provide sufficient thick barrier to prevent particles to form agglomerates. On the other side, when the chains are too long (from 10⁵-10⁷ g/mol), bridging flocculation may occur^{96,97,98,99}.

By far the most commonly used anionic polyelectrolytes are the alkali metal and ammonium salts of polyacrylic acid. For calcium carbonate suspensions sodium polyacrylate (NaPA), with a medium molecular weight, is a common polyelectrolyte dispersing agent. NaPA provides steric hindrance and at the same time its surface charge provides electrostatic stability, which prevents the agglomeration of particles^{100,101,99,102}.

1.3 PVC and CPVC

The pigment volume concentration (PVC) is one key-parameter for the majority of paints. The PVC value quantifies the filler loading of the system. The higher the PVC, the lower is the content of polymeric binder within the paint and the higher is the portion of filler particles (Equation 1.2). Variations in this ratio significantly affect the final properties, therefore it is one key-parameter to adjust the desired application properties 103,104,105,106. High PVC (PVC of 50 or higher) paints, which have higher pigment amounts, are generally less adhesive and more porous, whereas low PVC paints are expected to be glossier, more adhesive and less porous.

$$PVC = \frac{\text{Volume of the pigment}}{\text{Volume of pigment} + \text{Volume of solids binder}} x100$$
1.2

When the binder holding ability is overload, the critical pigment volume concentration (CPVC) is reached, and pigment and binder blend begin to create air interfaces or void. It was in the early 1940's when Asbeck and Van Loo¹⁰⁷ put forth the concept of critical pigment volume concentration as a fundamental physical transition point in a pigment-binder system at which the properties of a paint film change dramatically, mostly to the worse (see Figure 1.4). The determination of the CPVC of a latex/pigment blend is important because coherent latex/pigment films can only be obtained below the CPVC of the system.

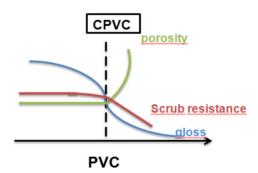


Figure 1.4. Dramatic change of the coatings properties above the CPVC.

The CPVC is not constant for all the binder-pigments pairs, therefore it is important to determine the CPVC for any given formulation. CPVC will depend on many aspects, such as, particles size, and particle size distribution¹⁰⁸. Many methods have been proposed to determine CPVC based on change of coating's properties, such as optical properties⁷⁵, mechanical properties¹⁰⁹, gas permeability¹¹⁰ and water permeability¹¹¹.

Moreover, theoretical CPVC values can be determined through oil absorption (OA) tests. The OA of a pigment is the grams of linseed oil per 100 g of pigment needed to form a paste-like texture. The equation that relates OA and CPVC is shown bellow:

$$CPVC = \frac{100}{1 + \frac{OA \cdot \varphi}{93.5}}$$
 1.3

where, OA is the oil absorption value, ϕ the density (g/mL) of the pigment and 93.5 accounts for the linseed oil density x 100.

This technique assumes that linseed oil and the binder are chemically similar. In the reality, deviations from this theoretical value occur due to the different interaction between polymer particles and pigment, which might cause pigment particles not to pack in the same way in the oil as in the latex binder. Equation 1.3 is valid for most solvent borne paints, while it deviates more for latex paints, since latexes have discrete particles while solvent borne paints no. In order to well understand the differences between solvent borne and latex paints it is worthy to compare the film-forming mechanism of these two paints 112,113 (Figure 1.5).

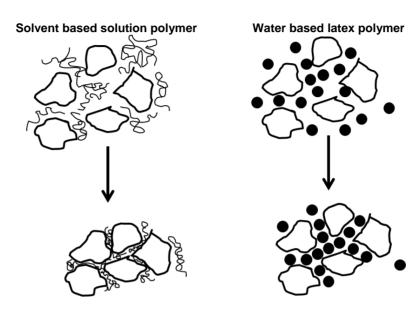


Figure 1.5. Differences in film formation process between solvent borne and water borne paints.

In solvent borne paints, polymeric chains are homogeneously distributed in the continuous phase around the pigment particles, and their concentration just increases as the solvent evaporates. Therefore, the pigment particles lock in the matrix of the binder as the film dries. A thin layer of binder polymer chains coats pigment particles preventing them from direct contact. However, latex are not dissolved in the medium (water), they are polymer particles dispersed in water. The film formation process is though very different. First, the particles come into close contact (in a structure called honeycomb) and afterwards the polymer chains inside the particles interdiffuse allowing them to coalesce into a coherent film as the water evaporates ^{114,38}. Due to the difference between being dissolved polymeric chains or polymer particles, the packing in a latex paint is less efficient than it is in a solvent paint. In a latex paint the whole pigment particles

surface can not be covered by the polymeric particles, and moreover pigments can be larger than the voids between the polymeric particles¹¹⁵.

To conclude, the CPVC calculated by the OA method is generally accurate for solvent borne paints, however in latex paints the real CPVC is lower than the theoretical one¹¹⁶.

1.4 Pigment binder interaction

Most of the surface paints and coatings that surround us in our daily basis are mainly pigment/binder blends. With the objective of improving the quality of paints, several papers have already published the study of the interaction between various types of binder and pigments. In 1976, Karel Rehacek characterized the pigment/binder interaction by the adsorption isotherms of the polymer (short castor oil modified G-alkyd resin) on various inorganic pigments surface and showed that the amount of binder absorbed was affected by the surface of the pigment and by the kind of binder¹¹⁷. In 1991, Javier Lara and Henry P. Schreiber also studied the interaction between rutile and organic pigments and polyester dispersions resins by adsorption¹¹⁸. However, at that time the influence on the final paint properties was not mentioned.

Years later, the effect of the interaction between the binder and pigments was studied on the final paint properties. For example in 2003 F. Tiarks et al., studied the influence of pure acrylic binders and styrene-acrylic binders on the dispersion of TiO₂ pigments⁴², and they concluded that pigment agglomeration could be caused by the type of binder employed or by the functionality of the dispersing agent chosen. In 2006, Shohreh Fatemi et al., investigated the

effect of acrylic binder and TiO₂ pigment and CaCO₃ filler amounts on the performances of paints for traffic use¹¹⁹. They concluded that using PVC values far above CPVC causes reduction of traffic paint quality. And more recently, in 2018, D K. Makepace et al. studied the mechanical properties of CaCO₃/latex blends¹²⁰, and they found out that the inclusion of nano-fillers leads to brittle fracture at lower filler volume fraction than when µm-size filler are used.

However, it has to be mentioned that most of the papers studying the interaction between pigments and different latex types have been performed after including all types of additives to the paint formulation (dispersants, rheology modifiers, tackifiers, defoarmers...). The effect that these additives have on the effective film formation and resultant quality of the film, cannot be neglected^{70,74,121,122,123}. As an example, in 2007, David Mahli et al., published a series of articles were they analysed the effect of a triblock polyether dispersant and surfactants on the colour of final paints 124,125,126 and the effect that different HEUR thickeners play on the spray applications, due to the change in viscosity¹²⁷. Regarding the triblock polyether dispersant, they found out that the placement of polyoxypropylene (PPO) segment internally in polyoxyethylene (PEO) triblock polymers produces significantly greater colour development than the placement of PEO groups internally in PPO/PE/PPO triblocks. They also found out that with three different colorants (carbon black, red and yellow pigments) sodium dodecyl sulfate surfactant provided poor colour development. On the contrary, good colour was achieved with carbon black pigment using nonylphenol oxyethlylene (EO) surfactant at low EO content, and with red and yellow colorants with high EO content. Regarding the effect of HEUR on spray applications, they concluded that with the addition of large hydrophobes in the terminal position of HEUR good spray characteristic were obtained.

Therefore, it has to beared in mind that all components are having some degree of interaction with each other in the waterborne paints and these complex interactions must be considered in the wet state, drying stage and dry state.

Tianhua Ding and co-workers tried to take out most of the additives of paints formulations, and they studied the interaction between CaCO₃/acrylic latex blends with the only use of a dispersing agent. They studied the effect of PVC, surface carboxylic groups, amount of NaPA, and latex particle size in drying kinetics, film formation and final paint properties ^{109,128,129,130}. They concluded that as the surface carboxyl group of the latex increased and the particle size decreased, the blends resulted in the formation of smaller pigment aggregates. They stated that NaPA could stabilize CaCO₃ filler particles and that the drying was faster when the PVC increased and at low amounts of the dispersing agent. However, the final solids content of the obtained blends was low (around 35 wt%).

None of the works presented in this section were able to prepare pigment/binder blends with the use of the minimum additives possible or without the use of any additive at high solids content and with applicable rheology. As mentioned above all the additives are going to have some degree of interaction between the components of the medium, and therefore will affect the final paint performances. Therefore, the isolation of the interaction between the CaCO₃ filler and acrylic latex is essential to gain an insight in how to improve the properties of coatings or to include more filler for obtaining the same properties reducing the final price of the paint.

1.5 Main motivation and objectives

As far as environment, safety and health are concerned, both industry and society are highly concerned. Due to this, water borne paints are gaining interest in our society and it is expected that they will continue to displace solvent borne systems in the near future. Therefore, research in this field is very important in order to achieve waterborne paints with no VOC and with good final performances for the required applications. Moreover, apart from fulfilling the requirements for a specific application, they have to be sold at a reasonable price. If the price is high, it will not be worthy from the industrial point of view. The final price of waterborne paints can be reduced by the addition of fillers without significant losses of the films properties up to a certain amount of filler addition.

Therefore, the study of the interaction between the binder and the filler, (which as mentioned before are the main components in paint formulations), is essential to improve the properties of the coatings and to obtain paints at an economical price. The objective of this work is to investigate the main factors affecting the interaction of acrylic polymer dispersions with calcium carbonate fillers. Until now, the interaction between these two components have been studied after the addition of all kind of additives, and the effect of these additives can not be neglected on the final paint properties. Therefore, the objective of this work has been to prepare different filler/acrylic polymer blends without the use of any additive, or using as less as additives possible, and to study the effects of several variables (filler and latex types, their surface coverage, particle size and filler/latex ratio), on the final film properties.

At the beginning of this research, the preparation of CaCO₃/acrylic latex blends with applicable rheology was only possible with the help of a dispersing agent and a thickener. Afterwards, thanks to the increase of the solids content of both the latex and CaCO₃ dispersion in water, blends were obtained with the only use of the dispersing agent, and the effect of the pH of the latex synthesis, the use of functional monomer, and the effect of polymer particle size was analysed. It has to be pointed out that when preparing fully formulated waterborne paints, the high affinity of the dispersing agent on the surface of CaCO₃ particles was observed, which hindered the effect of different latexes. Therefore, a new strategy for preparing CaCO₃/acrylic latex blends without the dispersing agent at high solids content was developed. Thanks to the removal of this component, the effect of the latex functional monomer and surfactant type on the final paint-like properties was possible to be analysed. Hence, CaCO₃/acrylic latex blends with applicable rheology were finally obtained without the use of any additive.

To summarize, from both academic and industrial perspectives, it is very important and meaningful to study the parameters that control the film quality of filler/latex blends. The aim is to isolate the study of the interaction between these two components, and to build a deeper understanding of the factors influencing the dispersion and adhesion of CaCO₃ fillers to acrylic binders.

1.6 Outline of the thesis

In **Chapter 2**, CaCO₃/acrylic latex blends were prepared with NaPA dispersing agent and with two different types of thickeners; a non-associative thickener and an associative one. Final paint-like films properties were analysed and the effect of each kind of thickener on the CPVC value was investigated.

In **Chapter 3**, latexes with different particle sizes, with and without the functional monomer and at different pH were synthesized. The effect of these variables were studied on the final properties of CaCO₃/acrylic latex films prepared with the help of NaPA. Moreover, in this Chapter a brief study is done to analyse different CaCO₃ samples.

In **Chapter 4**, the interaction between different acrylic latex with calcium carbonate filler was studied in fully formulated waterborne paints, with the combination of a design of experiment (DOE) and High-Throughput Experimentation (HTE). In this Chapter, the effect of the filler particle shape on packing efficiency was also studied.

Due to the need to avoid the use of additives, in order to isolate the study of the interaction between polymer-filler particles, in **Chapter 5** a new strategy was developed in which blends were prepared without the use of any additive. Latexes were synthesized with different amounts of different functional monomers and with different surfactants and these effects were analysed on final paint-like films. The supporting information of this Chapter is shown in Appendix IV.

In Chapter 6, the most relevant conclusions of the Thesis are summarized.

In order to avoid repetition of the experimental procedures and characterization, a detailed description of the experimental part is given in Appendix I, Appendix II Appendix III.

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Chapter 2. Influence of the type of thickener on the final properties of CaCO₃/Acrylic latex blends films

2.1 Introduction

As it was explained in Chapter 1, solvent borne paints exhibit a rheological profile that is favourable with respect to application and film formation. However, when a water based binder dispersion is mixed with a pigment dispersion, a completely different rheological profile is obtained. For such systems the viscosity over the whole shear rate is usually too low^{1,2,3}. Therefore, in order to achieve the desirable viscosity profile across the entire shear range of paint applications, thickeners are employed⁴.

The impact of these rheology modifiers on waterborne coatings has been widely studied. Much research has been carried out to study how the rheology of waterborne paints is affected by the addition of different amounts and types of thickeners^{5,6,7,8}. Some articles also published the effect of these thickeners on the final paint properties^{9,10}. However, no research investigating

the effect of different thickeners on the critical pigment volume concentration (CPVC) value has been published.

In order to reduce the final price of waterborne paints a high CPVC is highly desirable, to add as much filler as possible without the complete loss of the waterborne films properties. In this Chapter, the effect of two different thickeners on the CPVC value of CaCO₃/acrylic latex blends will be presented.

More precisely, in this work the CPVC has been determined for paint-like blends using two types of thickeners: Hydroxylethylcellulose (HEC) was used as non-associative thickener, and hydrophobically modified alkali soluble emulsion polymer (HASE) as associative thickener. HEC is a non-ionic cellulose derivative, whereas HASE is an anionic polyacrylate (copolymer of methacrylic acid and ethyl acrylate ester with a hydrophobic acrylic ester). These two kinds of rheology modifiers act in different ways; HEC thickener dissolves and swells in the water phase taking up the space in the paint, whereas HASE thickener contains hydrophobic groups that interact with each other and with the pigment and latex particles in the formulation to create a three dimensional network. The different mechanism of these two kinds of rheology modifiers for thickening was explained in a more detailed way in Chapter 1 (Figure 1.3), and the model chemical structure of these two thickeners is shown in Figure 2.1.

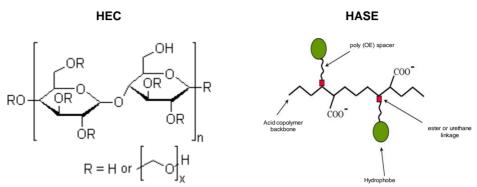


Figure 2.1. Model chemical structure of the two thickeners used along this chapter.

As far as thickeners are concerned, HEC undergoes little viscosity change over the different pH ranges. However, solutions possess the greatest stability in the pH range of 6.5 to 8. Below pH 3, solutions are less stable due to acidic hydrolysis and at high pH some oxidative degradation may occur. Besides, HASE thickeners are pH dependent and require a neutralizing agent such as ammonia, to deprotonate acid groups of the HASE thickeners, and to form a network with themselves and the particles of the medium, by ion-dipole interactions (Figure 2.2).

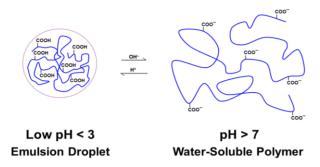


Figure 2.2. HASE pH dependence to thicken.

2.2 Experimental part

2.2.1 Materials

Methyl methacrylate (MMA, Quimidroga), butyl acrylate (BA, Quimidroga) and acrylic acid (AA, Fluka) monomers were used as supplied. Sodium persulfate (NaPS, Sigma-Aldrich) was used as thermal initiator. The surfactant used was Dowfax[®] 2A1 (alkyldiphenyl oxide disulphonate, Dow Chemicals, 45% active phase). Deionized water was used throughout the work. To increase the pH of the latexes a 25% solution of ammonia (Fluka) was used.

Ground calcium carbonate (GCC) was kindly supplied by Omya: Omyacarb®3-CL (with a purity of 98% and 30% of the particles with a size < 2 μ m). Sodium polyacrylate (NaPA, molecular weight (MW)= 5100 g/mol, Sigma-Aldrich) was used to disperse the CaCO₃ particles in water.

Hydroxylethylcellulose (HEC), NATROSOL® 250HR (Aqualon), was used as non-associative thickener and the hydrophobically modified acrylic polymer (HASE), THIXOL™ 53L, associative thickener, was kindly supplied by Coatex, Arkema.

2.2.2 Emulsion polymerization

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

Iniatially a 15 wt% solids content polymethyl methacrylate-co-butyl acrylate-co-acrylic acid (MMA/BA/AA at 49.5/49.5/1 of weight % composition) seed latex was synthesized by batch emulsion copolymerization at 75 °C and 240 rpm. The formulation used to prepare the seed latex is given in Table 2.1.

Table 2.1. Formulation used to synthesize the seed latex.

Compound	Charge (g)
MAA	63.17
ВА	63.17
AA	1.28
Water ^{a)}	718.23
Na ₂ S ₂ O ₈	1.28
Dowfax® 2A1b)	4.5

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

b) Active matter.

The charge of monomers, water and surfactant was added to the reactor and it was purged with nitrogen during 30 minutes. After reaching the desired temperature (75 °C) a shot of thermal initiator (NaPS) was added. After that, the latex was let to react batchwise during 2 hours. A seed latex with 15 wt% of solids content and 80 nm particle diameter (measured by Dynamic Light Scattering) was obtained.

Polymethyl methacrylate-co-butyl acrylate-co-acrylic acid (MMA/BA/AA at weight composition of 49.5/49.5/1) latexes were then synthesized with a target solids content of 50 wt% and a target particle size of 270 nm by seeded semi-batch emulsion polymerization. This polymerization technique was chosen because it allows good control of the reaction temperature, particle nucleation, final particle size, and particle size distribution^{11,12}.

The amount of seed required in the polymerizations to produce a latex with a certain solids content and with a certain average particle size can be estimated provided that the number of polymer particles remains constant during the polymerization by means of the following equation¹³:

$$m_{seed} = \frac{m_{latex}SC_{target}\overline{d}_{p,seed}^{3}}{SC_{seed}\overline{d}_{p,target}^{3}}$$
2. 1

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

Polymerization was carried out in semicontinuous at 75 °C and 240 rpm in the same setup described for the synthesis of the seeds. An initial charge containing the seed latex, a high amount of water and a small amount of monomers were added to the reactor. The initial charge was purged with nitrogen during 30 minutes. After reaching 75 °C a shot of NaPS was added. Then the preemulsion containing the monomers and the surfactant was fed during 4 hours and after that, the latex was let to react batchwise for 30 minutes. The formulation used is given in Table 2.2.

Table 2.2. Formulation used to synthesize the acrylic latex.

Compound	Initial Charge (g)	Stream (g)
Seed	23.48	-
MAA	1.94	85.63
BA	1.07	85.63
AA	-	1.75
Water ^{a)}	125.27	46.5
$Na_2S_2O_8$	1.75	-
Dowfax®2A1b)	1.4	-

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

2.2.3 Procedure to prepare CaCO₃/latex blends with the use of different types of thickeners

CaCO₃ / latex blends were prepared in two steps, which strategy is shown in Figure 2.3. In the first step the dispersion of the pigment, dispersing agent and thickener in water, the so-

b) Active matter.

called mill base, was prepared. In the second step the mill base was blended with the latexes at pH 9 and final blends were obtained.

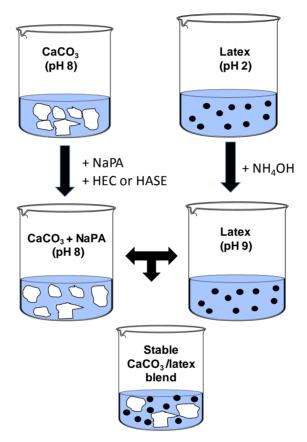


Figure 2.3. Strategy employed to prepare latex/CaCO₃ blends.

In order to obtain the mill base, first distilled water, thickener (HEC or HASE) and sodium polyacrylate (NaPA) dispersing agent were weighted in a 500 mL container and stirred using a

Dispermat high speed disperser blade under low shear (350 rpm). CaCO₃ was then added slowly into the container and the shear rate was increased (up to 1300 rpm) during the addition. After CaCO₃ addition, the mill base was left at constant shear for 30 min.

Afterwards, the mill base was blended (500 rpm) with the latex at pH 9 at different PVC values of 40, 50, 60 and 70. For all blends the total solids content (wt% of polymer + wt% of filler) was kept constant at 54 wt%, in order to be comparable. Tianhua Ding et al. 14,15 reported the same blends with similar compositions, but with lower solids content and without the use of any thickener. The increase of the solids content of the final waterborne paints is highly recommended 16 in order to be closer to industrial like paints.

2.2.4 Characterization

Conversion and solids content of the acrylic latexes were obtained gravimetrically. The average particle size of the latex and the zeta potential of the latex and calcium carbonate particles were measured by Dynamic Light Scattery Spectroscopy, DLS (Malvern® Zetasizer Nano). The glass transition temperature of the latex was analysed by Differential Scanning Calorimetry, DSC in a Q200 (TA instruments).

The particle size of CaCO₃ particles was measured by Dynamic Light Scattering, Malver Mastersizer 2000, without and in the presence of NaPA dispersing agent. First, the filler was diluted in DI water and then NaPA (0.2 to 1 wt% based on the weight of calcium carbonate

particles) was added. The mixture was stirred for 20 min and then sonified for 1 hour. An ice bath was used to reduce the temperature rise during the sonification process.

The viscosity of the mill base with and without NaPA was determined by Brookfield LV Viscometer. This equipment allows determining viscosities at rotational speeds of 50-200 rpm. In order to perform the measurements, the sample was placed onto the stage under a S06 disc spindle.

Stability of the blends was measured by Turbiscan Labexrt equipment and the drying kinetics of the blends films was followed with Adaptive Speckle Imaging Interferometry (ASII) with Horus® (Formulaction). Regarding the morphology of the obtained mill base and films, it was characterized by Scanning Electron Microscopy (SEM Hitachi TM3030) and by Environmentally Scanninc Electron Microscopy (eSEM-FEI QuantaTM 250). The gloss values were measured with a glossmeter (micro-TRI-gloss) at incident angle of 85°. Contact angle measurements were carried out in a Contact Angle System OCA (Dataphysic) equipment. The tensile tests were performed with TA.HD.Plus texture analyser.

2.3 Results and discussion

2.3.1 Seed and latex production

Poly(methyl methacrylate-co-butyl acrylate-co-acrylic acid) P(MMA/BA/AA) (49.5/49.5/1) latex was synthesized by semi-batch emulsion polymerization process to obtain a Tg value

around 15 0 C. This process is widely used in the industry to produce colloidal stable dispersions of polymer particles in water¹⁷. The characteristics of the seed and the final latex, regarding the solids content, the particle size and the glass transition temperature are shown in Table 2.3

Table 2.3. Properties of seed and final acrylic latex produced.

	Seed	Latex
Solids content (%)	15	50
dp (nm)	80	270
PDI	0.026	0.089
Tg (⁰C)	42	15

The seed was obtained with a solids content of 15% and a particle size of 80 nm and the final latex with a solids content of 49% and a particle size of 270 nm. The glass transition temperatures obtained for the seed and for the latex were 42 °C and 15 °C respectively. Taking into account the Fox equation for our polymer composition [P(MMA/BA/AA)] (49.5/49.5/1)], the glass transition of the latex should be 15 °C. As it can be observed in Table 2.3, the glass transition of the seed is higher than the one obtained by the Fox equation. This is attributed to the fact that the seed is synthesized by batch emulsion polymerization with monomers of very different reactivity ratios ($r_{MMA} \approx 1.8$; $r_{BA} \approx 0.30$). In a batch process, a MMA rich copolymer is obtained first and as the conversion increases, there is a drift in the comonomer composition toward the less reactive monomer (BA). Thus, at the end of copolymerization a quasi-pure PBA is produced after the MMA is depleted. The Tg reported corresponds to the MMA rich copolymer formed in the batch process. The low Tg of the homopolymer of BA is not recorded probably due

to the temperature at which the experiment is started (-50 °C). In the semi-batch process, an homogeneous copolymer is obtained due to the copolymerization under rather starved conditions. This results in a unique Tg in accordance with the value obtained by the Fox equation.

The conversion along the time for the seed and the final latex is depicted in Figure 2.4. As it can be observed, both the seed and the final latex reached full conversion.

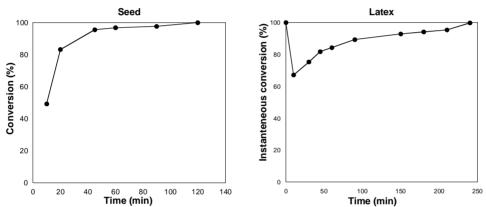


Figure 2.4. Conversion of the seed and the final latex along the time.

2.3.2 CaCO₃ particles (Omyacarb[®]-3CL)

The morphology of the surface of CaCO $_3$ 3CL sample was characterized by scanning electron microscope (SEM). As it can be seen in Figure 2.5, CaCO $_3$ 3CL particles show calcite morphology. According to the supplier 30% of the particles have a particle size lower than 2 μ m, which seems to be fulfilled.

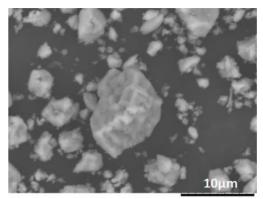


Figure 2.5. SEM image of the morphology of CaCO₃ 3CL particles.

Moreover, the theoretical critical pigment volume concentration (CPVC) was calculated for this pigment through the oil absorption (OA) number indicated by the supplier. The OA of a pigment is the grams of linseed oil that 100 g of pigment can absorb. The equation that relates OA and CPVC is shown below:

$$CPVC = \frac{100}{1 + \frac{OA \cdot \varphi}{93.5}}$$
 2.2

where, OA is the oil absorption value, ϕ the density of the pigment and 93.5 accounts for the linseed oil density x 100. The OA provided by the supplier was 30/100 g, therefore, from equation 2.2, the CPVC obtained for CaCO₃ 3CL was 54. The CPVC values calculated by

equation 2.2 are useful despite the lack of accuracy and precision in some cases, as this formula assumes that the wetting properties of linseed oil are similar to that of the binder polymer system.

Evidently, one important parameter affecting the CPVC of a paint is the use of solvent borne or waterborne binders¹⁸. As explained in the introduction, due to the polymer particle morphology in waterborne binders, the CPVC for latexes will be lower than the one for solvent borne counterparts.

2.3.3 Surface charge of CaCO₃ and acrylic polymers particles

In order to prepare CaCO₃/acrylic latex blends with different thickeners, first the stability of both CaCO₃ and polymer particles was measured in the whole pH range. This was done in order to choose a suitable pH for the preparation of stable CaCO₃/acrylic latex blends.

The stability of the calcium carbonate particles and the latex blend is closely bound to particle surface charge¹⁹. In fact, both compounds should have the same surface charge (negative or positive), to provide repulsive forces between particles and therefore to obtain a colloidal stable blend. The surface charge can be estimated using electrophoretic measurements, from where the zeta potential (ζ) can be easily obtained. In order to explain the ζ -potential, the electrical double layer (DL) must be first explained. The DL consists of two sections (see Figure 2.6), the Stern layer where the ions are strongly bound and the diffusion

layer, where they are less firmly associated. The zeta potential is the electric potential at the slipping plane, at the point in the bulk fluid away from the interface.

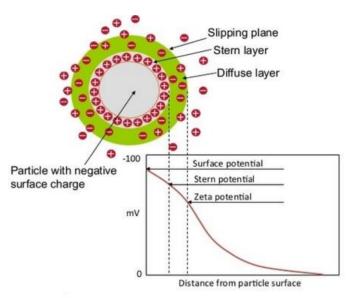


Figure 2.6. Electrical double layer and zeta potential²⁰.

The zeta potential can be calculated automatically from the electrophoretic mobility (μ_E), by Smoluchowski's equation²¹ (Equation 2.2):

$$\mathbf{Zp} = \frac{\mu_{E} \cdot \eta}{\epsilon_{0} \cdot \epsilon_{r}}$$
 2. 2

where, ϵ_0 is the permittivity of vacuum, ϵ_r , the dielectric constant of water, and η , the viscosity of the medium. The zeta potential can be negative or positive depending on the nature of the charge on the particles. The magnitude of the zeta potential is directly correlated to the colloidal stability. Colloids with high zeta potential (negative or positive) are electrically stabilized, while colloids with low zeta potentials tend to coagulate or flocculate.

Taking into account the recipe showed in Table 2.2, it can be said that latex particles used in this Chapter are stabilized by an anionic surfactant (Dowfax® 2A1) and by the acidic functional groups coming from acrylic acid, in order to prevent coagulation of the particles. In order to verify the surface charge of the acrylic latex, the zeta potential (Zp) of the latex, as a function of the pH of the medium was measured. The obtained result can be observed in Figure 2.7.

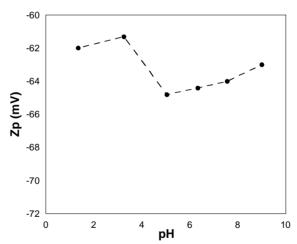


Figure 2.7. Zp of the acrylic latex as a function of the pH of the medium.

As it be seen in Figure 2.7, the surface of the acrylic latex showed a negative Zp all over the whole pH range. As mentioned above, the negative charge comes predominantly from the anionic surfactant on the surface of the particles, and from the persulfate moiety²². Moreover, it can be seen that increasing the pH of the medium the Zp became slightly more negatively. A higher negative value means that the particles present higher repulsion forces between them, which prevents flocculation/coagulation of the particles. This higher charge at high pH values, can be explained by the deprotonation of the carboxylic acid groups of the functional acrylic acid at basic medium.

The surface chemistry of calcium carbonate is more complex^{23,24,25}. The charge of the calcium carbonate particles were measured by different authors and the sign of the ζ is positive, negative, or variable according to the nature of the calcium carbonate particles, as reported by P. Moulin and H. Roques²⁶. Moreover, some studies reported that calcium carbonate crystals have an isoelectric pH of 9.6 in water^{27,28}, which means that the surface charge of the calcium carbonate depends on the pH of the aqueous media. If the pH is lower than the isoelectric pH of the calcium carbonate crystal, the surface charge of the particles is positive, zero if the pH is equal to the isoelectric point and negative above it. The surface charge of the CaCO₃ 3CL particles provided by Omya was measured by Zp measurements as a function of the pH of the medium (Table 2.4).

Table 2.4. Zp of CaCO₃ particles dispersed in water as a function of the pH of the medium.

рН	Zp(mV)
2.5	0
5	-1.44
7	-2.33
9	-4.78

In the case of calcium carbonate particles, the surface charge is caused by the dissolution of ions from the surface ($CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-}$). As it can be observed in Table 2.4, the surface charge of the $CaCO_3$ 3CL is almost zero at acidic pH, whereas, slightly negative at basic pH, which means that the isoelectric point for GCC 3CL sample was found around pH of 2.5. Decreasing the pH of the suspension, an increase in the solubility of $CaCO_3$ particles takes place due to the release of CO_2 in the solution^{29,30}:

CaCO₃ (s)
$$\longleftrightarrow$$
 Ca²⁺ (aq) + CO₃⁻² (aq)
H⁺ + CO₃⁻² \longleftrightarrow HCO₃⁻ + H⁺ \longleftrightarrow H₂O + CO₂ (g)

Figure 2.8. Reaction of CaCO₃ particles dissolving in water at acidic pH.

According to the Zp of the polymer particles (Figure 2.7) and the Zp of calcium carbonate particles (Table 2.4), the pH of 9 is a suitable medium to prepare stable calcium carbonate (filler) /acrylic latex (binder) blends. At this pH polymer and calcium carbonate particles showed

negatively charged surfaces, which will cause repulsive forces between them to obtain stable blends.

2.3.4 Determination of the optimum amount of NaPA needed to disperse CaCO₃-3CL particles

However, it has to be pointed out that the stability of calcium carbonate particles dispersed in water is not high enough because the electrophoretic mobility measurements showed low Zp values. Moreover, the density of calcium carbonate filler (d= 2.7 g/cm³) is high, which causes the sedimentation of particles in diluted medium. In industrial applications, the stability of pigment particles are commonly regulated through the adsorption of suitable dispersing agents³¹.

For calcium carbonate suspensions sodium polyacrylate (NaPA), with a medium molecular weight, is a common polyelectrolyte dispersant agent ^{32,33,34}. Sodium acrylate polymers have long chains which can act providing steric hindrance, and at the same time their surface charge provides electrostatic stability. Consequently, NaPA can prevent the agglomeration of particles³⁵.

In order to determine the optimum of NaPA dispersing agent amount needed to disperse the calcium carbonate particles, three different measurements were carried out; viscosity, zeta potential ζ and particle size (Figure 2.9, Figure 2.11 and Figure 2.12 respectively).

To obtain the optimum amount of NaPA by viscosity measurements, CaCO₃ particles were dispersed in water (with the maximum solids content possible: 75%), and different dispersions

were prepared with different amounts of NaPA (based on the weight of CaCO₃ particles). The obtained viscosities measured by the Brookfield viscometer are shown in Figure 2.9.

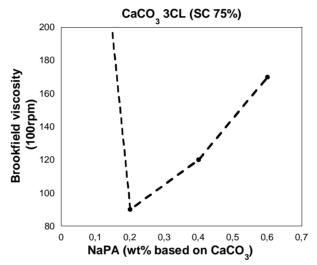


Figure 2.9. Viscosity change as a function of the amount of NaPA in $CaCO_3$ slurry.

As it can be observed in Figure 2.9, the viscosity decreased sharply with the addition of NaPA. This is because aggregation of particles might increase the viscosity by trapping water between aggregated particles, and when NaPA is added the viscosity decreases because the agglomerates break up and thereby water is released (Figure 2.10). The viscosity subsequently shows a gentle increase with increasing the amount of NaPA (above 0.2 wt% based on CaCO₃). When the amount of NaPA added is larger than the corresponding to the saturation adsorption, excess of NaPA exists, can swell in water and make the viscosity increase further.

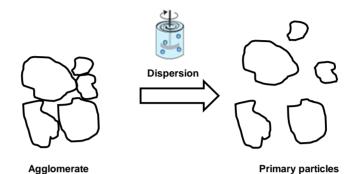


Figure 2.10. Illustration of the dispersion of particle agglomerates to primary particles.

The zeta potential of CaCO₃ particles dispersed in water as a function of the amount of NaPA added to the dispersion was also measured (Figure 2.11). As mentioned before, the zeta potential indicates the degree of electrostatic repulsion between charged particles, so a higher zeta potential value, either positive or negative, means more stability.

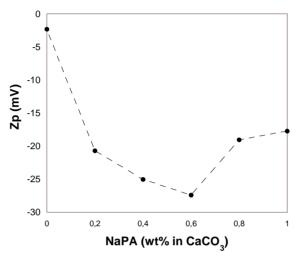


Figure 2.11. Zeta potential of CaCO₃ particles dispersed in water as a function of the amount of NaPA added (pH of 7).

The addition of NaPA made the Zp more negative as the concentration of NaPA increased (Figure 2.11). This is because the carboxylic groups of the NaPA molecules associate with the Ca⁺ ions, which neutralize the possible positive charge at CaCO₃ surface. A minimum Zp was detected at 0.6 wt% based on the weight of CaCO₃.

The particle size of CaCO₃ agglomerates was also measured as a function of the amount of NaPA added with respect to the weight of CaCO₃ particles (Figure 2.12).

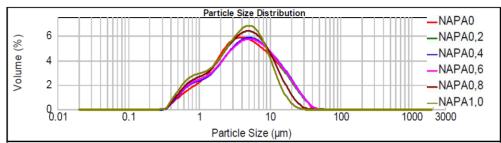


Figure 2.12. Particle size distribution of CaCO₃ particles varying the amount of NaPA added.

In Figure 2.12 it can be observed a significant shift to lower particle sizes above 0.8 wt% of NaPA. The average particle size of the pigment particles decreased, which means that thanks to the addition of the dispersing agent, the aggregates could be broken up.

Taking into account the three measurements described above (viscosity, zeta potential and particle size), it was decided as a compromise between the three of them to use 0.4 wt% of NaPA based on the weight of CaCO₃ particles, in order to well disperse the pigment particles. Jiansheng Tang et al. reported the same amount of NaPA for a precipitated calcium carbonate sample³⁶.

The stability of CaCO₃ particles dispersed in water with and without NaPA was then measured by Turbiscan Lab equipment (for further information see Appendix II) and by environmental scanning electron microscope (ESEM).

First, CaCO₃ particles with a solids content of 54 wt% were dispersed in water and then the dispersion was sonified for 15 minutes. In the case of the dispersion with NaPA, 0.4 wt% of

NaPA based on the weight of CaCO₃ was added. Afterwards, dilution of both concentrated dispersion was carried out to 5.4 wt%, and the obtained results are depicted in Figure 2.13, where the backscattered light of the dispersion for every hour during 5 hours of scanning (at 30 °C) was measured.

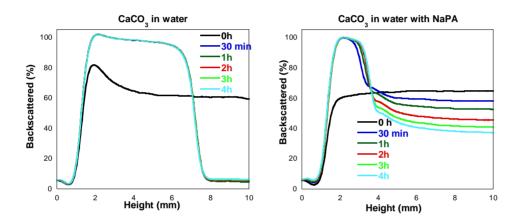


Figure 2.13. Stabilty of the CaCO₃ dispersion in water without NaPA in the left and with NaPA in the right (5.4wt%).

Both dispersions (CaCO₃ in water and CaCO₃ in water with NaPA) showed an increase of the backscattered light with time at the bottom of the vial (see Figure 2.13), indicating that sedimentation of filler particles was taking place after 1 hour. However, this sedimentation in the presence of NaPA was not full and instantaneous, indicating that the NaPA dispersing agent retarded CaCO₃ particles sedimentation, by better dispersing them. In order to visually see this effect, after measuring the stability by the Turbiscan equipment a picture of the vials was taken

(Figure 2.14). As it can be observed in Figure 2.14, with the addition of NaPA the complete sedimentation of CaCO₃ particles at the bottom of the vial was prevented.

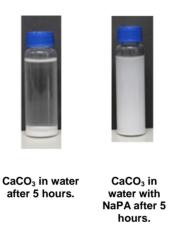
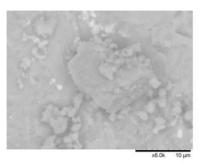


Figure 2.14. Stability of CaCO₃ in water without and with NaPA, after 5 hours.

Apart from stability measurements, ESEM images were also carried out in order to double check the dispersion of CaCO₃ particles. The obtained images are shown in Figure 2.15 and as it can be observed, the addition of NaPA enhances the dispersion of CaCO₃ particles, and allows to break down the pigment agglomerations to give primary pigment particles.

CaCO₃ dispersed in water



CaCO₃ dispersed in water with NaPA

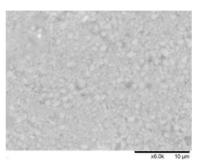


Figure 2.15. ESEM images of CaCO₃ particles dispersed in water with and without NaPA.

2.3.5 Determination of the amount of thickener used to prepare CaCO₃/Acrylic latex blends

As it is well reported in the literature, the rheology of waterborne paints is improved with rheology modifiers or thickeners in order to obtain suitable viscosity profiles³⁷. Moreover, it was seen in Figure 2.9 that the addition of the dispersing agent lowers the viscosity of the mill base, therefore it seems that the use of thickener is essential in order to avoid the sedimentation of CaCO₃ particles in the paints.

Paints viscosity depends on measurements conditions such as shear rate, because paints do not behave as Newtonian fluids. In Figure 2.16 the shear rate associated with the storage, levelling/sagging and brushing/spraying of paints can be observed³⁸. High viscosities at

low shear rate are desired to reduce sagging, whereas low viscosities are needed at high shear rate for brushing and spraying. For an easy application, paints should show a decrease in viscosity with increasing the shear rate, which is called shear-thinning behavior.

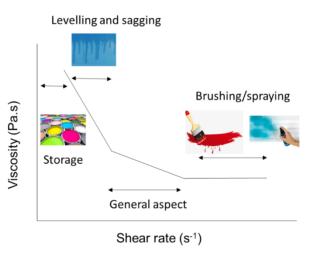


Figure 2.16. Relationship between viscosity, shear rate and paint properties.

The rheology of paints is highly affected by the thickener type and amount. In general, the amount of thickener used in paint formulation is between 0.1 and 1% of the total, and the amount needed can only be determined experimentally⁵.

In this work, a non-associative thickener (hydroxylethylcellulose HEC, comercial name NATROSOL 250HR) and an associative thickener (hydrophobically modified alkali-soluble

emulsions HASE, commercial name THIXOL[™] 53L) were used. In order to experimentally determine the amount of HEC and HASE to be used, latex/CaCO₃ blends were prepared with different amounts of the thickeners and the rheology of the obtained paints were measured (see Figure 2.17), in order to decide the most suitable thickener amounts. All blends were prepared with a solids content of 65 wt%, a PVC value of 45 and adding 0.4 wt% of NaPA dispersing agent based on the weight percent of CaCO₃.

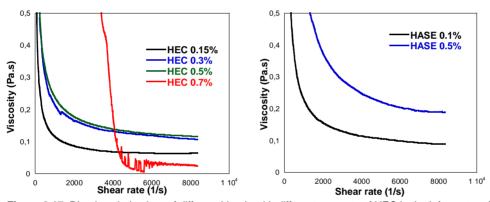


Figure 2.17. Rheology behaviour of different blends with different amounts of HEC in the lefts part and different amounts of HASE in the right part.

As it can be observed in Figure 2.17, all blends showed measureable shear thinning behaviour, except when high amount of HEC (0.7%) was added, in which the viscosity of the blend was out of range. Experimentally it was observed that a viscosity of around 0.1 Pa.s at high shear rates was enough to prevent particle sedimentation and to obtain good films. Therefore, and in order to obtain comparable latex/CaCO₃ blends, it was decided to use 0.5 wt%

of HEC and 0.1% of HASE thickener for the preparation of blends (as similar viscosities values were obtained at those thickener amounts).

Once the optimum amount of each thickener was determined, two different mill bases were prepared and the morphologies were characterized by SEM. The obtained images can be observed in Figure 2.18.

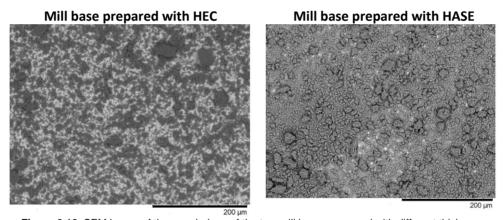


Figure 2.18. SEM image of the morphology of the two mill bases prepared with different thickeners.

As it can be observed in Figure 2.18, each thickener works differently. The associative thickener (HASE) binds CaCO₃ particles between them, whereas, the non-associative thickener (HEC) leaves gaps between the filler particles.

2.3.6 Characterization of CaCO₃/ Acrylic latex blends and films prepared with different types of thickeners

• Scanning electron microscopy (SEM) of the blends films

CaCO₃ /acrylic latex blends were cast into silicon molds and let to dry at 23 °C and 55% humidity for a week. Their visual appearance and the top surface pictures obtained by scanning electron miscroscopy (SEM) can be observed in Figure 2.19 and Figure 2.20, when employing HEC and HASE thickeners respectively.

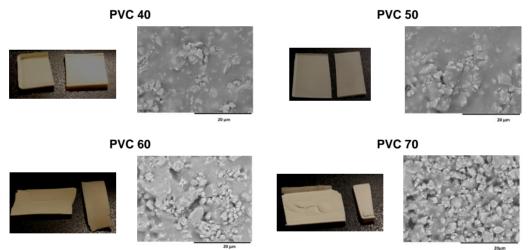


Figure 2.19. Photos and SEM micrographs of the CaCO₃/latex blends films containing HEC thickener at different pigment volume concentration (PVC) values.

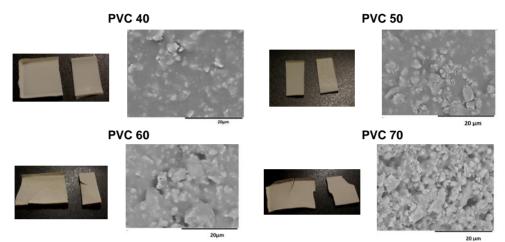


Figure 2.20. Photos and SEM micrographs of the CaCO₃/latex blends films containing HASE thickener at different pigment volume concentration (PVC) values.

Increasing the PVC, more CaCO₃ filler particles are present in the blends and this fact can be visually seen in the SEM images (Figure 2.19 and Figure 2.20). Above PVC 50, films were more brittle and some cracks could be observed during film formation. It is well known that above the critical pigment volume concentration (CPVC) films are discontinuous due to the presence of air pockets around pigment particles that replace the binder³⁹, which could be observed above PVC 50 for both HEC and HASE thickeners.

• Film formation of CaCO₃/acrylic latex blends by Horus

Adaptive Speckle Imaging Interferometry (ASII) optical technique, which is based on the diffusive wave spectroscopy (DWS), was used to analyse the film formation process of the blends. The Horus® was used to perform the analyses and the principle of the measurements can be seen in Appendix II. An example of the obtained graphs for CaCO₃/acrylic latex blends with HEC and HASE thickeners at the PVC value of 40 are shown in Figure 2.21, and the obtained values from the Horus measurements regarding the open time and set to-touch time are shown in Figure 2.21.

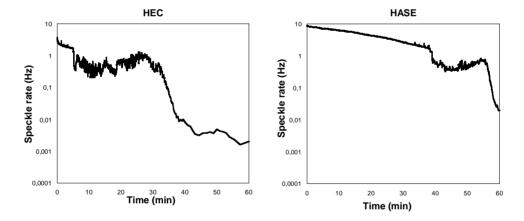


Figure 2.21. Drying kinetic profile obtained from the Horus, for CaCO₃/acrylic latex blends prepared with HEC and HASE thickeners for the PVC value of 40.

As it can be observed in Figure 2.21, the drying process of the blend is different depending on the thickener type used to prepare the blends. When employing HASE thickener for the preparation of blends the drying of the films is slower.

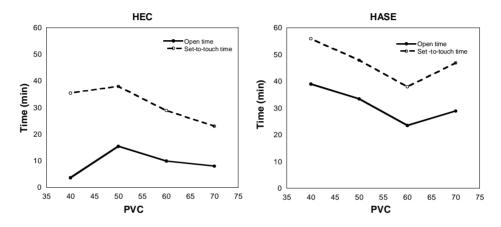


Figure 2.22. Open time and set-to-touch time for the CaCO₃/Acrylic latex blends prepared at different PVC values with HEC (left part) and with HASE (right part).

The open time is the time a coating remains workably wet before it begins to set. This parameter is a very important issue for waterborne coatings because traditional paints based on solvent borne exhibit open time values well above^{40,41,42}. In Figure 2.22, it can be observed that the open-time time is longer when preparing the paints with HASE thickener in comparison with paints prepared with HEC. The set-to-touch time, which is the time required for wet paint to reach the situation where none of the coating sticks to a finger that touches it, is also longer when employing HASE thickener.

Therefore, longer drying times were achieved when employing the associative HASE thickener. This can be attributed to the network that this thickener forms with the other particles of the medium, which can cause difficulties in evaporating water. Moreover, it has to be mentioned that when drying the mill bases prepared with different thickeners, a slight difference was also observed but not as big as in the final blends.

Contact angle value with water of CaCO₃/acrylic latex film

The water contact angle values were measured at the air-film interface. Just the polymer film was analysed initially as produced (non-cleaned) and after rinsing it with deionized water for 5 minutes. The obtained results can be observed in Table 2.5.

Table 2.5. Contact angle values measured for the polymer film before and after cleaning it with water.

Non-cleaned	Cleaned with water		
36 ± 2.3	73 ±3.4		

After cleaning the polymer film, higher contact angle values were observed (Table 2.5), indicating that at least some hydrophilic material was removed from the surface of the film and hence it became more hydrophobic. This hydrophilic material could correspond to the surfactant that during film formation could have migrated to the air-film interface and after cleaning, the surfactant could have been removed from the surface of the film.

The contact angle values for CaCO₃/P(MMA/BA/AA) blends films were also measured and results can be seen in Figure 2.23. The contact angle value of the films were measured as produced. They were not cleaned with water in order not to loose paint films integrity.

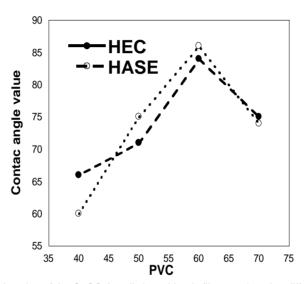


Figure 2.23. Contact angle value of the CaCO₃/acrylic latex blends films produced at different PVC values and with HEC or HASE thickener.

First, it has to be mentioned that the difference in contact angle values between the polymer film and paint film arises from the dispersion of calcium carbonate particles in the blends. Moreover, the contact angle value of the paint film is directly related to the roughness of the paint film surface.

In Figure 2.23, it can be observed that increasing the PVC (adding more filler particles to the system), the contact angle of the surface of the paint film increases. The higher the amount of filler in the system, the probability of formation of pigment clusters increases, therefore the surface roughness increases. However, it can be seen that at the PVC value of 70 the contact angle decreases. This fact can be attributed to the formation of voids in the coating filled by air, becoming the coating discontinuous and leading to the possibility of water being absorbed inside, which reduces the contact angle value. As it is well reported in the literature, after the CPVC the waterborne paint films properties turn out to worse⁴³.

Regarding the differences between the two types of thickeners, at low PVC values, when employing HASE the contact angle value of the paint film was lower; however, increasing the PVC value the contact angle value is higher when using HASE than when employing HEC thickener. This means that at high PVC the amount of HASE added was not the optimum amount to well disperse filler particles. Therefore, it can be concluded that at low PVC values the amount of HASE was better adjusted than at high PVC. Which suggests that when using associative thickener, the amount of thickener that needs to be added has to be more precisely adjusted depending on the PVC of the blends.

Gloss of CaCO₃/acrylic latex films

Gloss is one of the most important optical properties of coatings. The appearance of a surface depends on the manner in which incident light is reflected, absorbed, or transmitted by

the surface. Specular gloss of the CaCO₃/acrylic latex blends films was measured on black substrates at 85°, (for further information see Appendix III).

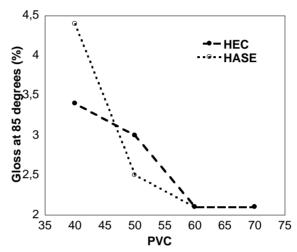


Figure 2.24. Gloss at 85° at the different PVC values for HEC and HASE thickeners.

Gloss is expected to increase with: (1) an increase in the refractive index of the surface, (2) an increase in the specular angle at which the measurement is made, and (3) an increase in the smoothness of the surface of the film⁴⁴.

Ground calcium carbonate and the acrylic latex have similar refractive index, 1.480 and 1.420 respectively, so changes in relative concentrations are not expected to produce significant changes in the refractive index of the mixture. Moreover, all measurements were made at the same incident angle. Therefore, the change in gloss will be due to differences in the smoothness of the surface on a microscale. The greater the concentration of GCC present, the greater the

number and dimensions of particle clusters that are formed. The formation of these clusters leads to an increase in the surface roughness (as seen in Figure 2.23 by the increase in the contact angle value), which results in reduced gloss (Figure 2.24). This tendency can be observed independently of the thickener employed.

Regarding the differences between the different thickeners employed, when using HEC at the PVC value of 60 the gloss levelled off at a very low gloss value and further increases of calcium carbonate filler amount did not affect the gloss. Because of the total loss of the optical properties, it can be concluded that the CPVC for this system was reached between PVC 50 and 60. However, when using HASE the gloss value levelled out at lower PVC values, which means that when using HASE thickener the CPVC was found between PVC 40 and 50.

Tensile-testing of CaCO₃/acrylic latex films

Strain-strain curves of the films cast from CaCO₃ / P(MMA/BA/AA) latex blends at different volume concentrations of the calcium carbonate pigment particles, and for two different thickeners are shown in Figure 2.25. As a rule, it can be observed that as the pigment volume concentration (PVC) increased, the stress-strain curves gradually changed from those characteristically obtained for typical elastomers to those of a brittle plastic material. In fact, for HEC thickener the change occurs above PVC 50 and for HASE thickener above PVC 40.

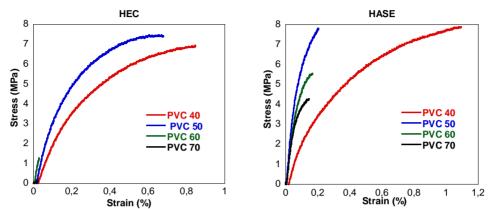


Figure 2.25. Stress-strain curves of CaCO₃/P(MMA/BA/AA) films at different PVC values for HEC and HASE thickeners.

Stress-strain curves were used to determine the strain at break and the toughness (Figure 2.26). The strain at break is the maximum elongation that a material can support before breaking. And the toughness, which is the area under the stress-strain curves, represents the energy per unit volume necessary to break the material. The toughness is related to material cohesion, and combines the resistance and ductility properties of a coating.

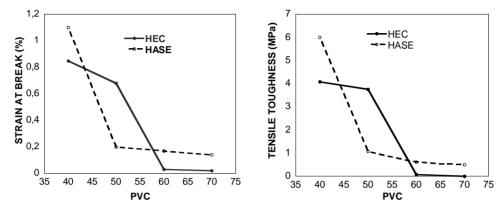


Figure 2.26. Strain at break and toughness of the films for different PVC values and for both thickeners.

The strain at break and the toughness decrease as the amount of GCC increases in the GCC/latex blends films. In fact, the decrease is known to become more important at the CPVC^{45,46}. As it can be seen in Figure 2.26, the mechanical properties dropped dramatically after reaching PVC 50 for HEC and PVC 40 for HASE. This behaviour confirms the results obtained from the specular gloss, that the CPVC is achieved before when employing HASE thickener.

The theoretical CPVC value for GCC/P(MMA/BA/AA) blends was calculated from equation 2 and it is around 54. This value would be in agreement with those obtained for the blend thickened with HEC by both gloss and tensile tests measurements. However, the CPVC obtained for the paints films produced with HASE thickener was below the theoretical value, which implies a negative effect of HASE thickener in the dispersion of CaCO₃/acrylic latex blend. This could be caused by the association of HASE thickener to the CaCO₃, which creates a net that hinders or

makes it more difficult to the polymer particles to distribute homogeneously in the blend, and consequently the final blend films properties obtained from this thickener to be worse.

2.4 Conclusions

In this chapter, the influence of the thickener on the critical pigment volume concentration (CPVC) value of latex/CaCO₃ blends has been studied. For carrying out this objective, P(MMA/BA/AA) latex was prepared by seeded semi batch emulsion polymerization and CaCO₃/P(MMA/BA/AA) blends were prepared with two different rheology modifiers, HEC and HASE, and using NaPA as dispersing agent in order to well disperse CaCO₃ particles.

First, the zeta potential of both polymer particles and calcium carbonate particles was measured and it was decided to prepare blends at the pH value of 9. Then, the optimum amount of NaPA needed to stabilized CaCO₃ was calculated. By different measurements (viscosity, zeta potential and particle size), it was concluded that 0.4 wt% of NaPA based on the weight of calcium carbonate particles was needed. Moreover, it was assessed that adding 0.4 wt% of NaPA, calcium carbonate particles were well dispersed. Finally, before preparing latex/CaCO₃ blends, it was also determined the amount of HEC and HASE thickeners in order to obtain final blends with good rheology profiles for storing, applications and final properties. Measuring the viscosity of some blends, it was seen that 0.5 wt% of HEC was needed, whereas, only 0.1 wt% of HASE.

Latex/CaCO₃ blends were prepared with the two different thickeners and at different PVC values. The effect of pigment volume concentration on the film morphology, contact angle, tensile

test and gloss measurements was studied. Tensile test, gloss measurements and morphology give an idea of the CPVC value. When using HEC non-associative thickener, mechanical properties and optical properties are completely lost above PVC 50, which means that the CPVC is between PVC 50 and 60. However, for HASE associative thickener, properties are lost above PVC 40, and therefore the CPVC was found to be between PVC 40 and 50. Because of this, it can be concluded that the nature of the thickener plays an important role in the CPVC value.

It has to be taken into account that HEC thickeners swell in the aqueous phase and therefore depends on the water content of the blends, but HASE thickeners depends on the type and the amount of the particles of the medium. At low PVC values, CaCO₃/acrylic films prepared with HASE showed better properties than when employing HEC thickeners, however this was not the case at high PVC values. At high PVC values more pigment particles are in the medium, and it seems that the network that the associative thickener forms between the particles can cause the agglomerations of some of the particles, as higher contact angle values, lower gloss and mechanical properties more brittle were observed. Therefore, when employing associative thickeners it is highly important to determine the optimum amount according to the PVC value. It has also be to pointed out that with this thickener longer drying times were achieved, which can cause poor final film properties due to water retention. Moreover, the network that this thickener forms with the CaCO₃ filler can make difficult to polymer particles to enter between them, and can cause the agglomeration of the filler particles.

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Chapter 3. Influence of the latex surface and

particle size on final paint-like blends with CaCO₃

3.1 Introduction

Due to its abundance, ground calcium carbonate (GCC) is used to lower the final price of

waterborne paints without significant losses of the films properties up to a certain amount of filler

addition1. As it has been mentioned, at the critical pigment volume concentration (CPVC) the

properties of the paint film change dramatically to worse.

However, it has to be pointed out that the CPVC of a pigment-binder system depends on

many aspects. Evidently, the first parameter affecting the CPVC is the use of solvent borne or

water borne binders2. On the other hand, the polymer particle size and the polymer particles

surface functionality will also affect the CVPC. In fact Klein et al. already found that smaller

particle sizes and the presence of acidic functionalities on the polymer particles surface favoured

higher CPVC values^{3,4,5,6}.

Thus, the study of the interaction between the binder and the pigment is essential to improve

the properties of the coatings. Several papers have already published the study of the interaction

between various types of binder and pigments by different methods^{7,8,9,10}. However, it has to be

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mentioned that most of the papers studying the interaction between pigments and different latex types have been performed after including all types of additives to the paint formulation (dispersants, rheology modifiers, tackifiers, defoarmers...), and it cannot be neglected the effect that these additives have on the effective film formation and resultant quality of the film^{11,12}. All components are having some degree of interaction with each other and these complex interactions must be considered in the wet state, drying stage and dry state¹³. In fact, as it has been shown in Chapter 2, the selection of only the thickener has an important effect on the CPVC of CaCO₃ on waterborne paints prepared with acrylate binders. In order to isolate the study of the interaction between the acrylic latex and the pigment, the challenge of this Chapter has been to prepare waterborne paints using only NaPA dispersing agent as additive and with applicable rheologies. These applicable rheologies have been pursued in order to mimic as much as possible the film formation conditions of real paints.

Therefore, high solids content waterborne paints based on polymer latex/filler blends have been prepared using only a dispersing agent as additive and the effects of several variables (latex type, their surface coverage, particle sizes and filler/latex ratio) on the film properties (scrub resistance, tensile properties, water uptake and gloss) have been investigated. Ground calcium carbonate (CaCO₃) and poly(methyl methacrylate-co-butyl acrylate) P(MMA/BA) have been used as extender and latex respectively and sodium polyacrylate (NaPA) has been added as dispersing agent, which is a common dispersant of the calcium carbonate as seen in the previous Chapter^{14,13,15}. The conditions to obtain satisfactory waterborne paints with CaCO₃ weight percentages as high as 70% have been established. Furthermore, the effect of CaCO₃ particle size and production procedure (GCC or precipitated calcium carbonate, PCC) on final film properties have been studied.

3.2 Experimental part

3.2.1 Materials

Methyl methacrylate (MMA, Quimidroga), butyl acrylate (BA, Quimidroga) and acrylic acid (AA, Fluka) were used as supplied. Sodium persulfate (NaPS, Sigma-Aldrich) was used as thermal initiator. The surfactant used was Dowfax® 2A1 (alkyldiphenyl oxide disulphonate, Dow Chemicals, 45% active phase). Deionized water was used throughout the work. To increase the pH of the latexes a 25% solution of ammonia (Fluka) was used. HCl (25 % solution) and NaOH (Sigma-Aldrich) were used for the titration of the latexes.

Two samples of ground calcium carbonate (GCC) were kindly supplied by Omya, Omyacarb®EXTRA-CL (with a purity of 97.5% and 90% of the particles with a size <2 μ m) and Omyacarb®3-CL (with a purity of 98% and 30% of the particles with a size < 2 μ m). In this work the names of GCC CL and GCC 3CL will be used to refer to them, respectively. One sample of precipitated calcium carbonate (PCC) was also kindly supplied by Cales de Llierca, CALPREC PA (average particle size of 1.7 μ m), which will be called PCC. Sodium polyacrylate (NaPA, molecular weight (MW)= 5100 g/mol, Sigma-Aldrich) was used to disperse CaCO₃ particles in water.

3.2.2 Synthesis of high solids content latexes

High solids content Poly(methyl methacrylate-co-butyl acrylate co-acrylic acid)
P(MMA/BA/AA) (49.5/49.5/1) latexes were prepared by seeded semi-batch emulsion
polymerization, as explained in Chapter 2. Latexes were prepared with 1% of AA and different

particle sizes: 120 nm, 300 nm and 600 nm, and with 300 nm without the acrylic acid functional monomer. Latexes were prepared at basic conditions with 1 wbm% of ammonia (see Table 3.1). Moreover, one latex was synthesized with 1% of AA and particle size of 300 nm at acidic conditions.

Table 3.1. Formulation of the latexes. Feeding time: 240 min.

	120 nm		300 nm		300 nm without AA		A 600 nm	
	Initial charge (g)	Stream (g)	Initial charge (g)	Stream (g)	Initial charge (g)	Stream (g)	Initial charge (g)	Stream (g)
Seed	388.1	-	31.12		31.12		3.97	
MMA	0.97	39.84	1.12	188.8	1.12	188.8	1.8	132.65
ВА	1.02	39.84	1.02	188.8	1.02	188.8	1.05	132.65
AA		8.0		2.4		-		2.7
Water	36.34	15.49	97.67	46.5	97.67	46.5	105.84	45.4
Dowfax 2A1		0.366		4.2		4.2		2.4
NH ₄ OH		0.8		2.4/-		2.4		2.7

3.2.3 Preparation of CaCO₃/latex blends using only NaPA additive

Waterborne paint-like blends were prepared in two steps. In the first step the dispersion of the pigment and dispersing agent in water, the so-called mill base, was prepared. In the second step the mill base was blended with the latexes at pH 9 and the final paints were obtained.

In order to obtain the mill base, first distilled water and sodium polyacrylate (NaPA) dispersing agent were weighed in a 500 mL container and stirred using a Dispermat high speed disperser blade under low shear (350 rpm). CaCO₃ powder was then added slowly into the container and the shear rate was increased (up to 1300 rpm) during the addition. After CaCO₃ addition, the mill base was left at constant shear for 30 min. The optimum dosage of NaPA needed to disperse correctly the CaCO₃ particles, was obtained measuring the dispersion viscosity with a Brookfield viscometer as a function of the amount of NaPA in a high solids content CaCO₃ slurry.

Afterwards, the mill base was blended (500 rpm) with the different latexes at pH 9. To study the interaction between the acrylic latex and calcium carbonate particles, different blends were prepared with this strategy, changing the nature of the latex in terms of particle size and functional monomer, the nature of CaCO₃ sample and for different PVC values of 30, 40, 45 and 50. Waterborne blends were then stored at standard atmospheric conditions (23 °C and 50% relative humidity) for 48 hours, before performing the films and their characterization.

3.2.4 Characterization

Conversion and solids content were gravimetrically determined. The average particle size was measured by Dynamic Light Scattering Spectroscopy, DLS (Malvern® Zetasier Nano). The microstructure of the final latex was determined by measuring the gel fraction in tetrahydrofuran (THF) by Soxhlet extraction and the molecular weight of the soluble part was analyzed by Gel Permeation chromatography (GPC). The carboxylic acid groups present in the surface of the

latex particles was calculated by titration after dialyzing the latexes. The details of the characterization procedures and methods are given in Appendix I.

The surface area of CaCO₃ was measured by nitrogen adsorption (BET) in a Micromeritics equipment (ASAP 2020).

The viscosity vs. shear rate of the final blends was measured using a TA rheometer (TA instruments AR 1500). Two microscopic techniques were used for the analysis of the samples. On one hand, the surface morphology of CaCO₃ particles and blends films was characterized by scanning electron microscopy (SEM) (TM 3030). And on the other, AFM pictures were obtained using an atomic force microscope Veeco Nanoscope IV multimode in tapping mode. The roughness profiles of the films were extracted from the height images of the AFM micrographs.

In order to measure the rest of the films properties, they were dried at 50 °C and 55% relative humidity on different moulds, depending on the test to carry out. To measure the water uptake, blends films were casted onto round silicone moulds. These films were then immersed in distilled water for seven days. Each day they were withdrawn from the glass container and carefully dried and quickly weighed, in order to analyse the evolution of the relative weight gained during immersion.

Relative surface gloss of the paint-like films was measured with a Glossmeter (micro-TRI-gloss) at incident angle of 85°. The mechanical properties of the films were measured by means of different techniques. Stress-strain tests were performed a week after the blend films were totally dry at 50 °C and 55% relative humidity, in silicone moulds. The hardness of the blend films was measured by Persoz pendulum hardness. The scrub resistance of the paint-like films was

determined by washability tests according to the ASTM D2486 standard method. For further information of these techniques, see Appendix III.

3.3 Results and discussion

3.3.1 High solids content latexes

The characterization of the obtained final latexes regarding the solids content, particle size, glass transition temperature, gel content and molecular weight can be observed in Table 3.2.

 Table 3.2. Characterization of the synthesized latexes.

	SC (%)	Dp (nm) (DLS)	Tg (⁰C) (DSC)	Gel (%)	Mn (g/mol)
MMA/BA 300 nm	59	295	16	55	142.000
MMA/BA/AA 300 nm	60.5	275	17	50	124.000
MMA/BA/AA 300 nm*	61	273	19	71	75.000
MMA/BA/AA 120 nm	61	119	17	60	75.000
MMA/BA/AA 600 nm	59	589	17	32	173.594

^{*}acidic conditions

After the synthesis, the final solids content for all latex was obtained gravimetrically and it was around 60 %. However, the latex with the particle size of 120 nm was synthesized at a

solids content of 25% and then it was concentrated using a rotavapor to attain the final solids content of 61%.

Polymer microstructure of the final latexes was analyzed in terms of gel content (or THF insoluble part) and molecular weight of the sol part. In table Table 3.2 it can be observed that gel was formed in all cases. In the emulsion polymerization of acrylates the gel is formed by intermolecular chain transfer to polymer followed by termination by combination ^{16,17,18}. On the one hand, increasing the polymer particle size the gel decreased: the superficial area per volume decreases, leading to a lower value in the average number of radicals per particles (ñ). Lower values of ñ, leads to a reduction of the rate of bimolecular termination between large molecules in the polymer particles, which reduced the gel formation.

On the other hand, the pH has also a strong influence on the polymer microstructure. When the reaction was carried out under basic conditions, the gel content was lower than at acidic conditions. When the polymerization is conducted at basic conditions higher amount of water soluble species are formed, which implies higher termination of oligoradicals in the aqueous phase and hence a reduction in the average number of radicals per particles (ñ), lowering the gel amount.

Furthermore, the gel content tends to decrease the sol molecular weight because the long polymer chains have a higher probability to suffer intermolecular chain transfer to polymer and therefore to be incorporated in the gel¹⁹.

In order to analyse the different incorporation of carboxylic acid groups on the particles surface, depending on the particle size and pH of the synthesis, titration with NaOH was carried out as explained in Appendix I. The results obtained are presented in Table 3.3.

Table 3.3. Carboxylic acid group percentage in the surface of the particles depending on the pH of the synthesis of the latex and particle size.

	-COOH in the surface (%)
MMA/BA/AA 120 nm	21.5
MMA/BA/AA 300 nm	15.5
MMA/BA/AA 300 nm acidic conditions	30
MAA/BA/AA 600 nm	12

Table 3.3 shows that as the pH of the polymerization media decreases, the amount of carboxylic groups on the surface of the particles increases. The pH affects the distribution of the acrylic acid monomer during the emulsion polymerization process, due to the dissociation of the carboxylic groups above the pKa, (pKa, acrylic acid= 4.25)²⁰. Hence, increasing the pH the acrylic acid would preferentially polymerize in the aqueous phase producing water soluble polymers, and lower amount of acrylic acid groups would be incorporated to the surface of the polymer particles.

Moreover, the lower the particle size of the latex the higher the surface area per volume of these particles, which allows a greater incorporation of acrylic acid groups in the surface of the particles (Table 3.3). On the contrary, for big particle size latex, low amount of carboxylic acid groups were found on the surface of the particles.

3.3.2 CaCO₃ samples

The SEM images of the three different CaCO₃ samples used in this Chapter can be observed in Figure 3.1.

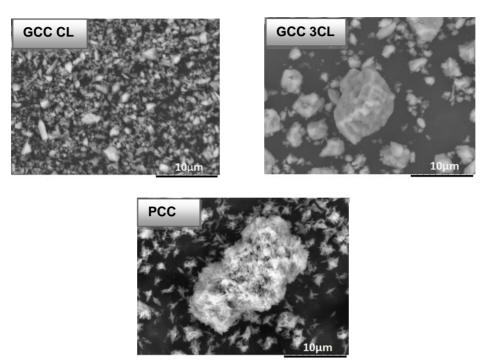


Figure 3.1 SEM images of GCC CL, GCC 3CL and PCC particles.

As it can be seen in Figure 3.1, GCC CL and GCC 3CL samples show calcite structure, whereas PCC sample has an aragonite structure. The SEM image of GCC CL sample shows that most of the particles have a size below 2 μ m, which is in agreement with the particle size provided by the supplier. Moreover, GCC 3CL particles are bigger than GCC CL and it seems that as provided by the supplier only 30% of the particles have a particle size lower than 2 μ m, the rest of the particles having a higher particle size. The individual CaCO₃ needles from PCC sample tend to form agglomerates. In the case of PCC sample, the particle size provided by the supplier, 1.7 μ m, approximates that observed by SEM for single needle-like particles.

The oil absorption values provided by the suppliers, the critical pigment volume concentration (CPVC) calculated from the oil absorption values, the BET surface area (calculated by the adsorption of N_2) and the maximum solids content in water calculated experimentally (as the amount at which more CaCO $_3$ cannot be dispersed in water), for each sample is shown in Table 3.4.

Table 3.4. Oil absorption value given by the supplier, theoretical CPVC and maximum solids content in water for each CaCO₃ sample.

	Oil absorption (g)	CPVC	BET surface area (m²/g)	Maximum solids content in water
GCC CL	40	49	8.2	70
GCC 3CL	30	52	2.4	75
PCC	45	43	7.3	47

As it can be observed in Table 3.4, higher solids content in water and CPVC can be achieved with GCC 3CL sample. Moreover, higher specific surface area was found for GCC CL filler. Slightly lower surface area was found for PCC in comparison with GCC CL, probably due to the formation of agglomerates (as it can be observed in Figure 3.1).

3.3.3 Preparation of waterborne paint-like blends with NaPA dispersing agent

In order to isolate the study of the interaction between the acrylic latex and the pigment, waterborne paint-like blends have been prepared using only NaPA as additive and with applicable rheologies. A first trial was done mixing MMA/BA/AA 300 nm latex (60 wt% s.c.) with a mill base of CaCO₃ (70 wt% s.c) as explained in the experimental part but without NaPA

dispersing agent. It has to be recalled that the maximum solids content dispersable of Omyacarb®-CL CaCO₃ particles in water is 70 wt%. Afterwards, the blend was casted into silicon molds and let to dry at 23°C and 55% humidity for two days. The obtained film can be seen in Figure 3.2.



Figure 3.2. Waterborne paint-like film prepared without additives, PVC 45, SC 65%.

As it can be observed, the obtained films were highly heterogeneous. Large agglomerates of CaCO₃ particles can be seen throughout the film. This means, that using this mixing procedure at least the use of a dispersing agent is needed in order to obtain a good dispersion of the pigment.

In the same way that it was done in Chapter 2 for Omyacarb 3CL pigment, the optimum amount of NaPA needed to disperse the Omyacarb CL was obtained from the evolution of the viscosity of a CaCO₃ slurry as a function of the NaPA content at high solids content (70 wt%) (Figure 3.3).

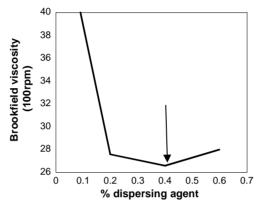


Figure 3.3 Viscosity change as a function of the amount of NaPA in the CaCO₃ slurry (70 wt%).

The viscosity of CaCO₃ slurry (70% solids content) decreased sharply with the addition of NaPA. This decrease is attributed to the water released from CaCO₃ aggregates when these particles are dispersed by the NaPA. The viscosity subsequently showed a slight increase with increasing the amount of NaPA. When the amount of NaPA added is larger than the one corresponding to the saturation adsorption, excess of NaPA exists, which could bridge between CaCO₃ particles or swell in water and consequently increase the viscosity¹⁵. Therefore, the optimum dosage of NaPA was established at 0.4 wt% based on the weight of CaCO₃ particles.

As mentioned above, adding NaPA the viscosity of the mill base decreases, which could lead to a precipitation of CaCO₃ in the final paint, like the one obtained when no further action was taken to improve the mixture between the latex and the mill base (see Figure 3.4). In this case the higher density of the CaCO₃ particles together with the low viscosity of the final blend led to a sedimentation of the filler particles at the bottom of the film.

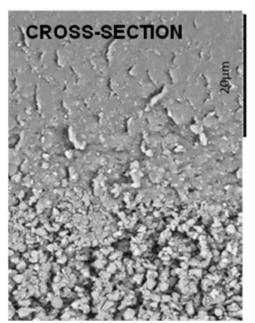


Figure 3.4. SEM cross-section images of latex/CaCO₃ blend film using NaPA.

In order to avoid this problem thickeners are commonly used in waterborne paints ^{21,22}. As it was seen in Chapter 2, the nature of the thickener plays an important role in the final properties of the film. Therefore, in this Chapter the use of thickeners was avoided. Taking advantage of the fact that the addition of NaPA leads to lower viscosity values, it was possible to increase the solids content of the CaCO₃ mill base to 75 wt% (the mixture formulation can be observed in Table 3.5). This allowed increasing the viscosity of the system and consequently avoiding CaCO₃ sedimentation during film formation, without the use of any thickener.

However, this high viscosity can lead to trapping air bubbles in the blend. In order to obtain undisturbed films, it was necessary to remove entrapped air bubbles from the mill base with a

deaeration equipment, which consisted on a container that could be closed by means of a flange. Anchor stirring was provided slowly for 20 minutes under proper vacuum. This way homogeneous and bubble free films could be obtained, and the interaction between binder and filler could be analyzed with the minimum amount of paint additives.

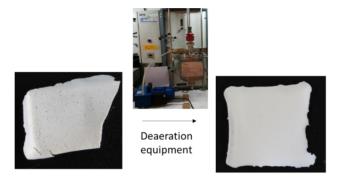


Figure 3.5. Preparation of final film without bubbles.

As it can be seen in Figure 3.5, the obtained film was homogenous after the deaeration of the paint-like blend. As a result, this strategy was followed in this Chapter, to study the interaction between the acrylic latex and calcium carbonate particles.

The formulating strategy employed was to mix the latex (when necessary neutralized to pH of 9) and CaCO₃ dispersion in water (with the help of NaPA) in different ratios, which would result in a final solids content of 60 %. The advantage of keeping the solids content equal is that it allows valid comparison to be made of dry film properties (e.g. scrub resistance, water uptake). The waterborne paint-like formulations can be observed in Table 3.5.

Table 3.5. Formulation of the latex/CaCO₃ mixture for different PVC values.

	Mill base			Latex		
PVC	CaCO₃	NaPA	H ₂ O	Polymer	H₂O	
30	34.05	0.18	11.35	32.64	21.76	
40	42.075	0.22	14.03	26.22	17.48	
45	45.9	0.24	15.3	23.1	15.4	
50	49.35	0.26	16.2	20.4	13.6	

Blends were stored at 23 °C and 50% humidity for 48 hours and then then films were prepared by drying in the oven at 50 °C and 55%, to ensure the coalescence of the polymer particles²³.

3.3.4 Waterborne paint-like blends: Comparison between different latexes

In this part of the Chapter blends were prepared using GCC CL as filler and with different types of latexes in terms of particle size and surface coverage.

Rheology

It is important to measure the rheology of the blends since the viscosity influences most of the applications properties. Figure 3.6 presents the viscosity versus shear rate for latexes. In the left graph latexes synthesized with 1% AA and different particle sizes are presented and in

the right graph latexes synthesized with 300 nm without AA and with 1% AA at basic and acidic conditions are presented. The measurements were performed at 25 °C.

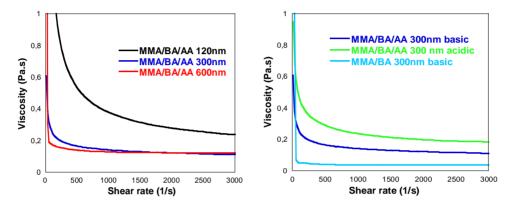


Figure 3.6. Rheology profile of the latexes with different particle sizes and AA at basic pH (left) and at different reaction pH with and without AA.

As it can be seen in Figure 3.6, the viscosity of the latexes show shear thinning (pseudoplastic) behaviour, characterized by the decrease of the viscosity as the shear rate increases. Regarding the differences in particle sizes, the latex synthesized with the smallest particle size presents higher viscosities. This is attributed to a lower interparticle space which leads to a higher interaction between particles. The big differences observed as a function of the particle size of the latexes, can be attributed to the fact that latexes are close to the maximum packing fraction, that for unimodal latexes is 0.64^{24,25}.

For a given solids content the viscosity of carboxylated latexes is supposed to increase when increasing the pH. At low pH the carboxylic groups are protonated and the surface layer containing carboxylic groups is compressed, while as the pH in the water phase is increased, the acid groups are ionized and the layer expands from the particle surface. This expansion has a

significant contribution on the hydrodynamic diameter of the polymer particles, leading to an effective increase in the volume fraction of the particles. However, in Figure 3.6 right graph, higher viscosity values can be observed for the latex synthesized at acidic pH. Two factors can affect this behaviour: On one hand the final solids content strongly affects the viscosity of the latex, and the solids content of the acidic latex was slightly higher (61% vs 60%, Table 3.2). It has to be mentioned, that as the solids content approaches the maximum packing fraction (which as mentioned above for unimodal distribution is 0.64), the viscosity sharply increases²⁶. On the other hand, the amount of carboxylic acid groups on the surface of the latex synthesized at acidic conditions is higher, which would contribute to a larger extent to the hydrodynamic volume of the particles. Moreover, it can also be observed that the latex synthesized without the functional monomer had lower viscosity. This latex does not present the acrylic acid groups on the surface of polymer particles, leading to a lower surface potential and hence a lower particle interaction.

The rheology profile for blends prepared at different PVC value and with different latexes are shown in Figure 3.7. It has to be pointed out that although the MMA/BA/AA acidic latex was synthesized at acidic conditions, the latex was then neturalized for the preparation of the blends.

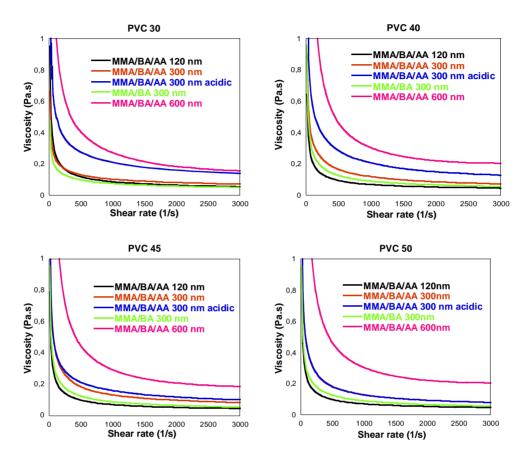


Figure 3.7. Rheology profile of the blends prepared with GCC-CL at different PVC values, with different latexes.

For all blends (Figure 3.7), shear thinning behaviour was observed, which means high viscosity in the low shear region to avoid settling and instability during storage and transport of the paint and low viscosities in the high shear rate region which corresponds to the application. The viscosity of waterborne paints is mainly given by the volume fraction, the size of the particles, the polydispersity of the particles and the interaction between them. In this case, the volume fraction is the same for all the blends, so the rest of variables will have to be considered to understand the differences between them.

As it can be observed in Figure 3.7, blends prepared with the latex of 600 nm particle size presented higher viscosity profiles. For bimodal distributions, a greater difference between the large and the small particles results in a lower viscosity, because the small particles fill better into the voids of the large particles. For blends prepared with the latex of 600 nm the difference between larger filler particles and smaller polymer particles is less, and therefore the viscosity is higher than for the other blends, as can be seen in Figure 3.7. Giving the same particle size of the latex (300 nm), higher viscosity was observed for blends prepared with the latex synthesized at acidic conditions. This might suggest a better interaction between the latex and calcium carbonate filler, thanks to a higher incorporation of AA in the surface of the polymer particles. On the contrary, lower viscosity was observed for blends prepared with the latex synthesized without the functional monomer, suggesting a weaker interaction in this case.

AFM

AFM phase images of the blends films dried at 23 °C and 55% humidity are represented in Figure 3.8. AFM taping mode phase images were obtained due to the great differences in viscoelastic properties of calcium carbonate particles and the polymer in the film.

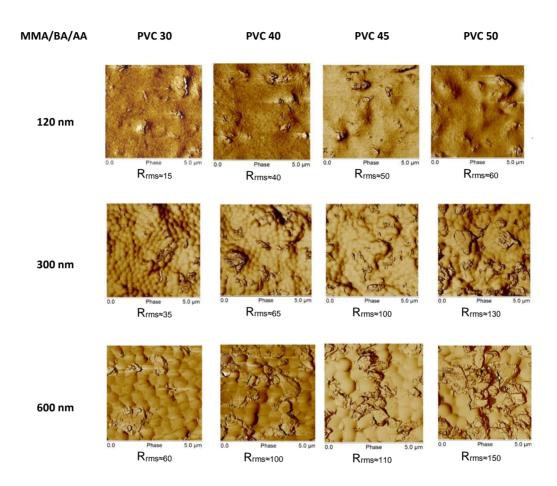


Figure 3 8. AFM phase images of the blends films at different PVC values, prepared with latexes synthesized with 1% AA and different particles sizes. R_{rms} values (nm) have been obtained from the height images.

The regular spheres represent latex particles, whereas the irregular forms constitute calcium carbonate particles. The roughness profiles (R_{rms}) of the films were extracted from the height images of the AFM micrographs (for further information see Apendix III). The roughness of the surface affects coating properties such as gloss.

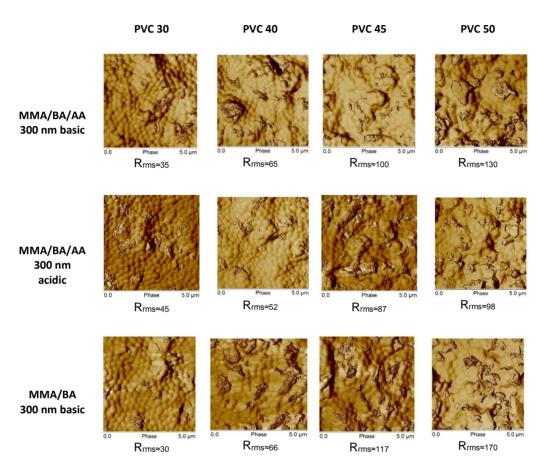


Figure 3.9. AFM phase images of the blends films prepared with GCC CL at different PVC values, with latexes synthesized without AA and with 1% AA at basic and acidic conditions. R_{rms} values (nm) have been obtained from the height images.

As it can be seen in Figure 3.9, in all cases the roughness of the surfaces increased increasing the PVC value. At high PVC values, more calcium carbonate agglomerates can be observed on the surface, which decreased the smoothness of the films. For a given PVC value,

the roughness increased as the particle size of the latex used to prepare the blend increased. This means that the surface of the films prepared with 600 nm particle size latex were rougher and films prepared with 120 nm particle size latex smoother.

As it can be observed in Figure 3.9, paint-like films prepared with the latex synthesized in acidic conditions (with the exception at PVC value of 30) present less rough surfaces than paint-like blends prepared at basic conditions. Therefore, the enrichment of the polymer particles of carboxylic groups for the case in which the latex was synthesized at acidic conditions, led apparently to a better compatibility between the binder and the extender, and therefore to less rough surfaces.

Moreover, similar roughness values were observed at low PVC values for blends prepared with 300 nm particle size latex, with and without the acrylic acid functional monomer. However, at high PVC values, blends manufactured without the functional monomer were rougher. Suggesting a worse interaction between the binder and the CaCO₃ particles when the functional monomer is not employed in the synthesis of the latex.

Gloss

Specular gloss of pure latex and blends films was measured on black substrates at 85 ⁰ geometry and the obtained results are presented in Figure 3.10. The values obtained showed a standard deviation of ±2.

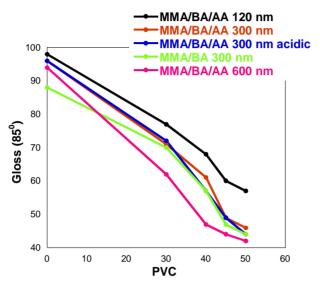


Figure 3.10. Gloss value for the pure latexes (PVC 0) and waterborne blends.

It can be observed that the gloss value for blends films was lower than the one for pure latex films. Among the latexes, lower gloss value was observed for the latex synthesized without the presence of the acrylic acid functional monomer. The formation of the film was worst without the presence of the carboxyl groups on the latex particles, which decreased the gloss of the film. For the blends containing CaCO₃, it can be seen that the gloss was reduced as the PVC value increased; thereby increasing calcium carbonate concentration in the paint-like films, gloss decreases²⁷. The greater the concentration of filler present, the greater particle agglomerates are formed. The formation of the agglomerates leads to increased roughness on the surface of the film, as it was observed by AFM images (Figure 3.8 and Figure 3.9), which results in a reduction of gloss. It can also be observed that the gloss of the paint-like films was higher for those blends prepared with the smaller particle size latex. As mentioned before, gloss is a surface

property that depends on the smoothness of the surface and as observed by AFM images, blends prepared with the smallest particle size latex were smoother. This smoothness does not come just from the smaller binder particle size, but from the better filler particles dispersion in the blend, which does not push their appearance on the film surface. Therefore polymer particle sizes have a strong effect on paint gloss, as seen by AFM too.

However, the presence of AA functional monomer did not present significant differences when the gloss of the paint-like film was the measured property. Even if as observed by AFM images, paint-like film prepared with the latex at acidic conditions showed a smoother surface compared to the paint-like film prepared with the latex at basic conditions, no big differences were observed in the gloss value from one to another (Figure 3.10).

Lastly, it is well known that gloss is lost above the CPVC^{28,3}. Above PVC 40, the gloss value for all paints films dropped significantly except for the paints prepared with 120 nm and 600 nm particle size latex. For blends prepared with 600 nm latex the biggest drop was found between PVC 30 and 40, while for blends prepared with 120 nm latex, no big drops were detected below PVC 45. This means, that the CPVC for this system can be achieved at higher PVC values for 120 nm latex and at lower PVC for 600 nm latex.

Water uptake

Another important characteristic of waterborne paints is their resistance to absorb water. To measure this, water uptake of the latexes and paint-like films were followed during time (as explained in Apendix III) and the obtained results for the latexes and blends prepared are shown in Figure 3.11, Figure 3.12 and Figure 3.13.

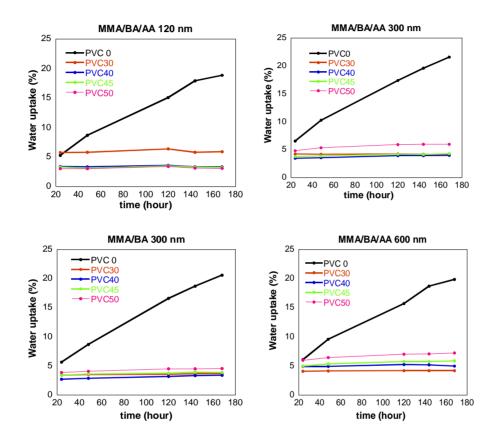


Figure 3.11. Water uptake of the latexes and blends prepared with latex of different particle size and with and without AA functional monomer, during a week.

As it can be observed in Figure 3.11, the water uptake of the latex films was very similar independently of the final particle size. Latex films absorbed around 20% of water in one week.

However, the absorption of the paint-like films was much lower (around 5% in one week) and it remained constant after the initial uptake. Moreover, no clear differences were observed from one paint to another at different PVC values. Nevertheless, it has to be pointed out that none of the blend films disintegrated during immersion, which suggest a good cohesion of films.

The water uptake results from the latexes synthesized under different pH conditions are shown in Figure 3.12, and the blends prepared with both latexes and at different PVC values are depicted in Figure 3.13.

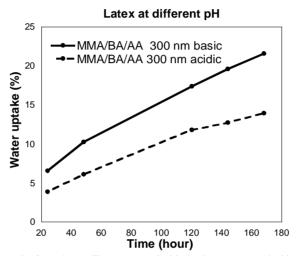


Figure 3.12. Water uptake for polymer films prepared with the latex prepared with 1% AA at acidic and basic conditions.

As it can be observed in Figure 3.12, the water absorption profile is different depending on the pH used in the synthesis of the latex. Water uptake of the films results from the interplay between the existence of hydrophilic pockets or aggregates inside the film, the capacity of those pockets for water absorption and their accessibility. As it can be observed, the latex synthesized under basic conditions absorbed higher amount of water. Therefore, the amount of absorbed water at the end of the experiment varied significantly depending on the pH conditions of the latex. When the latex was synthesized under acidic conditions the formation of water soluble oligomers was less favoured, and therefore, the film from the latex absorbed less water comparing with the film formed from latex synthesized under basic conditions.

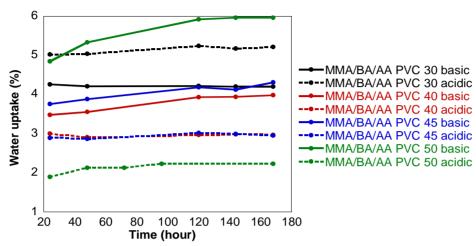


Figure 3.13. Water uptake for blends prepared with acidic and basic latex at different PVC values.

Regarding the water absorption of blends, as it can be observed in Figure 3.13 a clear tendency among the different PVC values cannot be observed. Moreover, blends prepared with the latex at acidic conditions absorb less water, with the exception of the paint prepared with a PVC value of 30. These results might suggest that the interaction between the acrylic latex and the calcium carbonate particles is better when higher carboxylic groups are present in the surface of the latex particles prepared at acidic conditions.

Water uptake of the films demonstrated that despite the high content of CaCO₃ pigment inside the films, films were cohesive and after being immersed in water for one week, they did not lose their integrity.

Mechanical properties

The effect of the particle size, the pH of the synthesis and the functional monomer of the latex on the mechanical properties of the waterborne paint-like film was studied at different PVC values. For this purpose, tensile test, hardness and scrub resistance measurements of the blends films were carried out.

Tensile test

Strain-stress curves of the blends films prepared with the different latexes and GCC CL at different PVC values are shown in Figure 3.14 and the obtained elongation at break, toughness and Young's modulus in Figure 3.15.

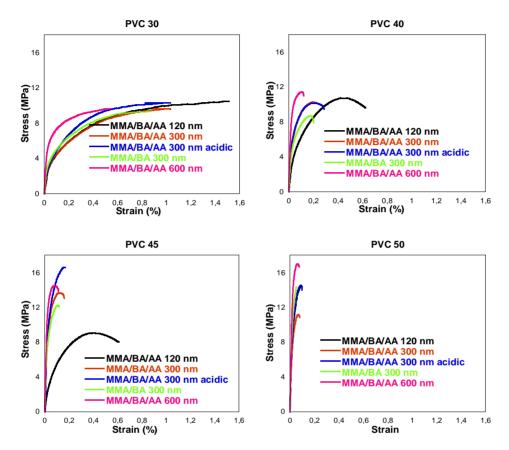


Figure 3.14. Tensile test of the blends films prepared with GCC CL and different latexes at different PVC values.

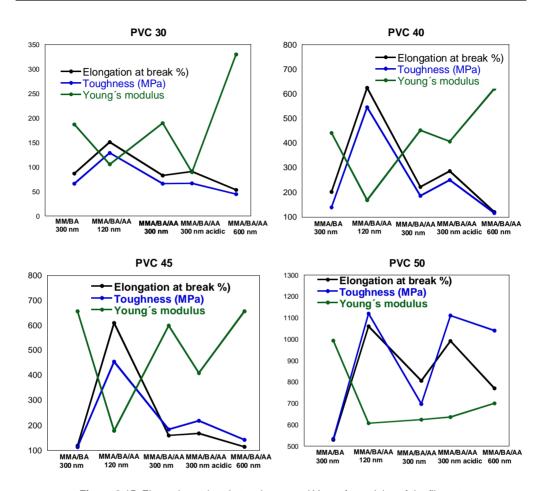


Figure 3.15. Elongation at break, toughness and Young's modulus of the films at PVC values of 30, 40, 45 and 50.

Figures 3.14, Figure 3.15 show that the elongation at break of the paint-like films decreased increasing the PVC value. It can also be observed that increasing the PVC value, the Young's modulus for all paint-like films increased. These results show that increasing the PVC value, paints films become more brittle, because the increase of the pigment amount in the system reinforces the polymer matrix. For all PVC values it can be clearly seen that paints

prepared with the smallest latex particles achieved higher elongation at break and lower Young's modulus. The opposite was observed for blends prepared with the larger particle size latex, smaller elongation at break and a higher Young's modulus. It can also be observed that the mechanical properties of the paint-like films prepared with the latex of 120 nm at the PVC of 45 were not still completely lost, as opposed to the other films. This means that with the latex of the smallest particle size, higher PVC can be achieved without a complete loosing of mechanical properties. The particle size of the latex strongly affects tensile test properties and as previously reported by Klein et al.²⁹, smaller latex particles can provide a better interaction with the filler because of larger total surface area.

Moreover, it can be observed that blends prepared with the latex synthesized at acidic conditions showed slightly better mechanical properties. Higher elongation at break can be achieved preparing blends with this latex, and it seems that the mechanical properties preserve better at higher PVC values. On the opposite, when blends were prepared with the latex synthesized without the functional monomer the mechanical properties were worse (lower elongation at break). This means that a better interaction between the polymer particles and the CaCO₃ particles is obtained when the latex is synthesized with the functional monomer and at acidic pH. This is attributed to a higher incorporation of the acrylic acid functional groups (see Table 3.3) on the surface of the polymer particles that enhance the dispersion of the CaCO₃ particles.

It can be argued that the difference in the mechanical properties of the films obtained from blends can come from the differences already present in the latexes. Figure 3.16 presents the tensile test measurements of the films obtained from the pristine latexes.

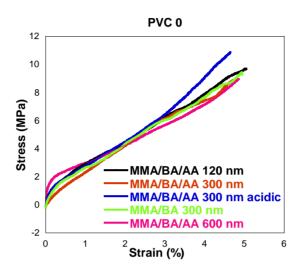


Figure 3.16. Tensile test of the films form the different latexes.

As it can be seen in Figure 3.16, no clear differences can be observed between the different latexes. And the small differences can be attributed to differences in microstructure, like different gel content or different molecular weights, already observed in Table 3.2. Therefore, the existence of different mechanical properties of the blends come from the different interaction between the polymer particles and the CaCO₃ particles.

Hardness

The hardness is defined as the resistance of a coating to a mechanical force, such as pressure, rubbing or scratching. In practice, different testing methods can be used and in this case, pendulum hardness was employed¹².

The hardness of paint-like film depends on several factors such as binder type and pigments used in the paint. In this case hardness was analysed as a function of the particle size of the latex, the functional monomer of the latex, the pH of the synthesis of the latex and the PVC value. The hardness of the latexes and the paint-like films are presented in Figure 3.17.

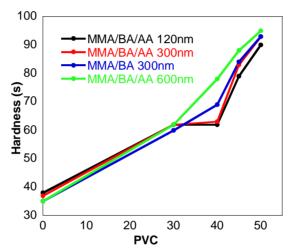


Figure 3.17. Hardness as a function of the PVC value for the different films obtained from the latexes and waterborne paint-like blends.

As it can be observed in Figure 3.17, similar hardness values were observed for the films obtained from the four latexes. The hardness of the films increased with increasing the pigment concentration in the paints. Adding pigment to the soft matrix the rigidity of the paint film increased. Moreover, blends prepared with the biggest particle size latex were more rigid, whereas, blends prepared with the smallest particle size latex, were slightly more elastic. Blends prepared with the latex of 300 nm without the acrylic acid functional monomer presented slightly higher hardness than the blends prepared with the functional monomer. Therefore in this case

both the beneficial effect of the smaller particle size and of the presence of the AA functional monomer could be detected in the final films.

Scrub resistance

The scrub resistance of the films prepared with different latexes varying particle size and functional monomer and with GCC CL at different PVC ratios are plotted in Figure 3.18.

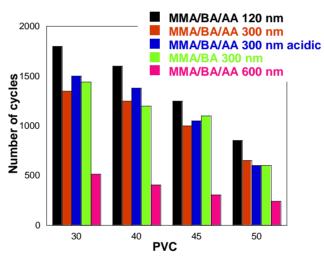


Figure 3.18. Scrub resistance of waterborne paint-like films, prepared with different latex and GCC CL at different PVC values.

As it can be seen in Figure 3.18, the scrub resistance for all films decreased with increasing the PVC value. This result is expected because paints with low PVC have enough amount of binder to keep the pigment particles strongly bound. It can also be observed that those blends prepared with the latex of the smallest particle size (120 nm) presented better scrub resistance. This means that this latex had high pigment-binding capacity which is related to

higher scrub resistance. In the same way, the compatibility of the pigment with the latex of 600 nm seems to be worse as these films presented much less scrub resistance.

No significant differences were observed for films prepared with or without the acrylic acid functional monomer. Moreover, the scrub resistance for films prepared with the acidic latex are slightly better. A better interaction is observed in this case due possibly to a higher amount of functional carboxylic groups in the surface of the particles, which leads a more cohesive films, and thus to more scrub resistant paint film.

3.3.5 Waterborne paint-like blends: Comparison between CaCO₃ samples

In the previous results it was observed that better properties as a whole were obtained when preparing blends with the latex of 120 nm particle size. Because of this, in the following sections, blends were prepared using this latex and employing other samples of CaCO₃ particles, more precisely with a precipitated calcium carbonate (PCC) and Omyacarb®3CL. This last CaCO₃ was already used in Chapter 2. Blends were prepared at the PVC value of 45, because it was already seen that when preparing blends with the latex of 120 nm and GCC CL pigment, this PVC was just below the CPVC (section 3.3.4).

PCC at PVC 45

Precipitated calcium carbonate (PCC) is a synthetic calcium carbonate produced industrially by bubbling carbon dioxide into a solution of calcium hydroxide. PCC is used as functional

pigment, to provide mainly the optical function of whiteness, brightness and opacity. In fact, this pigment is used in many examples of the literature to replace the expensive TiO₂^{30,31,32}.

The procedure employed to make the blend of PCC with 120 nm latex at PVC 45 was the same as the one explained in section 3.4.3. For this pigment, the mill base was prepared with 0.4% of NaPA based on PCC weight and the use of dispersant gave the possibility to increase the solids content of PCC in water up to 55% (in order to obtain high viscosity and to avoid the use of thickeners).



Figure 3.19. Paint-like film produce using PCC at the PVC value of 45, with the latex of 120 nm.

The obtained film (Figure 3.19) was whiter than the films obtained with the CL sample. Nevertheless, cracks were obtained in the film, which means that for this pigment the CPVC has been surpassed at the PVC value of 45 (the theoretical CPVC for PCC is 43, Table 3.4). As the film showed these cracks, further characterization of this film was not carried out.

• PCC + CL (10/90 ratio) at PVC 45

To improve the properties of the paint films obtained with the calcium carbonate CL sample, it was decided to prepare one blend adding 10% of PCC and 90% of GCC CL at PVC of 45, which blend has a theoretical CPVC of 43.5. The films obtained in the presence and absence of PCC are shown in Figure 3.21.

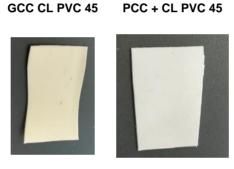


Figure 3.20 Film using CL only and PCC + CL (10/90) at PVC value of 45, with the latex of 120 nm particle size at 60 wt% solids content.

As it can be observed in Figure 3.21, a whiter film was obtained when adding 10% of PCC to GCC-CL. The resulting film was characterized in terms of scrub resistance, gloss and water uptake and compared with the results obtained previously using only CL pigment (Table 3.6 and Figure 3.22).

Table 3.6 Scrub and gloss at 85° using CL pigment and using the mixture of PCC + CL (10/90), at PVC 45, with 120 nm particle size latex.

	CL	PCC + CL
Scrub	1250	+2000
Gloss	60±2	50±2

Adding 10% of PCC the scrub resistance of the film improved significantly from 1250 cycles before breaking for 100% CL, to more than 2000 cycles for 10/90 (PCC/CL). The gloss value decreased slightly. This can be attributed to an irregular particle packing in the coating, which leads the incident light deflected in different directions. This effect was already seen by Nitin Kumar and co-worker with a scalenohedral PCC³³.

The water absorption was also measured and the obtained evolution profile along a week is represented in Figure 3.21.

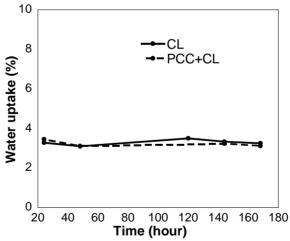


Figure 3.21. Water uptake of paint-like films using CL pigment and using the mixture of PCC + CL (10/90), at PVC 45, with 120 nm particle size latex.

Regardless the addition of 10% of PCC pigment, the water uptake evolution was similar (Figure 3.21). Therefore, adding only 10% of PCC scrub properties are improved significantly, however it must be mentioned that PCC is much more expensive than CL, as seen in Chapter 1. Moreover, the CPVC for PCC pigment is achieved at lower PVC values, which means that lower amount of this pigment can be added to the system.

3CL at PVC 45, 50 and 55.

Finally, blends were also prepared with calcium carbonate GCC-3CL sample. The CPVC for this pigment is 54, therefore blends were prepared at the PVC values of 45, 50 and 55 and compared with the blends prepared with CL at PVC of 45 and 50, using the latex of 120 nm particle size. For this pigment the mill base was prepared with 0.4% of NaPA based on the weight of 3CL and increasing the solids content in water to 83 (as explained before, it is possible to increase the solids content due to the addition of the dispersant agent). The gloss values are presented in Table 3.7, the AFM images in Figure 3.23 and the mechanical properties with the water uptake measurements in Figure 3.24.

Table 3.7. Scrub resistance and gloss for blends prepared with CL and 3CL pigment.

_	CL		3CL		
	PVC 45	PVC 50	PVC 45	PVC 50	PVC 55
Gloss at 85 ⁰	60	57	5	5	3.7

The gloss of the films was very different from one filler to the other. Blends prepared with the 3CL sample showed lower gloss values than blends prepared with GCC CL. This fact is attributed to a narrow particle size distribution of CL sample which increase the gloss³⁴.

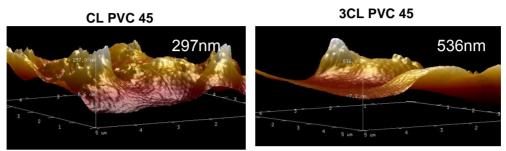


Figure 3.22. AFM images of the film surface for CL and 3CL at PVC value of 45.

By AFM images it can be appreciated that the average height of the film roughness when using CL was 297 nm, whereas when using 3CL it was 536 nm (Figure 3.22). As it was seen in Figure 3.2, the particle size of GCC 3CL sample is higher than the particle size of GCC CL, and therefore films obtained from GCC 3CL are rougher. The higher roughness of GCC 3CL also explains the lower gloss achieved with this pigment sample 35.

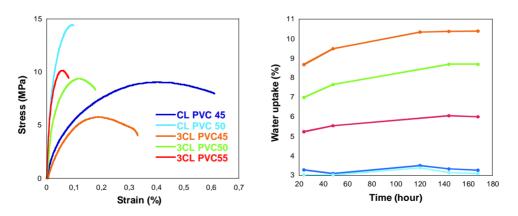


Figure 3.23. Mechanical properties and water uptake for CL and 3CL blends.

Analysing the mechanical properties (Figure 3.23), at the PVC value of 45 using CL the elongation at break was greater than using 3CL, this fact can be attributed to the smaller particle size of CL comparing with 3CL³⁶. However, at the PVC value of 50 the result is the opposite. This is because the CPVC for CL is reached at the PVC value of 45 while for 3CL coherent films can be obtained above PVC 45. Regarding the water uptake, the absorption was significantly higher for blends prepared with 3CL pigment, as it can be observed in Figure 3.23. This means that the packing of CL particles create a network, in which the water finds more difficulty in passing.

Although better final properties can be achieved with CL, 3CL allows preparing films at higher PVC values without the cracking of the films. Therefore, and for applications where high quality paints are not necessary, 3CL filler can be a better choice than CL as higher filler concentrations can be added in the waterborne formulation, reducing the price of final paints.

3.4 Conclusions

In this study, the interaction of acrylic latex and GCC CL pigment particles was studied as a function of the nature of the binder, in terms of different particle sizes, the functional monomer and surface coverage. In order to isolate as much as possible the study of such interaction, the amount of additives added to the waterborne paint were reduced to just the dispersing agent to obtain an applicable paint. Therefore, only sodium polyacrylate was used as dispersing agent in its optimal amount. Paints at different PVC values from 30 to 50 with CaCO₃-CL sample were produced and the effect of the different binder types was analyzed on the final film properties (gloss, water uptake and mechanical properties).

It was found that films prepared with the acrylic acid monomer showed slightly better properties than paints prepared without the functional monomer. Moreover, better properties were achieved when paint-like blends were prepared with the latex synthesized under acidic conditions in comparison with paint-like blends prepared with the latex synthesizes at basic conditions. This is attributed to a higher incorporation of the carboxylic acid functional group in the surface of the polymer latex when the latex was synthesized at acidic pH.

Regarding the latex particle size, better final properties were obtained when using the latex with the smallest particle size, which proves a better interaction between the acrylic latex of smallest particle size and calcium carbonate particles. As a result, films with higher PVC values without complete loosing of the properties could be obtained with the latex with acrylic acid and smaller particle size. In fact, such film presented a water uptake value around 3% after one week of immersion in water, a gloss of 57 at 85°, and cohesive nature at PVC 50, or 71% weight percent of CaCO₃.

Blends were also prepared with a different GCC of higher particle size (GCC 3CL) and with a PCC sample, in order to study the differences between these. On the one hand, it was observed that lower CPVC is achieved when using PCC, however with the addition of only 10% of PCC, films produced better scrub resistance and whiteness (as observed in the final films), of course at the expense of the price, as PCC is a functional pigment. On the other hand, the final properties obtained with 3CL are worse than when employing CL, but this filler allows the production of higher PVC values, which gives waterborne paints with lower film prices.

3.5 References

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Chapter 4. Industrial like waterborne paint formulation

4.1 Introduction

The final properties of a coating are affected by a wide range of components. Among them, the binder, the filler and the thickeners to name but a few. All these components can be varied, and moreover they can be added at different amounts in order to obtain the desirable final properties for a certain application¹. Therefore, for a specific final application there are a considerable high amount of variables and alternatives that make the number of possible combinations a huge work to carry out their characterization in the laboratory by conventional methods. To face this problem, the design of experiments (DOE) is crucial, as it has the capability of investigating the effect of components at different levels with fewer experiments than in a conventional way^{2,3,4}. Furthermore, in the recent years researchers have started to use high throughput experiments (HTE) in the field of polymers and coating formulation^{5,6,7,8}, whose aim is to simultaneously produce the maximum possible number of paints as quickly and as economically as possible⁹. This is possible by automated laboratory robots and fast intelligent data processing.

In order to better understand the role of each component in coating applications, the combination of both the design of experiment (DOE) with High-Throughput Experimentation (HTE) has been demonstrated to be successful in both academic and industrial research^{10,11,12,13}. For instance, in 2015, Bohórquez et al. showed the interest of combination of both techniques to

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understand the interaction of a complex polymer colloid in pigmented paints¹⁴. And in 2016, Minari et al. showed the successful optimization of waterborne coatings based on bio-based hybrid films containing casein¹⁵. In the same year, The Dow Chemical company published an article where they explained the use of both techniques for developing new industrial coating products¹⁶.

The steps that must be carried out to combine both the design of experiments with the highthroughput experiments are shown in Figure 4.1.



Figure 4.1. Steps of the combination of DOE and HTE.

In this Chapter, the combination of DOE with HTE has been carried, with the aim to study the interaction between different acrylic latex with calcium carbonate fillers in fully formulated waterborne paints. To do so, acrylic latexes have been synthesized with different functional monomers and different surfactant types and two different experimental designs have been conducted. The first one, to analyse the effect of latexes synthesised with different functional monomers on the final paint properties (in this case, paints were duplicated with the addition of TiO₂ (50 g/L) and the second one to analyse the effect of latexes synthesized with different surfactants on the final paint properties.

Apart from this, in this Chapter the effect of the particles shape on packing efficiency will be presented. To study this, polystyrene beads with the same average particle size of one of the

CaCO₃ used in this work were synthesized. Paints were prepared replacing the irregular CaCO₃ by regular polystyrene beads and the effect was studied by analysing the final paints properties.

4.2 Experimental part

4.2.1 Materials

Methyl methacrylate (MMA, Quimidroga), butyl acrylate (BA, Quimidroga), acrylic acid (AA, Fluka), methacrylic acid (MAA, Quimidroga) and acrylamide (Aldrich) were used as supplied. Sodium persulfate (NaPS, Sigma-Aldrich) was used as thermal initiator. The surfactants used were Dowfax 2A1 (Dow Chemical, 45%), Laternul PD-104 (Kao Group, 20%) and Sipomer Pam-200 (Solvay). The structure and the molecular weight of the surfactants employed can be observed in Table 4.1. Deionized water was used throughout the work. To increase the pH of the latexes a 25% solution of ammonia (Fluka) was used. Hydrochloric acid (HCI, 25 % solution) and sodium hydroxide (NaOH, Sigma-Aldrich) were used for the titration of the latexes.

Table 4.1. Structure and molecular weight of the different surfactants used in this work.

Surfactant	Structure	Molecular weight (g/mol)
Dowfax 2A1	SO ₃ Na SO ₃ Na O R	575
Sipomer Pam-200	HO OH	500
Latemul PD-104	H ₂ C=C-CH ₂ CH ₂ O-CH ₂ CH ₂ O-CH ₂ CH ₂ CH ₂ O-S-C-CH ₃ O-S-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-	1674

Information taken from¹⁷

Three CaCO $_3$ of different particle sizes were used, namely 0.8 µm (84 % < 2 µm), 5 µm (27% < 2 µm) and 15 µm (27% < 10 µm) supplied by Omya. TiO $_2$ was used also as pigment and was supplied by Cristal. The additives used were the following: a biocide, antifoam, dispersant, thickener, surfactant and a coalescing aid (confidential information).

4.2.2 Synthesis of high solids content latexes

High solids content Poly(methyl methacrylate-co-butyl acrylate) P(MMA/BA) (50/50) latexes were synthesized by seeded semi-batch emulsion polymerization, in order to afterwards prepare the waterborne paints. The procedure followed was the same as the one explained in

Chapter 2, and latexes were prepared in this way with different functional monomers and different surfactant types.

- Four latexes were synthesized at acidic pH with different functional monomers. All functional monomers were added in 1 wbm% and Dowfax 2A1 0.8 wbm% was used as surfactant. The monomers employed were AA, MAA, Acrylamide, and one latex synthesized with both AA and Acrylamide adding 1wbm% of each one in the synthesis. The formulation used in these reactions is the same as the one given in Table 4.2, changing the functional monomer for each latex.
- P(MMA/BA/AA) (49.5/49.5/1) latexes were synthesized with different surfactant types at the same concentration in water (6.84 mmol/L). The surfactants employed were Dowfax 2A1, Laternul PD-104 and Sipomer Pam-200. Synthesis were carried out under basic conditions for Laternul and Dowfax surfactant and at neutral conditions for Sipomer. The formulation used is the same as the one given in Table 4.2 changing only the type and final amount of surfactant.

Table 4.2. General formulation of the latexes with dp=270 nm.

Compound	Initial charge (g)	Stream 1 (g)
Seed 1	31.125	-
MMA	1.12	118.8
ВА	1.02	118.8
Functional monomer	-	2.4
Water	97.67	46.5
Na ₂ S ₂ O ₈		-
Dowfax 2A1	-	4.2

Feeding time: 240 min, SC 60 %, 0.5 wbm% NaPS initiator shot

4.2.3 Use of DOE with HTE to prepare waterborne paints

In order to prepare waterborne paints a design of experiments has been carried out and according to that design, waterborne paints were prepared with the help of high throughput technology.

The design of experiments is the plan used to collect significant data. In this step the variables, the levels and the responses have to be defined. The variables are the factor of interest and each factor contains two or more levels. Levels can be numerical (can be expressed as a number or continuous scale) or categorical (names, words, numbers on a non-continuous scale). For example, a component concentration is defined as numerical level, whereas a type of additive as categorical level. The response is a measured property believed to be impacted by the experimental factor (variables and levels). In Table 4.3, it can be observed the scheme of the DOE used in this study:

Table 4.3. Specifications of the DOE used.

VARIABLES	LEVELS	RESPONSES
PVC	From 60 to 75	
Binder	Different acrylic latexes	-Gloss, average scattered, whiteness,
Filler	Three different calcium carbonate of different particle sizes	spreading rate, scrub resistance.
TiO ₂	With or without	

Paints were prepared at the PVC range from 60 to 75, and with three calcium carbonate of different particle sizes (0.8 μ m, 5 μ m and 15 μ m). Two different designs were carried out, the

first one with four different latexes with different functional monomers (AA, MAA, AA/Acrylamide, and Acrylamide) and the second one with three latexes with different surfactant types (Dowfax 2A1, Laternul PD-104 and Sipomer Pam-200). The formulation of the waterborne paints was carried out on the base of a quadratic experimental design, because each factor interact with all other in contributing to the response. The design of experiments can be represented as follows, for each latex (Figure 4.2):

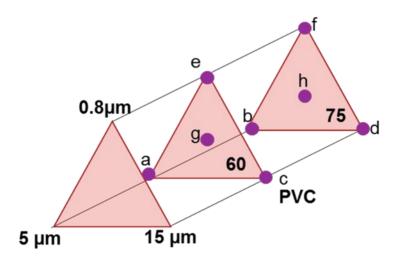


Figure 4.2. Design of the experimental plan for the system employed.

The experimental design will cover all the area shown in Figure 4.2, but the purple points are the key points, where:

- a) Is the experiment using the 5 μm CaCO₃ at PVC 60.
- b) Is the experiment using the 5 µm CaCO₃ at PVC 75.
- c) Is the experiment using the 15 μm CaCO₃ at PVC 60.

- d) Is the experiment using the 15 μm CaCO₃ at PVC 75.
- e) Is the experiment using the 0.8 µm CaCO₃ at PVC 60.
- f) Is the experiment using the 0.8 μm CaCO₃ at PVC 75.
- g) Is the experiment using a mixture of the three different CaCO₃ at PVC 60.
- h) Is the experiment using a mixture of the three different CaCO₃ at PVC 75.

When using latexes with different functional monomers paints were duplicated adding titanium dioxide (50 g/L) and ethoxylated hydroxyethylcellulose (EHEC) was used as thickener, whereas, when using latexes with different surfactants, paints were prepared directly with the addition of titanium dioxide (50 g/L) and hydrophobically modified alkali soluble emulsion polymer (HASE) thickener was employed. The slurries, which is the pigment dispersed in water, with the corresponding additives (the exact amount is confidential information) were prepared at a solids content of around 75. Paints were then prepared with the formulation obtained from the DOE at a solids content of 35% in an automatic robot (high throughput experiments, confidential information). First the remaining additives and the slurry were added and mixed at 2000 rpm for 100 s. Afterwards, the latexes were added and everything was mixed at 1600 rpm for 120 s. According to the DOE experiments, in order to cover all the area shown in Figure 4.2 and to obtain reliable data (because some of the paints must be repeated to prove reproducibility) a total of 150 paints were prepared in the first campaign and 74 paints in the second one.

After the preparation of paints, the paints films were characterized by HTE. The obtained results from the HTE are fitted into a mathematical model, and this allows the description of the interaction between the formulation variables and the properties measured.

4.2.4 Waterborne paints with PS beads

The objective of this part was to study the effect on packing of irregular shaped 0.8 μ m CaCO₃ vs spherical PS beads. For that purpose, PS beads with a particle size of 0.8 μ m were synthesized by emulsion polymerization. These hard irregular CaCO₃ or spherical PS were added as fillers to waterborne paints, either alone or combined with 5 μ m CaCO₃ particles.

In order to study the packing effect of the fillers, four paints were prepared at the PVC value of 60 with a solids content of 35% and adding 50 g/L of TiO₂. For each of the paints the following fillers were used:

- 1. 0.8 μm CaCO₃
- 2. 0.8 µm PS beads
- 3. 0.8 / 5 μm CaCO₃ blend (50/50)
- 4. 0.8 μm PS / 5 μm CaCO₃ blend (50/50)

For the preparation of these paints, the slurry was prepared with the corresponding additives (the exact amount is confidential information), and then the latex at pH 9 was blended with the slurry. It has to be pointed out that as the coalescing agent can influence the deformation of PS beads particles, paints were prepared without using any coalescence agent. In order to ensure the complete coalescence of the latex particles, a lower glass transition temperature (0 °C) acrylic latex was used for the preparation of these paints (confidential information).

4.2.5 Characterization

Conversion and solids content of the final latexes were gravimetrically determined. The average particle size was measured by Dynamic Light Scattering Spectroscopy, DLS (Malvern®

Zetasier Nano) and the glass transition temperature by differential scanning calorimetry (DSC) in a Q200 (TA instrument). The microstructure of the final latex was determined by measuring the gel fraction in tetrahydrofuran (THF) by Soxhlet extraction. The carboxylic acid groups present in the surface of the latex particles was calculated by titration after dialyzing the latexes. The details of the characterization procedures and methods are given in Appendix I.

Scanning Electron Microscopy (Jeol FESEM) was used to analyze the morphology of CaCO₃ samples and Environmental Scanning Electron Microscopy (eSEM-FEI QuantaTM 250) to analyze the final paints. Two different techniques were used to analyze the roughness of the paint surfaces; Atomic Force Microscopy (AFM, Veeco Nanoscope V multimode) and profilometer (nanofocus). The final paint properties (gloss, average scattered, spreading rate at 98%, whiteness and scrub resistance after 200 cycles) were characterized by the global test analyzer of AkzoNobel. The information about these techniques is described in Appendix III.

4.3 Results and discussion

4.3.1 High solids content latexes

Characterization of final latexes with different functional monomers.

Table 4.4 presents the particle size, solids content, Tg, amount of carboxylic groups on the surface of the particles based on the total carboxylic groups and the gel content for the latexes synthesized with different functional monomers.

Table 4.4. Characterization of final latexes with different functional monomers.

	dp (nm) (DLS)	SC (%)	Tg ºC (DSC)	Carboxylic acid groups in the surface of the particles (%)	Gel (%)
MMA/BA/AA	275	60	16	20	50
MMA/BA/MAA	271	60	17	32	53
MMA/BA/Acrylamide	271	61	15	-	28
MMA/BA/AA/Acrylamide	282	60	16	18	60

As it can be observed in Table 4.4, similar particle sizes and solids content were obtained independently of the functional monomer used.

Since the polymerizations were carried out under starved conditions, high instantaneous conversion along the polymerization process and final full conversions were achieved. Moreover, the copolymer compositions were very similar for all the latexes and hence the expected glass transition temperature (15°C according to Fox equation) was obtained for all the cases.

In order to analyze the amount of carboxylic acid groups on the particles surface, their titration with NaOH was carried out as explained in Appendix I. The hydrophobicity of the functional monomers plays an important role during the emulsion polymerization. The higher the hydrophobicity, as in this case for MAA, the less oligoradicals are going to be formed in the aqueous phase and more functional groups are going to be incorporated on the surface of the latex particles. This is why the latex with MAA functional monomer presents a higher fraction of carboxylic acid groups on the surface of the particles.

The polymer microstructure of the final latexes was analysed in terms of gel content (or THF insoluble part). The obtained final gel content is quite high for all cases, and the lowest gel

content was achieved when employing acrylamide functional monomer. A possible explanation is that when adding acrylamide the pH of the medium increases. When the polymerization is conducted at more basic conditions higher amount of water soluble species are formed, which implies higher termination of oligoradicals in the aqueous phase and hence a reduction in the average number of radicals per particles (ñ). In emulsion polymerization of acrylates, gel is formed by intermolecular chain transfer to polymer followed by termination by combination. Therefore, lower values of ñ, led to a reduction of the rate of bimolecular termination between large molecules in the polymer particles, which reduced the gel formation.

Characterization of MMA/BA/AA final latexes synthesized with different surfactants (6.84 mmol/L).

To analyse the effect of the surfactant employed in the production of waterborne paints, acrylic latexes were synthesized with one conventional surfactant and with two different polymerizable surfactants. The conventional surfactant was the anionic surfactant Dowfax 2A1, which contains two ionic charges per molecules. The polymerizable surfactants employed were Sipomer Pam-200 and Latemul PD-104, the first one with a methacylate double bond and a phosphate group and the second one with a vinyl double bond and a sulphate anionic group (see Table 4.1).

The synthesis were carried out at basic conditions except when using Sipomer Pam-200. For Sipomer Pam-200 pH conditions were kept neutral, because at very acidic or basic conditions the hydrolysis of the ester linkage and the phosphate group might occur¹⁸. The final latexes characteristics regarding particle size, solids content and gel content are shown in Table 4.5.

Table 4.5. Characterization of the latexes with different surfactants.

	dp (nm) (DLS)	SC (%)	Gel (%)
MMA/BA/AA (Dowfax 2A1)	272	63	53
MMA/BA/AA (Sipomer Pam-200)	277	62	51
MMA/BA/AA (Latemul PD-104)	249	62	63

As it can be observed in Table 4.5, no big differences were observed with latexes synthesized with Dowfax 2A1 and Sipomer Pam-200 surfactants; however, lower particle sizes and higher gel content were obtained when using Laternul as surfactant. Moreover, all latexes were successfully synthesized at high solids content.

4.3.2 CaCO₃ samples

The morphology of the different CaCO₃ filler samples and TiO₂ pigment used in this work was characterized by SEM (Figure 4.3).

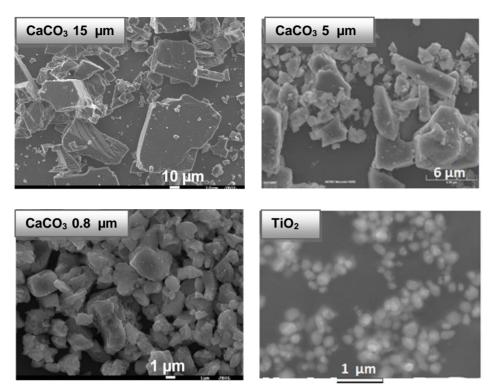


Figure 4.3. SEM images of the morphology of the different CaCO₃ and TiO₂ used.

TiO₂ presents much lower particles sizes than the calcium carbonate samples, being the average particle size below 500 nm. On the other hand the SEM images of the three different calcium carbonates are shown, which apparently seem to be in agreement with the particle size provided by the supplier: 15 μ m (27% < 10 μ m), 5 μ m (27% < 2 μ m) and 0.8 μ m (84 % < 2 μ m).

4.3.3 Waterborne paints

4.3.3.1 Waterborne paints prepared with latexes synthesized with different functional monomers

> Final properties obtained from HTE

As it was mentioned in the experimental part, for the preparation of the paints first of all a design of experiments was done. Taking into account this design, waterborne paints were prepared with the help of the paint robots at AkzoNobel and the properties of waterborne paints films were determined using AkzoNobel global test methods (HTE). Finally, the statistical analysis of the obtained paint properties was carried out. For this, paint properties were modelled by using a linear-linear model. Thanks to the model, the region of optimum paint formula can be determined. The model analysis is displayed in Table 4.6, where the R-squared (R²) for each response is shown. R² values are derived from the difference between the predicted result of an experiment (based on a model) and the actual result. In general, the higher the R², the better the model fits the data.

Table 4.6. R^2 values for the properties of the paints prepared with latexes synthesized with different functional monomers (without and with TiO_2).

	R ²		
RESPONSE	Paints with latexes synthesized with different functional monomer	Paints with latexes synthesized with different functional monomer (with TiO ₂)	
Gloss 85 ⁰	0.76	0.79	
Average Scattered	0.96	0.99	
SR (98%)	-	-	
Whiteness	0.85	0.78	
Scrub	0.89	0.89	

As it can be seen in Table 4.6 all responses are above or close to 0.77, which is a enough value in order to prove good alignment and model fit.

Therefore, by the combination of DOE and HTE and afterwards the statistical analysis of the data, it would be possible to determine which mixture from 0-100% of each calcium carbonate and which acrylic latex gives the best paint performance.

Gloss

Specular gloss of waterborne films were measured at 85 $^{\rm 0}$ geometry and the obtained results are presented in Figure 4.4, for paints prepared with latexes synthesized with different functional monomers.

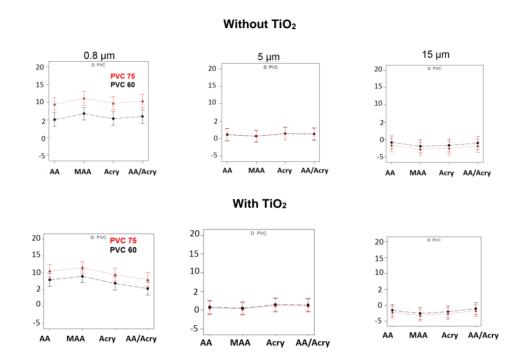


Figure 4.4. Gloss value for paints prepared with latex synthesized with different functional monomers, for two different PVC, different CaCO₃ particle sizes, without and with TiO₂.

In Figure 4.4 it can be observed that the gloss value was lower as the particle size of the CaCO₃ filler increased. Therefore, higher gloss values were achieved when using the calcium carbonate of the lowest particle size¹⁹. However, no big differences were observed with the addition of 50 g/L TiO₂.

It can be also observed that when the particle size of the $CaCO_3$ filler is $0.8~\mu m$, the gloss was increased as the PVC increased; this was surprising since increasing the PVC the amount

of calcium carbonate is increased and the gloss value should decrease, as it has been seen in Chapter 3²⁰. The only possible explanation for this fact could be the presence of agglomerates in some of the final waterborne paints at PVC 75 with 0.8 µm CaCO₃, which could lead to their faster sedimentation, leaving a more glossy just polymeric film on the top of the film.

Not big differences were observed from one functional monomer to another when employing the calcium carbonate of 5 µm and 15 µm particle sizes. However, a slight tendency towards lower gloss values when employing the acrylamide can be observed when paints were prepared with the calcium carbonate of the lowest size and with TiO₂. Differences more remarkable were expected to be seen between the different functional monomers employed, however this was not the case. This can indicate that the use of all kind of additives is hindering to see the effect of the different functional monomer. The dispersing agent (NaPA) used is well known to have high affinity with the surface of CaCO₃ particles²¹, therefore this component could have hindered the effect of the different functional monomers.

Average scattered

The average scattered of the paints films is an indicator of the opacity. The opacity quantifies the ability of the paint to obscure the substrate. In Figure 4.5, the average scattered value can be observed for paints prepared with latexes synthesized with different functional monomers.

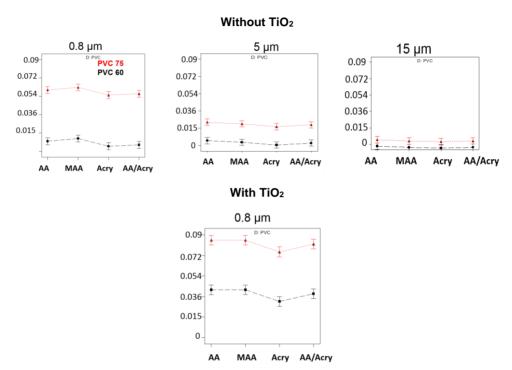


Figure 4.5. Average scattered for paints films prepared with latex synthesized with different functional monomers.

As it can be in Figure 4.5, paints films were more opaque when using the calcium carbonate of the smallest particle size and at higher PVC values (increasing the amount of filler in the system). Moreover, when employing the CaCO₃ of 0.8 µm it can be observed that those paints prepared with the acrylamide functional monomer presented slightly lower opacity values. This suggests a weaker interaction of the calcium carbonate particles with polymer particles containing the acrylamide functional monomer.

With the addition of TiO₂ (50 g/L) the final paints films were more opaque, as the scattered value increased significantly. TiO₂ is a functional pigment used to provide high opacity to the final paints films²², and this effect was noticeable, as the average scattered is more or the less the double for both PVC values with the addition of this pigment.

Whiteness

The whiteness of the paint is the colour property. The whiteness values for paints obtained from latexes prepared employing different functional monomers with and without the TiO_2 pigment can be observed in Figure 4.6,

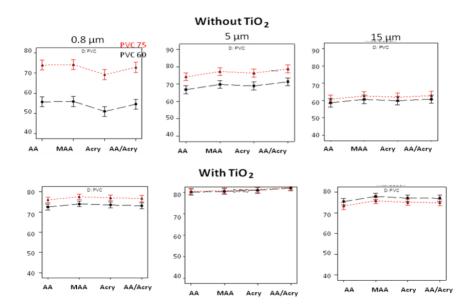


Figure 4.6. Whiteness values for paints films prepared with latexes synthesized with different functional monomers.

As expected the whiteness value is higher when using the calcium carbonate of the smallest particle size, when increasing the PVC value and for paints prepared with TiO₂.

The only little differences can be observed in the absence of TiO₂ and when employing the smallest particle size calcium carbonate, where the waterborne paints prepared with the acrylamide functional monomer have the lowest whiteness value. In the rest of the cases, no differences were observed from one functional monomer to another, this might suggest that the addition of NaPA makes a screen on the effect of different functional monomers of the latexes.

Weight lost after 200 scrub cycles

Wet scrub resistance simulates cleaning a wall to try to remove a mark. After the paints panels were subjected to 200 scrub cycles the amount of paint lost was measured by weight. Therefore, higher values means that more material is lost and therefore lower resistance to scrub. In Figure 4.7 it can be observed the scrub for paint films prepared with latexes containing different functional monomers.

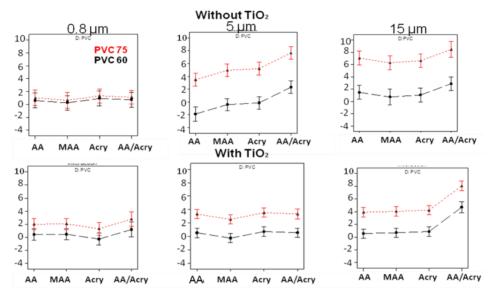


Figure 4.7. Weight lost after 200 cycles for paints films prepared with latex synthesized with different functional monomers.

In Figure 4.7, it can be observed that worse scrub resistance is obtained when preparing paints with higher particle size calcium carbonate and at higher PVC values. In general, worse scrub resistance is obtained for paints prepared using the latex prepared with AA/Acrylamide functional monomers. In this case, the latex contains two functional monomers which are very hydrophilic and will tend to copolymerize to give a significant level of water soluble polymers. In a neutralized paint, this will be totally water soluble; therefore when these panels are scrubbed this part will be lost.

> Other characterization apart from HTE

AFM

The roughness of the surface of the paints was analysed by AFM images. AFM peak force tapping mode was used due to the great differences in the viscoelastic properties of calcium carbonate particles and the polymer in the film. The roughness of the paint surface is very important because this can give an idea about the dispersion of CaCO₃ particles in the film. This can affect coatings properties such as gloss. The roughness profiles of the films were extracted from the height images of the AFM micrographs of the paints and the calculated average roughness are shown in Table 4.7.

Table 4.7. Roughness value for the surface of the paints prepared with latexes synthesized with different functional monomers, at the PVC value of 60 and 0.8 µm CaCO₃.

Rrms (nm)	Without TiO ₂	With TiO ₂
AA	77	93
MAA	50	
Acrylamide	206	197
AA/Acrylamide	100	107

As it can be observed in Table 4.7, the roughness of the surface of the films depends on the functional monomer employed during the synthesis of the latex. Those paints prepared using the latex containing the acrylamide functional monomer were rougher, whereas, paints prepared using the latex synthesized with MAA smoother. It has to be mentioned that not big differences were observed in the roughness values with the addition of 50g/L of TiO₂ to the paint formulation. In Table 4.8, the obtained AFM images for paints films surface can be observed.

Table 4.8. AFM images for paints prepared with latex synthesized with different functional monomers, at the PVC value of 60, and using CaCO₃ of 0.8 µm particle size.

Functional	Paint without TiO ₂	Paint with TiO ₂
monomer		
AA	0.0 Peak Force Error 5.0 μm	0.0 Peak Force Error 5.0 μm
MAA	0.0 Peak Force Error 5.0 µm	
Acrylamide	0.0 Peak Force Error 5.0 μm	0.0 Peak Force Error 5.0 μm
AA/Acrylamide	0.0 Peak Force Error 5.0 μm	0.0 Peak Force Error 5.0 μm

Profilometer

In order to measure the roughness of the surface of the paints, apart from AFM, profilometer measurements were conducted. The equipment gives directly the root mean square height (Sq) values, which value quantify the roughness of each waterborne paint surface. In this technique, the equipment sends light to an area of the surface, and the sensor detects heightened light intensity; finally, the spectrometer represents the heights of the surface through a 3D graph of colour differences. Profilometer measurements were conducted for paints prepared with latexes synthesized with different functional monomers, at two different PVC of 60 and 75, for 0.8 µm CaCO₃. As an example, some of the graphs are depicted in Figure 4.8 and the obtained Sq values in Table 4.9.

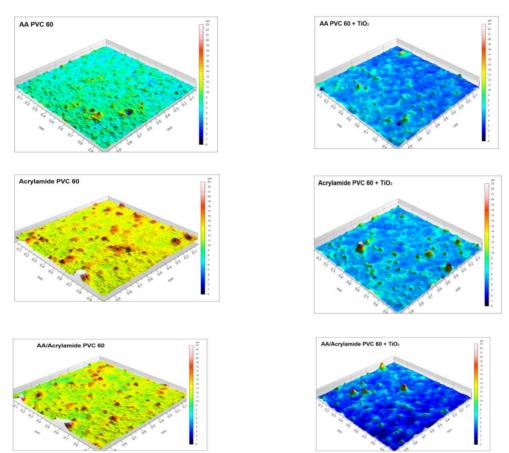


Figure 4.8. Profilometer 3D graphs for paints prepared with latexes synthesized with different functional monomers, at the PVC values of 60 for 0.8 µm CaCO₃

Table 4.9 Sq (μ m) values for paints prepared with latexes synthesized with different functional monomer, at the PVC values of 60 and 75 for 0.8 μ m CaCO $_3$.

	Sq (µm)	
	PVC 60	PVC 75
AA without TiO ₂	1	1.4
AA with TiO₂	1.2	1.5
MAA without TiO ₂	1	1
MA with TiO ₂	-	1.2
Acrylamide without TiO ₂	1.8	2.2
Acrylamide with TiO₂	1.8	2.4
AA/Acrylamide without TiO ₂	1.7	2
AA/Acrylamide with TiO ₂	1.9	1.9

Paying attention to Table 4.9 two different conclusions can be withdrawn. On the one hand, increasing the PVC (adding more filler particles to the paint formulation), the roughness of the paint surfaces increases. On the other hand, depending on the functional monomer employed the roughness values are different. Paint films prepared with the latex synthesized with the acrylamide functional monomer were rougher. On the contrary, those paints prepared with the latex synthesized with AA or MAA functional monomer were smoother. This tendency was the same as the one observed by AFM, confirming that AA and MAA functional monomers interact better with CaCO₃ filler particles than Acrylamide.

Regarding the differences between the different functional monomer employed, results reveals that when employing the acrylamide functional monomer the final paint properties are worse. However, no big differences were found between AA and MAA functional monomers. The dispersing agent (NaPA) might had hindered to see this effect.

Final paints films appearance

The final paint films appearance when using MAA/BA/AA latex with Dowfax 2A1 0.8 wbm% at the PVC value of 60 is shown in Figure 4.9. Photos are shown for paints prepared with the different calcium carbonate particle sizes (0.8 μm, 5 μm and 15 μm) and with the blend of the three calcium carbonates, without TiO₂ when using EHEC thickener.

Without TiO₂

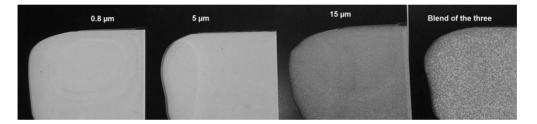


Figure 4.9. Paints at the PVC value of 60, when using MMA/BA/AA latex and EHEC thickener.

As it can be observed in Figure 4.9, white spots were observed in some of the final paints films. This can be very clearly seen when the paint was prepared with the blend of the three different calcium carbonates. Therefore, a problem of stability was occurring, as a phase separation between the latex and the filler particles was observed.

Two types of flocculation are well reported in the literature: bridging^{23,24} and depletion flocculation^{25,26}. Bridging flocculation occurs when associative polymer macromolecules connect pigment particles causing phase separation, whereas, in depletion flocculation the pigment particles are phase separated due to the exclusion from the polymer solution phase (see Figure

4.9)²⁷. More precisely, the depletion flocculation occurs when in a fully formulated paint dispersion, a water soluble polymer molecule finds itself restricted due to the interface with surrounding species. This restriction reduces the entropy, and therefore they tend to migrate out of the particles region where they can configure at higher entropy. Due to this fact, a concentration gradient is formed, which causes an osmotic pressure difference that forces the colloidal particles together.

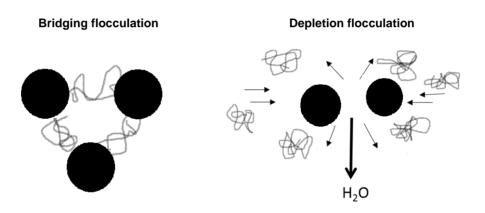


Figure 4.10. Illustration of the two types of flocculation: bridging and depletion

In practice, depletion flocculation is the most commonly seen effect because the bridging usually occurs at additive levels much lower than the ones in coating formulations. The depletion flocculation occurs when: 1) non-adsorbing polymer is added, 2) adsorbing polymer is added well above the adsorption saturation point, 3) the added polymer adsorb weakly onto particles^{28,29,30,29}.

In order to avoid the depletion flocculation issue, paints were prepared changing the nature of the thickener from a non associative thickener (EHEC) to an associative one (HASE). The visual appearance of the obtained paints are presented in Figure 4.11.



Figure 4.11. Paints prepared with MAA/BA/AA latex at the PVC value of 60, with the blend of the three calcium carbonates and with TiO₂. In the left using EHEC thickener and in the right HASE thickener.

When paints were prepared with the non-absorbed polymer (EHEC), the paint can was not homogenous. Depletion flocculation can give rise to the appearance of some agglomerates (as it can be observed in Figure 4.11), this phenomenon is defined as syneresis³¹. However, when paints were prepared with the absorbed polymer (HASE), this problem was solved. Edward Kostansek and co workers reported in some works the use of phase-diagrams to visualize the regions of latex dispersion and flocculation as a function of the amount of surfactants and thickeners used, for both non-adsorbed and absorbed polymers³². From their research they found that when using non-associative thickeners (the latexes they used had the same

compositions that the ones in this Chapter), depletion flocculation happened in all region, except when the lowest concentration of thickener was employed. However, this was not the case for associative thickener, where they found more regions were the latex was well dispersed^{33,23}.

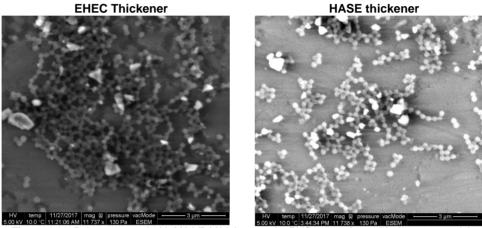


Figure 4.12. Paints prepared with MAA/BA/AA latex at the PVC value of 60, with the 0.8 μ m calcium carbonate and with TiO₂. In the right using EHEC thickener and in the left HASE thickener.

As it can be observed by the ESEM images (Figure 4.12), when paints were prepared with the associative thickeners particles are better dispersed. Therefore, and with the aim to avoid depletion flocculation, preparation of paints with latexes synthesized with different surfactants was performed using HASE thickener instead of EHEC thickener.

4.3.3.2 Waterborne paints prepared with latexes synthesized with different surfactants

> Final properties obtained from HTE

Gloss

In Figure 4.13, it can observed that gloss values for paints prepared with latexes synthesized with different surfactants.

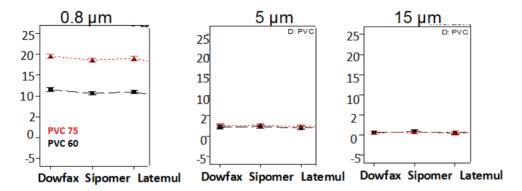


Figure 4.13. Gloss value for paints prepared with latex synthesized with different surfactant, for two different PVC and different CaCO₃ particle sizes.

As it can be observed in Figure 4.13, no differences were observed from one paint to another. Therefore, independently of the surfactant type used in the synthesis of the latex, the final gloss value of the paints was the same, which results were surprising. As the dispersing agent is placed strongly on the surface of CaCO₃ particles in order to prevent their agglomerations^{34,35}, it was thought that the use of this component was hindering the effect of

different surfactants. In the same way that it was previously observed with latexes synthesized with different functional monomers.

Spreading rate at 98%

The spreading rate is the area covered with a litre of paint, therefore, higher values means that more material can be covered with the same amount of paint. The spreading rate at 98% contrast ratio was calculated for paints prepared with the latexes synthesized with different types of surfactants in the presence of the TiO₂ and it is shown in Figure 4.14.

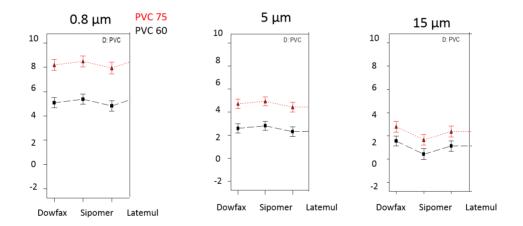


Figure 4.14. Spreading rate at 98% for paints prepared with latex synthesized with different surfactants.

In Figure 4.14 it can be appreciated that the spreading rate at 98% is higher when using the lowest particle size calcium carbonate and at high PVC values. Moreover, no big differences can

be observed from one surfactant to another. Which results reveals ones again that the use of NaPA is not allowing to see the differences between the different surfactants employed.

Whiteness

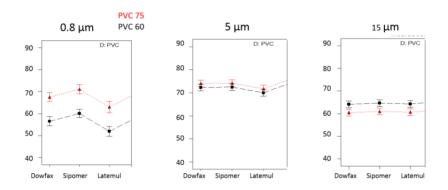


Figure 4.15. Whiteness values for paints films prepared with latex synthesized with different surfactants.

As it can be seen in Figure 4.15, the biggest difference between the different surfactants employed comes for Laternul PD-104, when the smallest particle size of calcium carbonate is used. In the other cases no differences can be observed, due to the use of NaPA which hinders the effect of the different surfactant.

· Weight lost after 200 scrub cycles

In Figure 4.16 the scrub resistance for paints prepared using latexes synthesized with different surfactants is depicted.

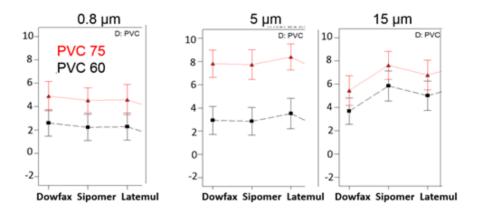


Figure 4.16. Weight lost after 200 scrub cycles for paints films prepared with latex synthesized with different surfactants.

When preparing paints with the highest particle size CaCO₃, the scrub resistance was worse for those paints prepared with the latex synthesized with Laternul PD-104 and Sipomer Pam-200 surfmers.

Other properties apart from HTE

Profilometer

Profilometer measurements were also performed for paints prepared with latexes synthesized with different surfactants at the PVC value of 75 for the different calcium carbonate particle sizes. The obtained roughness (sq) values are depicted in Figure 4.17.

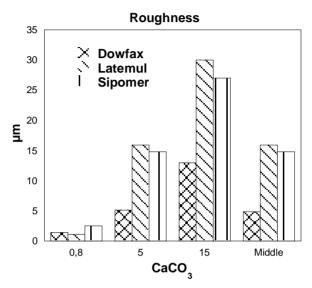


Figure 4.17. Roughness values for paints films prepared with latexes synthesized with different surfactant types for the different CaCO₃ particle sizes at the PVC value of 75.

As it can be observed in Figure 4.17 and as expected, paints prepared with the higher particle size calcium carbonate (15 μ m) were rougher, whereas paints prepared with the smallest particle size calcium carbonate (0.8 μ m) smoother. Moreover, with the blend of the three calcium carbonates, an average surface roughness was obtained.

Regarding the different types of surfactants, those paint films prepared with the latexes synthesized with the polymerizable surfactants (Laternul and Sipomer) were rougher than the paint films prepared using the latexes synthesized with the conventional surfactant (Dowfax). This can be due to a worse compatibility of CaCO₃ with the binders prepared with the copolymerizable surfactants, because the polymer particles are covered by covalent bound

surfactants, so the network that associative thickeners create might be blocked, which could cause the increase in roughness. Another plausible explication is the interaction between different surfactants with the associative thickeners. In fact, many researches have been done on how rheology is affected by the types and amounts of surfactants employed^{36,37,38}. Surfactants can either decrease or increase the viscosity of associative polymers, depending on their structure. Moreover, a competitive adsorption process between the surfactants and thickeners molecules is observed, which depends on the concentration and characteristics of both surfactants and thickeners³⁹.

Taking everything into account when polymerizable surfactants were employed the final paint properties tuned out to be worse. However, as in the case for the different functional monomers the differences from one to another were not that remarkable, due to the addition of the dispersing agent and other additives.

4.3.3.3 Waterborne paints with PS beads

PS beads were synthetized with a Tg of 98 °C (measured by DSC) in order to prepare waterborne paints using hard PS beads as filler instead of CaCO₃. The objective was to compare the regular packing of spherical PS beads versus the irregular packing of CaCO₃ by analysing the final paint properties. To achieve this objective, four different paints were prepared as explained in the experimental part;

- 1. 0.8 μm CaCO₃
- 2. 0.8 µm PS beads
- 3. $0.8 / 5 \mu m CaCO_3 blend (50/50)$
- 4. 0.8 μm PS / 5 μm CaCO₃ blend (50/50)

AFM

The roughness of the surface of the prepared paints films was measured by AFM and the obtained images are shown in Figure 4.18. Images were taken after drying the paints at ambient temperature.

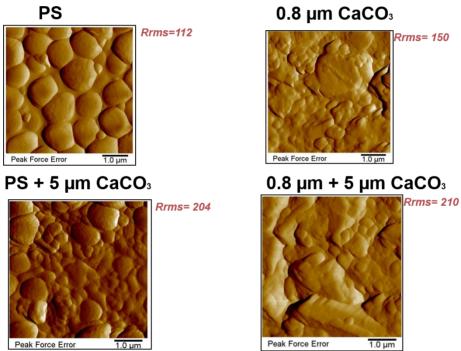


Figure 4.18. AFM images and roughness values for paints films prepared with PS, CaCO₃ or combination of both.

As it can be observed in Figure 4.18, the roughness of the final paints films was lower when using the PS beads as filler alone in comparison with the calcium carbonate filler of similar

average particle diameter. However, similar roughness values were obtained when replacing calcium carbonate for PS beads in paints where it was blended with 5 µm CaCO₃.

Profilometer

The roughness of the paint surface was also measured by profilometry and the obtained 3D graphs are shown in Figure 4.19.

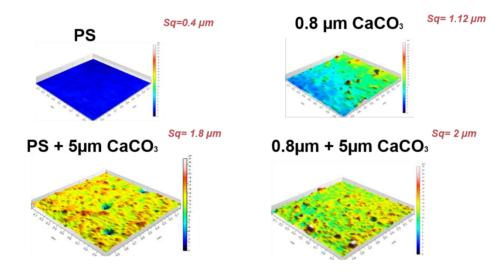


Figure 4.19. Profilometer 3D graphs and the roughness values for paints films prepared with PS, CaCO₃ or combinations of both.

As it can be observed in Figure 4.19, when replacing CaCO₃ filler with PS filler in the waterborne formulation, the final paint film roughness was lower. However, not big differences were observed in the roughness values when replacing calcium carbonate for PS filler particles

in a paint where it was blended with 5 μ m CaCO₃. This roughness values showed the same trend as the roughness values obtained by AFM.

Some other characterizations

In order to deeper study the effect of the way of packing the filler in the final paints properties, gloss at 60°, the whiteness and the spreading rate at 98% was measured and the obtained results are shown in Table 4.10.

Table 4.10. Gloss at 60°, whiteness and spreading rate for paints films prepared with PS, CaCO₃ or combination of both.

	Gloss 60 ⁰	w	SR (98%)
PS	2.75	91.47	2.85
CaCO₃ 0.8	2.41	77.43	5.35
PS/5 CaCO₃	2.28	88.50	2.64
CaCO ₃ 0.8/5 CaCO ₃	2.27	80.67	4

As it can be observed from Table 4.10, higher gloss value was obtained for PS alone compared with CaCO₃, but similar gloss values with the blends. Gloss is a surface property that depends on the smoothness of the surface. As it was observed by AFM and profilometer, in Figures 4.18 and 4.19 respectively, when preparing paints with the PS alone as filler, the surface of the paint film was smoother, therefore this paint presented a higher gloss value.

Regarding the whiteness, higher whiteness was obtained in all cases when using the PS beads instead of 0.8 μ m CaCO₃. Last but not least, the hiding powder was higher for 0.8 μ m CaCO₃ than for the PS beads. The refractive indexes of the polystyrene (1.55-1.59) and the

calcium carbonate (1.61) are similar, therefore, the increase in the spreading rate can be attributed to the possibility of having some degree of porosity, which would increase the hiding capacity, when using the calcium carbonate, because this filler packs irregularly.

Spherical PS beads and irregular CaCO₃ pack in different ways and thus, the final paints properties are different. Waterborne paints films were smoother, more glossy and whiter when replacing CaCO₃ for PS beads. These results open a window of opportunities to try to modify the morphology of CaCO₃ with the aim to improve final paint properties.

4.4 Summary and conclusions

In this Chapter, different high solids content (60 wt %) P(MMA/BA) acrylic latexes were synthesized, changing the functional monomer and the type of surfactant. A design of experiments (DOE) with the combination of high throughput experiments (HTE) were carried out in order to prepare the less amount of paints and to be able to understand the effect of the different functional monomers and different surfactants when preparing waterborne paints with three different particle sizes of calcium carbonate.

As regards the differences between the different functional monomers, when employing acrylamide the roughness of the paints surface increased (as showed by AFM and profilometer measurements). Moreover, with this functional monomer in some of the cases slightly lower gloss value, worse opacity, lower whiteness and worse scrub resistance were found. However, big differences or a clear tendency could not be observed from one functional monomer to another. Better results were expected when employing MAA functional monomer. Due to the differences

in hydrophobicity the polymer particles with MAA have higher amount of carboxylic acid on the surface of the particles, which enhances the interaction with CaCO₃ particles. Unfortunately, this tendency could not be observed. The dispersing agent (NaPA) might had hindered this effect and together with the other additives, and moreover waterborne paints were formulated well above the CPVC, at which point all the waterborne paint properties turn out to worse.

It has been observed that thickeners can cause the destabilization of a system, in fact depletion flocculation was observed when EHEC thickener was used. This problem was solved when using HASE thickeners instead of EHEC. Therefore, the choice of a specific thickener is highly important to obtain stable systems.

As far as the paints prepared with different surfactants are concerned, the surface roughness was higher when preparing paints with the polymerizable surfactants. Moreover, slightly lower gloss value and worse scrub resistance was found for these surfactants. The differences in other properties were not observed, probably and in the same way as with paints prepared with the different functional monomers, due to the high PVC values at which the paints are prepared (above CPVC) and due the addition of the dispersing agent and other additives.

Regarding the differences between the different three CaCO₃, better performances were achieved with the CaCO₃ of the smallest particle size. Even at the PVC of 75, the final properties were better than for the other filler samples at the PVC value of 60. This means that with this filler, higher amount of filler can be added, reducing by this way the final cost of the waterborne paint.

Last, PS beads with a similar particle size to the 0.8 µm CaCO₃ were synthesized. Paints were prepared using these PS beads as filler in order to study the effect of regular packing versus irregular packing in the final paint properties. It was seen that if CaCO₃ would be round some properties such as whiteness and gloss values could be improved.

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Chapter 5. Isolation of the interaction between CaCO₃ and different latex surfaces in paint-like blends

5.1 Introduction

Waterborne acrylic polymers are commonly modified with small amounts of functional monomer such as N-methylolacrylamide, acrylic (AA), methacrylic (MAA) or itaconic acid (IA) in order to improve their mechanical properties and to increase their compatibility with other materials¹. Although they are only used at relatively low levels in the emulsion polymerization process, these functional monomers can lead to a significant enhancement of the final paint properties^{2,3,4}. Moreover, the absence of these type of monomers can cause the destabilization of the system.

Another raw material that influences the stability of the system during the emulsion polymerization process is the surfactant^{5,6,7}. Surfactants are absorbed on the polymer particles and they provide stabilization of polymer particles during the polymerization and longer shelf life of the product. However, conventional surfactants can have a negative effect on product properties because of the fact that the physically adsorbed surfactant can be desorbed during storage. Furthermore, when the latex is applied as a film, the adsorbed surfactant can migrate

towards the film-air or the film-substrate interface, or can accumulate in pockets. These facts affect the performance of the film formed, like water resistance, gloss and film appearance^{8,9}. In order to overcome these drawbacks, during the last years a promising approach has been considered, where the surfactant is chemically incorporated into the polymer particles during the polymerization process, so that desorption of the surfactant from the polymer particles or migration in the resulting polymer film is disabled¹⁰. Polymerizable surfactants maintain the amphiphilic structure of a conventional surfactants, but they contain also a C=C double bond in their structure and therefore they can copolymerize with the monomers during the course of the polymerization¹¹.

Therefore, the surface properties of the latex can be varied by the incorporation of different functional groups into latex particles¹² or employing different types of surfactants¹³, and these possible variations seem promising in order to achieve an optimum compatibility between the pigment and binder particles.

In the present Chapter, different acrylic latexes have been synthesized to afterwards use them as binder for waterborne paints. More precisely, acrylic latexes P(MMA/BA) have been synthesized with different amounts of different functional monomers (AA, MAA and IA) and with different types of surfactants (conventional and polymerizable surfactants). In this Chapter, latexes with the acrylamide functional monomer were not prepared, because in the previous Chapter it was seen that the properties of the final waterborne paints films with this functional monomer were worse. Moreover, latexes prepared with the different amounts of MAA functional monomer and employing the conventional surfactant were dialyzed, with the objective to remove all possible water soluble species components and to study how paint-like properties are affected by the presence of these components.

In the previous Chapter, it was observed that NaPA was able to hinder the effect that latexes with different functional monomers and different surfactants have on the formulation of waterborne paints with CaCO₃ filler, due to the high affinity of this component with CaCO₃ particle surface. In order to better study the compatibility between different latexes with calcium carbonate particles, the objective of this Chapter has been to prepare CaCO₃/acrylic latexes blends without the use of any additive and with applicable rheology. This has been possible thanks to the direct addition of CaCO₃ powder to diluted latex.

Different blends have been prepared at different pigment volume concentration (PVC) values, and the obtained properties of both the blends and the paint-like films were characterized. Finally, the interaction between different latexes and calcium carbonate filler was studied by NMR measurements, by investigating the absorption capacity of polymer particles on the surface of CaCO₃ particles.

5.2 Experimental part

5.2.1 Materials

Methyl methacrylate (MMA, Quimidroga), butyl acrylate (BA, Quimidroga), acrylic acid (AA, Fluka), methacrylic acid (MAA, Quimidroga) and itaconic acid (IA, Sigma-Aldrich) monomers were used as supplied. Sodium persulfate (NaPS, Sigma-Aldrich) was used as thermal initiator. The surfactants used were Dowfax 2A1 (Dow Chemical, 45%), Latemul PD-104 (Kao Group, 20%) and Sipomer PAM-200 (Solvay). Deionized water was used throughout the work. To increase the pH of the latexes a 25% solution of ammonia (Fluka) was used. HCl (25% solution) and NaOH (Sigma-Aldrich) were used for the titration of the latexes.

Ground calcium carbonate (GCC) supplied by Omya, Omyacarb®EXTRA-CL (with 97.5% of the particles with a size <2 μ m) was used for the preparation of paint-like blends. Moreover, for the adsorption studies by NMR, a pure CaCO₃ was obtained from Sigma-Aldrich (with a 99.995% of purity).

5.2.2 Synthesis of acrylic latexes

Poly(methyl methacrylate-co-butyl acrylate) P(MMA/BA) (50/50) latexes were synthesized by seeded semi-batch emulsion polymerization (in the same way as reported in Chapter 2), in order to afterwards prepare the waterborne paints. Different latexes were prepared with different amounts of different functional monomers and with different surfactants:

Seven latexes were synthesized at acidic pH with three different functional monomers (AA, MAA and IA) and one latex was synthesized without the use of any functional monomer. AA and MAA functional monomers were added at 1, 3 and 5 wbm%, whereas IA only at 1 wbm%. In all these cases Dowfax 2A1 0.8 wbm% was used as surfactant and 0.5 wbm% NaPS initiator shot was employed at the beginning of the reaction with the exception of the latex synthesized with IA function monomer. In this case the initiator amount was doubled and it was divided in three different shots (t=0, t=120 min and t=240 min), in order to obtain high conversions at the end of the reaction. The formulation used in these reactions is the same as the one given in Table 5.1, changing the functional monomer and its amount for each latex.

Latexes were also synthesized with different surfactant types at the same concentration in water (6.84 mmol/L). The surfactants employed were Dowfax 2A1, Latemul PD-104 and Sipomer Pam-200. Synthesis were carried out under acidic conditions for Latemul and Dowfax surfactant and at neutral conditions for Sipomer. The formulation used is the same as the one given in Table 5.1, changing only the type and final amount of surfactant. For the three different surfactants, different latexes were prepared with 1 wmb% of AA, 1wbm% of MAA and without the use of any functional monomer. Moreover, one more latex was prepared using Latemul as surfactant and 1 wbm% of MAA adding a lower amount of this surfactant in the synthesis (2.19 mmol/L).

Table 5.1. General formulation of the final latex with dp= 300nm.

Compound	Initial charge (g)	Stream 1 (g)
Seed 1	31.125	-
MMA	1.12	118.8
BA	1.02	118.8
Functional monomer (1, 3 and 5 wbm%)	-	3/9/15
Water	97.67	46.5
$Na_2S_2O_8$		1.5
Dowfax 2A1	-	0.589

Feeding time: 240 min and SC 50%.*Reaction time for IA was 360 min and double amount of NaPS was used in that case.

5.2.3 Preparation of CaCO₃/acrylic latex blends without the use of any additive

Waterborne paints were prepared without the help of any additive. The strategy followed was the next one; all latexes were neutralized at the pH of 9 and were diluted. Then CaCO₃ powder was directly added with the help of the Dispermat (1300 rpm). High shear is needed to break-up the pigment particle agglomerates. In order to obtain undisturbed paint films, entrapped air bubbles were removed with a deaeration equipment (Figure 5.1).

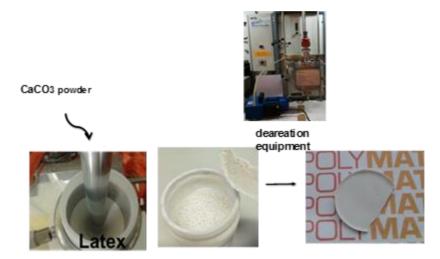


Figure 5.1. Strategy employed to synthesize waterborne paints without the use of any additive.

The direct addition of CaCO₃ powder to diluted latex gives the possible to disperse calcium carbonate particles in the medium, without the need of preparing a mill base where the use of NaPA is unavoidable to well disperse pigment particles. Paint-like blends were prepared employing this strategy at the different PVC values of 30, 40 and 50, with a solids content of 60 wt%.

5.2.4 Preparation of CaCO₃/acrylic latex blends without the use of any additive: after dialyzing the latexes

During the discussion of the results obtained in this Chapter, it was seen that the water soluble oligomeric species of the latexes could be having some kind of effect in the interaction with CaCO₃. Therefore, latexes prepared with 1 wbm% and 5 wbm% of MAA functional monomer and employing Dowfax 2A1 (0.8 wbm%) were cleaned, with the objective to remove all possible water soluble components and therefore better study the interaction between the latex particle surface and CaCO₃ particles. To carry out this, latexes were diluted at a solids content of 30%, and afterwards the latexes were cleaned by means of dialysis. Dialysis of the latexes was carried out until the conductivity of the water phase remained constant. After dialysis the solids content of the latexes was increased by evaporation of water in the rotavapor. Waterborne paints were prepared with these two latexes with the same strategy used in 5.2.3, at the PVC value of 40.

5.2.5 Characterization

Conversion and solids content of the final latexes were gravimetrically determined. In order to assess the polymerization of the polymerizable surfactants ¹³C-NMR measurements were carried out of the pure surfactants (Latemul PD-104 and Sipomer Pam-200) and of the latexes after polymerization, and the C double signal intensity were checked (details in Appendix I). The average particle size was measured by Dynamic Light Scattering Spectroscopy, DLS (Malvern® Zetasier Nano) and the glass transition temperature by differential scanning calorimetry (DSC) in a Q200 (TA instrument). The fraction of carboxylic acid groups present in the surface of the latex particles was calculated by titration after dialyzing the latexes and the amount of carboxylic acid groups in the water phase was measured by means of gravimetric analysis. The details of

the characterization procedures and methods are given in Appendix I. The molar mass of the water-soluble oligomers was determined by aqueous SEC-MALS/RI using 0.01 M NaNO₃ solution as the mobile phase. The columns were calibrated using water-soluble polyethylene glycol (PEG) standards with molecular weights in the range 2 000-21 000 (g/mol).

The rheology of the paint-like blends were analyzed in a AR 1500 rheometer. Scanning Electron Microscopy (SEM) (TM 3030) was used to analyze the morphology final paint-like films. Atomic Force Microscopy (AFM) (Bruker Dimension Icon with nanoscope V controller) was used to analyze the roughness of the blends surfaces. The final paint-like properties were analyzed in terms of contact angle measurements, gloss measurements, mechanical properties (tensile test and scrub) and water absorption. Further information can be found in Appendix III.

Moreover, the interaction between acrylic polymers of different nature and calcium carbonate filler particles was determined by using ¹H- NMR spectroscopy (Bruker Avance-500). For this, CaCO₃/acrylic latex blends were prepared with deionized water and the supernatant was characterized by ¹H-NMR spectroscopy in a Bruker AVANCE-500 spectrometer.

5.3 Results and discussion

5.3.1 Acrylic latexes

Poly(methyl methacrylate-co-butyl acrylate) P(MMA/BA) latexes were synthesized by semibatch emulsion polymerization, with different amounts of different functional monomers and different surfactants. Characterization of the final MMA/BA latexes synthesized at acidic conditions with different amounts of functional monomers.

Since the polymerizations were carried out under starved conditions, high instantaneous conversion along the polymerization process and final full conversions were achieved for all latexes with the exception of the synthesized with the itaconic acid (IA) functional monomer. In this case the instantaneous conversion was lower than for AA and MAA for all 4h of reaction and the final conversion was 90% as it can be observed in Figure 5.2.

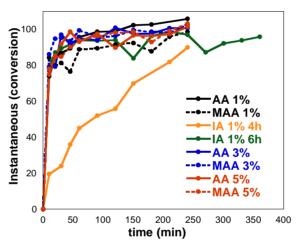


Figure 5.2. Instantaneous conversion of P(MMA/BA) latex with different amounts of different functional monomers.

IA has a negative influence on the conversion and this effect has been widely analysed on the literature^{14,15}. For latexes made with both acrylate esters and itaconic acid, the major role of the IA is in the earliest stages of emulsion polymerization, because IA can affect the termination of copolymer oligomeric radicals in two ways. First, because itaconic acid is slower to polymerize

than the acrylate esters, its presence is likely to reduce the propagation rate in the aqueous phase (see the reactivity ratios in Table 5.2). Second, the incorporation of IA into the copolymer oligomers produces a huge increase in the water solubility, therefore the possibility of two oligomeric radicals to terminate with each other in the water phase increases.

Table 5.2. Copolymerization reactivity ratios.

Monomer 2	r1	r2
MMA	0.73	1.28
IA	1.10	0.23
IA	1.29	0.34
	MMA IA	MMA 0.73 IA 1.10

Information taken from 14

Moreover, in some articles it has been postulated that the itaconic acid induced the decomposition of persulfate and that higher conversions are obtained when replacing persulfates with an azo initiator¹⁶. As the use of NaPS was important in order to make the comparison with the other latexes, it was decided to increase the amount of NaPS in order to maintain the radical flux. In fact, when the double amount of NaPS was used, the final conversion increased form 90% to 96%. Moreover, the reaction time for this latex was increased to six hours. It has also been reported that as the amount of itaconic acid increased, the conversion was lower¹⁷. Due to this fact, latexes with IA were not synthesized with 3 and 5 wbm%.

Table 5.3 presents the solids content, particle size, Tg, amount of carboxylic groups coming from the functional monomers in the water phase and on the surface of the particles, the gel content and the molecular weight for the latexes synthesized with different amounts of different functional monomers.

Table 5.3. Characterization of final latexes with different functional monomers.

	SC (%)	Dp (nm) (DLS)	Tg (⁰C) (DSC)	-COOH in water (%)*	-COOH in surf (%)*	Mol COOH/m² surface
Without M	47.5	277	15			
AA 1%	47.6	273	17	19	39	1.08 x 10 ⁻¹¹
AA 3%	47	276	17	21	32	2.1 x 10 ⁻¹¹
AA 5%	46	286	17	27	56	5.58 x 10 ⁻¹¹
MAA 1%	46	280	18	6	52	1.3 x 10 ⁻¹¹
MAA 3%	47.6	281	23	3	39	3.05 x 10 ⁻¹¹
MAA 5%	47.5	274	26	4	71	6.5x 10 ⁻¹¹
IA	51.5	269	16	70	20	1.36x10 ⁻¹²

^{*}Carboxylic acid groups in the water phase and in the surface of the particles.

As it can be observed in Table 5.3, generally, similar particle sizes and solids content were obtained independently of the functional monomer used.

Moreover, as the copolymer compositions were very similar for all the latexes, a glass transition temperature of around 17 $^{\circ}$ C was achieved for most of the cases. In the case of MAA functional monomer higher glass transition temperatures were found, rising from 18 $^{\circ}$ C to 26 $^{\circ}$ C when increasing the functional monomer from 1 to 5 wbm%.

In order to analyse the amount of carboxylic acid groups on the particles surface, their titration with NaOH was carried out as explained in the experimental part. Latexes with MAA functional monomer present more carboxylic acid groups on the surface of the particles, followed by AA and IA presents the lowest amount on the surface. The hydrophobicity of the functional monomers plays an important role during the emulsion polymerization. The higher the hydrophobicity, in this case for MAA, the less oligoradicals are going to be formed in the aqueous

phase and more functional groups are going to be incorporated on the surface of the latex particles 18,19,20.

The amount of carboxylic acid groups in the water phase were calculated gravimetrically.. As it can be observed in Table 5.3, MAA remains mainly in the surface of the particles, whereas IA resides mainly in the water phase during emulsion polymerization. Therefore, as the polarity of the functional monomer is decreased IA>AA>MAA, less oligomers were found in the aqueous phase. Similar results were obtained by Mauricio Pinheiro et al., for the semicontinuos emulsion polymerization of S/Ba with 1 wbm% of IA, where they found that IA resides mainly in the aqueous phase¹⁵.

Moreover, the molar mass of the water-soluble oligomer were measured by aqueous GPC after separating the continuous phase from the polymer particles by centrifugation and the obtained results can be observed in Table 5.4.

Table 5.4. Molar mass of the water-soluble oligomers of the latexes synthesized with different amounts of different functional monomers.

arriounts of differen	Mn (g/mol)	PDI
AA 1%	1 400	1.3
MAA 1%	2 300	1.1
IA 1%	800	1.6
AA 3%	1 300	1.3
MAA 3%	1 900	1.3
AA 5%	1 100	1.8
MAA 5%	1 300	14

As it can be observed in Table 5.4, increasing the hydrophicity of the functional monomer (MAA<AA<IA) and the amount of functional monomer, the molar mass of the water-soluble

oligomer was lower. As the concentration of the carboxylic acid groups in the water phase increases, the propagation rate coefficient (kp) decreases, therefore the termination events can be more probable and the final molecular weights are lower²¹.

In addition, it has to be pointed out that the molecular weight of the dispersing agent (NaPA) used in the previous Chapter is 5100 g/mol. Therefore, the water-soluble oligomers that are being formed during the polymerization of MMA/BA with the acidic functional monomers are shorter than the CaCO₃ dispersing agent used in the previous Chapters.

> Characterization of MMA/BA/AA final latexes synthesized with different surfactants (6.84 mmol/L).

In this part, one conventional surfactant and two different polymerizable surfactants were employed. The conventional surfactant was the anionic surfactant Dowfax 2A1, and two polymerizable surfactants were employed; Sipomer Pam-200 and Laternul PD-104.

The synthesis of the latexes was carried out at acidic conditions except when using Sipomer Pam-200 (in order to avoid the hydrolysis of the phosphate group), employing the same concentration of surfactant in water; 6.84 mmol/L. Moreover, a latex was also synthesized with Latemul PD-104 surfactant at a lower concentration in water of 2.19 mmol/L. After polymerization, the conversion of the polymerizable surfactants was followed by ¹³C-NMR. The signal corresponding to the unsaturated carbon of the initial polymerizable surfactants, completely disappeared in both cases, which prove that both surfactants have completely polymerized (the obtained spectrums are showed in Appendix IV).

The final latex characteristic regarding the particle size, the solids content and the glass transition temperature is shown in Table 5.5.

Table 5.5. Characterization of the latexes with different functional monomers.

	SC (%)	Dp (nm) (DLS)	Tg (°C) (DSC)
Dowfax AA	50.1	290	16
Dowfax MAA	51	281	18
Dowfax without functional monomer	51.5	277	17
Latemul AA	51.1	291	14
Latemul MAA	51.4	292	17
Latemul without functional monomer	50.6	286	14
Sipomer AA	52.5	279	15
Sipomer MAA	52	290	15
Sipomer without functional monomer	52	278	15
Latemul (2.19 mmol/L)	50	278	15

As it can be observed in Table 5.5, similar final solids content, particles sizes and glass transition temperatures were achieved independently of the surfactant or functional monomer employed during the synthesis.

AFM phase images of the cross-section of the films made from latexes synthesized with different surfactants employing AA as functional monomer are shown in Figure 5.3.

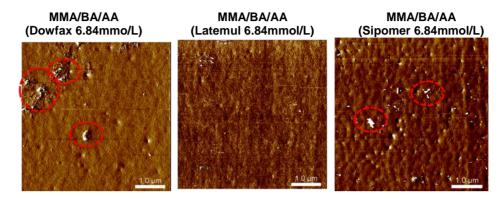


Figure 5.3. AFM cross-section images for latex synthesized with different surfactants types.

As it can be observed in Figure 5.3, some aggregates (white domains) could be observed within the films containing Dowfax 2A1 and Sipomer Pam-200. These aggregates could be a mixture of water-soluble and surfactant molecules agglomerations and were not observed when the latex was synthesized with Latemul PD-104 surfactant. This might suggest that Latemul PD-104 was better incorporated into the polymer backbone. Moreover, these latexes were centrifuged and the amount of polymer remaining solubilize in the water phase was measured. In the case of the latex synthesized with Sipomer Pam-200 more water soluble species were found, which suggests that Sipomer Pam-200 may homopolymerize and remain solubilized in the water phase.

5.3.2 CaCO₃/acrylic latex blends without the use of any additive

The effect of the different amounts of different functional monomers and different type of surfactants was studied on the final properties of CaCO₃/acrylic latex films. Blends were prepared at different PVC values of 30, 40 and 50, when using latexes synthesized with different amounts of different functional monomers, whereas at the PVC of 40 when employing latexes synthesized with different types of surfactants.

· Visual appearance of the paints

All of the paints prepared had good visual appearance except for the paints prepared with latexes synthesized without any functional monomer. In this case paints coagulated, as it can be observed in Figure 5.4.







Figure 5.4. Visual appearance of the final waterborne paints prepared using the latex synthesized without any functional monomer.

Moreover, this effect was more or less noticeable depending on the surfactant employed during the latex synthesis. Higher amount of coagulum was obtained when preparing the latexes with the polymerizable Sipomer Pam-200 surfactant, then for Dowfax 2A1 and last for Laternul PD-104, which produced the least coagulated paint. According to this, it can be concluded that the use of functional monomer is a must in order to prepare stable blends with this procedure. It has to be pointed out, that this effect was not observed previously, as NaPA dispersing agent was used in all the previous Chapters. Therefore, thanks to the preparation of blends without the use of any dispersing agent, the influence of the latex particles surface is more significant. As a result, just the paints prepared with functional monomers bearing latexes were further characterized.

· Rheology of the blends

The rheology of the latexes synthesized with different amounts of different functional monomers were measured, and the obtained graphs can be observed in Appendix IV. According to these measurements, higher viscosity profiles were obtained when increasing the amount and the hydrophilicity of the functional monomers.

It is important to measure the rheology of the CaCO₃/acrylic latex blends, since the viscosity influences most of the applications properties. Figure 5.5 and 5.6 present the viscosities versus shear rate for the final paints at different PVC values. The measurements were performed at 25 $^{\circ}$ C.

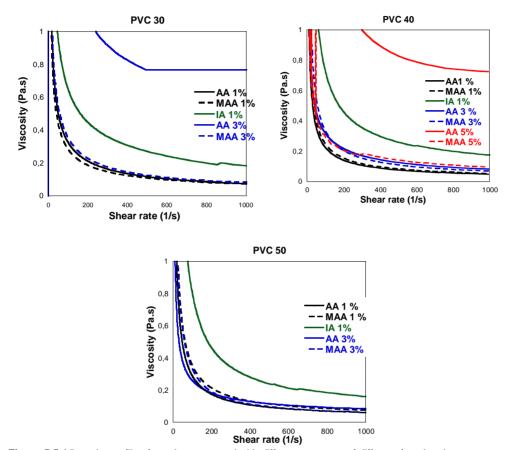


Figure 5.5. Viscosity profiles for paints prepared with different amounts of different functional monomers at different PVC values.

For all paints (Figure 5.5), shear thinning behaviour was observed; which means high viscosity in the low shear region to avoid settling and instability during storage and transport of the paint and low viscosities in the high shear rate region which corresponds to the application. As it can be observed in Figure 5.5, when preparing paints with the IA functional monomer, the

viscosity of the final paint increased significantly. Moreover, it seems that as the amount of functional monomer is increased, the final viscosity of the paint also increased and that paints prepared with the AA functional monomer presented higher final viscosities than paints with MAA. All of this facts can be explained with the same effect; the higher the amount of soluble oligomer are present in the final paint film, the higher the final viscosity of the paint is. These soluble oligomers act as thickeners of the paints. This trend was the same for the viscosity of the latexes (Appendix IV).

The rheology of the latexes synthesized with different surfactants can be observed in Appendix IV. Those latexes synthesized with the polymerizable surfactants presented higher viscosity than latexes synthesized with the conventional Dowfax surfactant. The rheology profiles for paints prepared with latexes synthesized with different surfactants and functional monomer for the PVC value of 40 can be seen in Figure 5.6.

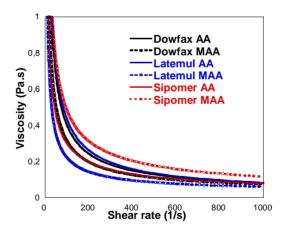


Figure 5.6. Viscosity profile for the latexes with different surfactants and functional monomer at the PVC value of 40.

The final rheology profile of the paints differs depending on both the surfactant and functional monomer type employed in the synthesis of the latex (Figure 5.6). Paints prepared with the Sipomer Pam-200 surfactant and with MAA functional monomer presented the highest viscosities, whereas paints prepared with Laternul PD-104 surfactant and with MAA functional monomer presented the lowest viscosities.

. SEM images of the blends films

CaCO₃/acrylic latex blends were then cast into silicon molds and left to dry at 50 °C and 55% humidity for a week in order to ensure full coalescence of polymer particles. The cross-section of the obtained films were observed by scanning electron microscopy. All SEM images of the paints films were similar, and as no differences were observed from one to another, a representative SEM images of the paints films employing MMA/BA/AA (49.5/49.5/1) and Dowfax 2A1 is shown in Figure 5.7. Moreover, for the sake of comparison, the same paint film SEM images are shown but when employing sodium polyacrylate (NaPA) dispersing agent to prepare the waterborne-like paints (the strategy followed in Chapter 3).

Whole film cross-section

MMA/BA/AA (49.5/49.5/1) (Dowfax 0.8 wbm%) with NaPA

MMA/BA/AA (49.5/49.5/1) (Dowfax 0.8 wbm%) without NaPA

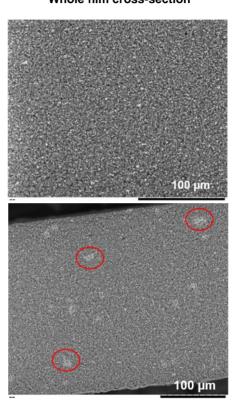


Figure 5.7. SEM images of the cross-section of final films for P(MMA/BA/AA) (49.5/49.5/1) when employing NaPA and in the absence of NaPA for the PVC value of 40.

First of all what it was noticeable is the appearance of white domains when the use of NaPA was supressed. In order to verify what these white spots were, EDX measurements of one of these zones were carried out, as well as EDX measurements of a zone without the white spots. The results of the EDX measurements can be observed in Figure 5.8. The images at the top

correspond to an area of a white spot, whereas the images at the bottom to an homogenous area. Moreover, in the left the obtained elements with different colours are represented and in the right the obtained elements by weight percent.

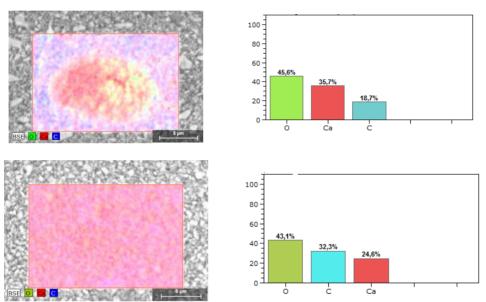


Figure 5.8. EDX images. Blends prepared without the use of NaPA dispersing agent and when employing MAA/BA/AA (49.5/49.5/1) latex with 0.8 wbm% of Dowfax 2A1.

From Figure 5.8, it can be seen that when doing an EDX of the white spots Ca/C ratio is higher than the one obtained from and homogenous zone. Threfore, it can be concluded that the white spots correspond to calcium carbonate particles agglomerations. This means that in order to fully disperse calcium carbonate particles, the use of the dispersing agent is highly recommended. However, as the objective of this Chapter was to study the interaction between different latexes nature (in terms of functional monomer type, different amount of functional

monomer and different types of surfactant), the use of NaPA was avoided. As it was shown in Chapter 4, this component can hinder the interaction of different latexes with CaCO₃ particles

As mentioned above, all the waterborne films SEM images were similar. Unfortunately, this was not the case when preparing films using the latexes synthesized with Sipomer Pam-200 surfactant. The SEM images of films prepared with latexes synthesized with this surfactant are shown in Figure 5.9.

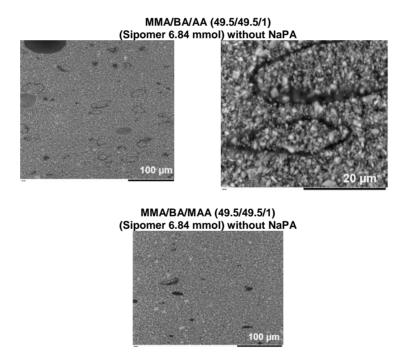


Figure 5.9. SEM imagines of films when employing in the synthesis of the latex Sipomer Pam-200 as surfactant.

In Figure 5.9, it can be observed that the SEM images had strange forms when employing Sipomer Pam-200 surfactant in the synthesis of the latex. The dark zones were analysed by EDX, but no extra concentration of P was found in those areas, probably due to the low concentration of the P element in the whole polymer. These dark zones, could be because of the presence of oligomers that maybe attached to polymer particles and therefore can not migrate.

. AFM images of the films

AFM phase images of the paint-like films dried at 50 $^{\circ}$ C and 55 % humidity are shown in this section with 5 μ m x 5 μ m image areas. AFM tapping mode phase images were obtained due to the great differences in the viscoelastic properties of calcium carbonate particles and the polymer in the film.

The AFM cross-section images of the paint-like films can be observed in Figure 5.10, for films prepared with latex synthesized with 6.84 mmol/L of different surfactants and AA or MAA functional monomer at the PVC value of 40.

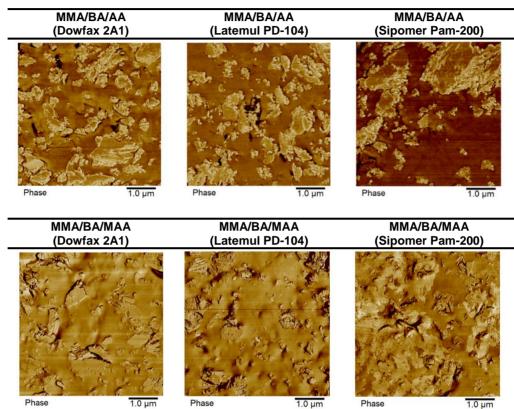


Figure 5.10. AFM phase images of the cross-section of films prepared with latexes synthesized with different surfactants at the PVC value of 40.

From the AFM images of Figure 5.10 it seems that calcium carbonate particles are better dispersed when the latex was synthesized with Laternul PD-104 surfactant, as the particle agglomerations seem to be slightly smaller than for films prepared with Dowfax 2A1 and Sipomer Pam-200. Moreover, it seems that the worst dispersion of CaCO₃ particles is obtained when Sipomer Pam-200 surfactant is used, because a region of particle agglomerations can be observed and at the same time a region where filler particles are not present.

In order to perform the quantifications of these AFM images, the area of each CaCO₃ agglomeration in the paint-like films was measured, with the help of a commercially available software, Image Pro Plus 7.9. The measurement of the individual agglomerate average area allows to know the level of CaCO₃ particles dispersion in the paint-like films. For each paint-like film, four different AFM images were taken and the average and the deviation of the area of each CaCO₃ agglomeration was measured.

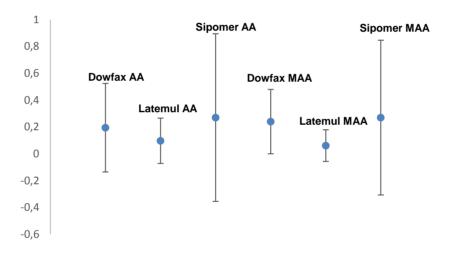


Figure 5.11. Average of the area of CaCO₃ particles (μm²) inside films. Blends were prepared with different surfactants.

In Figure 5.11, it was observed that higher areas and deviations was observed when Sipomer Pam-200 was used as surfactant. On the opposite, lower area and deviation was achieved when using Laternul PD-104. This means, that particles are better dispersed when the paint is prepared with the latex synthesized with Laternul PD-104 surfactant.

In Figure 5.12, the AFM images of paint-like films prepared with latexes containing different amounts of functional monomer for the PVC value of 40 can be observed.

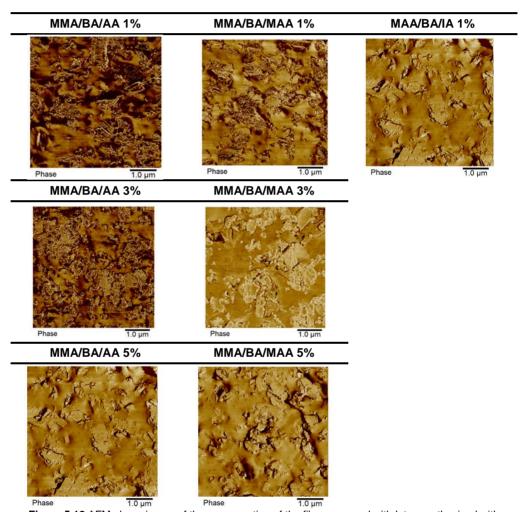


Figure 5.12.AFM phase image of the cross-section of the films prepared with latex synthesized with different amounts of different functional monomers at the PVC value of 40.

In Figure 5.12 it can be observed that particles are less agglomerated when 1 wmb% of functional monomer was employed. The same image analysis of the CaCO₃ agglomerates was also carried for these images and the results are shown in Figure 5.13. It can be observed that the average area and the deviation of the CaCO₃ pigment particles is lower for paint-like films prepared with AA and MAA 1 wt%. However, no big differences were found between the other paint-like films. The lower CaCO₃ agglomerates size for lower functional monomer concentrations can suggest that the presence of soluble oligomers produced in the synthesis of the latex, harms the dispersion of calcium carbonate particles. Previously, in Table 5.4, it was pointed out that the molar mass of the water-soluble oligomers was lower than the molecular weight of the NaPA dispersing agent (used in Chapters before). This is the reason why the dispersing agent is able to well disperse calcium carbonate particles, while the water-soluble oligomers not. This fact is probably because smaller oligomers can move easily to attach to the calcium carbonate particles, which keep off polymer particles to be absorb onto the surface of calcium carbonate particles. Moreover, these oligomers are not long enough to provide steric stabilization, and can cause the agglomeration of some of the particles.

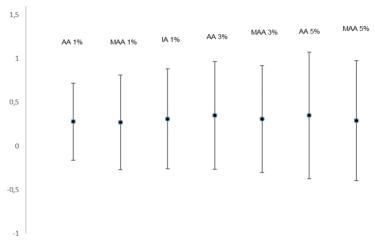


Figure 5.13. Average of the area of CaCO₃ particles (μm²) inside the films. Blends were prepared with different amounts of different functional monomers.

Contact angle values

Contact angle measurements of the polymer film, paint-like films and CaCO₃ compact powder were carried out. Furthermore, in order to study the migration of the water soluble species to the water in the polymer film, just the polymer film was analysed initially as produced and after rising it with deionized water for 5 minutes.

To measure the contact angle of the filler, CaCO₃ discs were prepared by compression of the powder with a pressure of 10⁹ Pa. Four discs were prepared and the contact angle value achieved was 19±4, which means that this filler has a hydrophilic nature. Polymer film and paint-like films were prepared at 350 µm wet thickness in glass substrates and were let to dry at 50 °C

and 55 % of humidity for a week. Table 5.6 presents the water static contact angle values for the films cast from latexes synthesized with different amounts of different functional monomers and their paint-like films.

Table 5.6.. Contact angle of the different latex synthesized with different amounts of different functional monomers and the obtained films for the PVC values of 30, 40 and 50 (Dowfax 2A1 was used as surfactant in all cases).

	Polymer flm	Polymer after rinsing	PVC 30	PVC 40	PVC 50
MMA/BA/AA 1%	20 ±2	77 ±3	72 ±2	83 ±2	91 ±3
MMA/BA/MAA 1%	31 ±2	77 ±3	70 ±2	78 ±3	89 ±3
MMA/BA/IA 1%	41 ±3	81 ±4	78 ±2	91 ±2	96 ±3
MMA/BA/AA 3%	29 ±1	75 ±2	74±2	90 ±1	99 ±2
MMA/BA/MAA 3%	18 ±2	73 ±4	72±2	87 ±1	93 ±2
MMA/BA/AA 5%	50 ±3	67 ±2	-	92 ±2	-
MMA/BA/MAA 5%	21 ±2	73 ±2	-	85 ±2	-

Polymer films presented very different contact angle values, and a clear tendency can not be observed. This could be because of the different hydrophilic nature of the functional monomers and due to the different water soluble species formed during the polymerization. After rinsing the polymer films with water for five minutes, the contact angle value increased in all the cases, which means that water soluble species were removed after rising the film. Moreover, after rinsing the polymer films, it can be observed that increasing the amount of functional monomer, the contact angle value slightly decreased, due to a higher amount of hydrophilic part in the latexes.

The theory of wetting rough surfaces is well developed and two different situations are considered depending if the liquid penetrates the interior of the cavities or not²². According to Cassie-Baxter model, the liquid does not penetrate in the cavities of the rough surface, whereas in the model of Wenzel the liquid penetrates into the cavities of the rough surface²³. As the roughness increases, the energy needed to wet the cavities increases and the Cassie's case becomes more favourable. Therefore, an increase in contact angle can be directly related to a higher roughness in paint-like film surface.

It has to be taken into account that the differences in contact angle values between the polymer film and the paint-like films can be related to the interaction between acrylic polymers with CaCO₃ particles. Depending on the interaction between these two components, they will pack in different ways, which will affect the roughness of the surface as a consequence, the contact angle values. Regarding the contact angle value of the paint-like films at different PVC values, different tendencies can be observed. First, increasing the PVC value, the contact angle increased as well, which means that surface became rougher as more filler particles are present in the surface (same tendency showed in Chapter 3). Secondly, increasing the amount of functional monomer in the synthesis of the latexes, paint-like surface presented a higher contact angle value, which mean that they became rougher. Therefore, the use of higher amount of functional monomer during the synthesis of the latex does not allow a better dispersion of the CaCO₃ filler particles. Moreover, differences in the contact angle values were observed depending on the functional monomer used in the synthesis of the latex. Itaconic acid presented the highest contact angle value, and methacrylic acid the lowest. The use of the methacrylic acid

functional monomer lead to an enhanced interaction between the polymer particles and CaCO₃ particles, giving a smoothner final paint-like film.

In Table 5.7 the different contact angle values of the polymer films and paint-like films can be observed depending on the surfactant used during the synthesis of the latex.

Table 5.7. Contact angle value for the films prepared from the latex synthesized with different surfactants and with both MAA and AA functional monomers and for films at the PVC value of 40.

	Polymer film	Polymer film after rinsing	PVC 40
Dowfax 2A1 AA	65 ± 1	71 ± 1	83 ± 1
Dowfax 2A1 MAA	62 ± 1	73 ± 1	78 ± 2
Latemul PD-104 AA	76 ± 1	75 ± 2	83 ± 2
Latemul PD-104 MAA	74 ± 1	76 ± 1	74 ± 2
Sipomer Pam-200 AA	72 ± 2	72 ± 1	90 ± 1
Sipomer Pam-200 MAA	72 ± 1	72 ± 1	88 ± 1

^{*}surfactants (6.84 mmol/L)

In Table 5.7, the different contact angle values of the latex and films can be observed depending on the surfactant used during the synthesis of the latex. Regarding the contact angle values of the latex, in the films containing the conventional surfactant Dowfax 2A1, lower contact values were obtained, suggesting that when Dowfax is used as surfactant migration to the air-film interface occurred. When the films were rinsed with water, higher contact angle values were obtained, indicating that the migrated surfactant was removed from the air-film interface.

However, in the films containing Laternul PD-104 and Sipomer Pam-200 no differences in contact angle values were observed before and after rinsing the films with water. These results indicate that no migration of Laternul PD-104 and Sipomer Pam-200 surfactant occurred to the

air-film interface. Therefore, the aggregates observed in AFM cross-section image (Figure 5.3) for the latex with Sipomer Pam-200 could be surfactant oligomers that could not migrate to the surface (maybe oligomers that are chemically bounded). Otherwise, the contact angle value would have been lower. However, the aggregates observed for latex with Dowfax 2A1 can be composed of mobile surfactant molecules, that could also migrate to the surface of the latex, due to the increase in contact angle value observed after rinsing the films with water.

Paying attention to the contact angle values of the paint-like films, it can be observed in Table 5.7 that similar values were obtained when using conventional Dowfax 2A1 and the polymerizable Laternul PD-104 surfactant, however higher contact angle values were observed when using the polymerizable Sipomer Pam-200 surfactant. It seems that the compatibility of this surfactant with calcium carbonate filler particles is not as good as with the rest of surfactants. It is important also to point out than when using MAA as functional monomer instead of AA, the paint films surface were smoother.

Gloss

Specular gloss of paint-like films was measured on black substrates at 85° geometry. The obtained results when preparing paint-like films with different amounts of different functional monomers are presented in Table 5.8 and paint-like films prepared with latex synthesized with different surfactant types in Table 5.9.

Table 5.8. Gloss value at 85° for paint-like films prepared with latexes synthesized with different amounts of different functional monomers for the PVC values of 30, 40 and 50.

	PVC 30	PVC 40	PVC 50
MMA/BA/AA 1%	70 ±4	51 ±1	33 ±1
MMA/BA/MAA 1%	75 ±1	52 ±1	35 ±1
MMA/BA/IA 1%	64 ±2	39 ±2	18 ±3
MMA/BA/AA 3%	63 ±2	46±1	28 ±1
MMA/BA/MAA 3%	71±2	45 ±1	34 ±1
MMA/BA/AA 5%	-	37 ±1	-
MMA/BA/MAA 5%	-	48 ±2	-

Gloss is a surface property that depends on the smoothness of the surface. As it can be observed in Table 5.8, increasing the amount of functional monomer in the synthesis of the latex the gloss values decreased. This means that CaCO₃ filler particles are worse dispersed in the medium when the amount of the functional monomer in the latex synthesis is increased. As seen before in Table 5.3, increasing the amount of functional monomer in the synthesis of the latex the water soluble oligomers increased as well. Therefore, it can be concluded that water soluble oligomers are not able to act as an additional dispersing agent, fact that was also observed by S.Kirsch et al in 2001²⁴.

When using IA as functional monomer, lower gloss values were observed, whereas when using MAA functional monomer higher gloss values could be obtained. Increasing the PVC value the gloss decreased, because more filler particles are in the system. The results observed in Table 5.8 are correlated with the results obtained from the contact angle values. When rougher surfaces were detected, the gloss value of the paint-like surface was lower.

Table 5.9. Gloss values for paint-like films prepared with latexes synthesized with different types of surfactants (6.84 mmol/L).

	PVC 40
MMA/BA/AA 1% (Dowfax 2A1)	41 ±1
MMA/BA/MAA 1% (Dowfax 2A1)	50 ±1
MMA/BA/AA 1% (Latemul PD 104)	43 ±1
MMA/BA/MAA 1% (Latemul PD 104)	49±1
MMA/BA/AA 1% (Sipomer PAM 200)	30±1
MMA/BA/MAA 1% (Sipomer PAM 200)	48±1

As it can be observed in Table 5.9, paint-like films prepared with the latexes synthesized with Sipomer Pam-200 were less glossy. This means that when using this surfactant the latex is not able to disperse well calcium carbonate particles. Moreover, slightly higher gloss values were obtained when using Latemul PD-104 surfactant in the synthesis of the latexes. This suggests that better latex-calcium carbonate interaction is obtained when Latemul PD-104 was used to synthesize the latexes.

Mechanical properties

The effect of the functional monomer and surfactant type of the latex on the mechanical properties of the paint-like films was studied at different PVC values. For this purpose, tensile test and scrub resistance measurements of the polymer and CaCO₃/latex blends films were carried out.

Tesile test

The stress-strain curves of the latex films synthesized with different amount of different functional monomer can be observed in Appendix IV. Similar curves were achieved, however when employing MAA functional monomer the resulting films were more brittle. The stress-strain curves of the paint-like films are depicted in Figures 5.14. it has to be mentioned that mechanical properties for all paint-like films at the PVC value of 50 and for paint-like films prepared with latexes synthesized with 5 wbm% of functional monomer at PVC 40 were not conducted, because paint-like films were above CPVC and coherent films were not obtained. Moreover, when films were prepared with the latex synthesized using the IA functional monomer at the PVC value of 40, a coherent film was not obtained either, which means that the paint-like film was already above the CPVC.

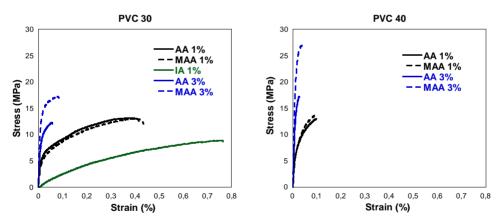


Figure 5.14. Mechanical properties of paint-like films prepared with latex synthesized with different amounts of different functional monomers at PVC values of 30 and 40.

In Figure 5.14, it can be observed that at high PVC values the mechanical properties are dramatically worse. It seems that higher elongation can be achieved when the latex was synthesized with IA functional monomer, this can be attributed to a hydro plasticiser effect of the remaining non converted functional monomer. It can also be observed that increasing the amount of functional monomer the mechanical properties of the final paint-like film are worse. Moreover, slightly higher maximum elongation and higher toughness values were achieved when the paint-like films were prepared with latex synthesized with MAA functional monomer, fact that is more visible employing higher amounts of functional monomers. This could suggest a better interaction of these latexes with calcium carbonate particles, as the film elongates more and the energy that must be applied to break these paint-like films is higher

The mechanical properties of the latexes synthesized with different surfactants were similar and the obtained curves can be observed in Appendix IV. In Figure 5.15, the strain-stress values for films prepared with different types of surfactants employing AA and MAA functional monomers are shown. In this case, paint-like films prepared with the latex synthesized with Sipomer PAM-200 and MAA functional monomer was not possible to be measured, as the film showed cracks after the drying processes. This means that, in this system the CPVC was already surpassed at the PVC value of 40.

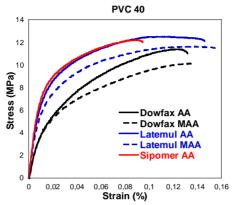


Figure 5.15. Mechanical properties for the paint-like films prepared with latexes synthesized with different types of surfactants and functional monomers at the PVC value of 40.

As it can be observed in Figure 5.15, the Young's modulus for all the paint-like films were similar, and only slight differences can be observed in the maximum elongation and in the toughness values for the different paint-like films. Very slightly higher elongation and toughness values were obtained when employing Laternul PD-104 surfactant in the synthesis of the latex. On the contrary, paint-like films prepared with the latex synthesized with Sipomer Pam-200 showed the worse properties, lowest maximum stress and toughness value. Moreover, as mentioned above good films were not possible to make with this surfactant and MAA functional monomer. Therefore, it can be concluded that weaker interactions are observed between calcium carbonate particles with latexes prepared with Sipomer Pam-200 surfactant.

Scrub resistance

The scrub resistance of the paint-like films prepared with different latexes synthesized with different amounts of different functional monomers at the different PVC values of 30 and 40 are plotted in Figure 5.16. At the PVC value of 50 the scrub resistance measurements were not possible to be conducted. As mentioned before, at this PVC the system is above the CPVC and thick enough coherent paint-like films were not possible to be obtained.

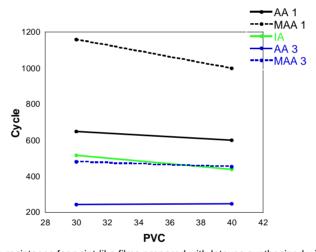


Figure 5.16. Scrub resistance for paint-like films prepared with latexes synthesized with different amounts of different functional monomer at different PVC values.

As it can be observed in Figure 5.16, the scrub resistance for paint-like films prepared with higher amount of functional monomer was lower; which means that the interaction between polymer particles and filler particles is worse. Moreover, MAA functional monomer showed better

wet scrub resistance, and IA functional monomer the worst scrub resistance, for 1 wbm% of functional monomer.

The scrub resistances for the paint-like films prepared with different types of surfactant and functional monomers at the PVC value of 40 can be observed in Table 5.10.

Table 5.10. Wet scrub values of the different paint-like films prepared with latexes synthesized with different types of surfactants (6.84 mmol/L)

	PVC 40
MMA/BA/AA 1% (Dowfax 2A1)	765 ±50
MMA/BA/MAA 1% (Dowfax 2A1)	1155 ±36
MMA/BA/AA 1% (Latemul PD-104)	1021 ±47
MMA/BA/MAA 1% (Latemul PD-104)	1602 ±30
MMA/BA/AA 1% (Sipomer Pam-200)	657 ±37
MMA/BA/MAA 1% (Sipomer Pam-200)	508 ±42

Paying attention to Table 5.10, two different conclusions can be drawn. On the one hand, paint-like films prepared with the latex synthesized with MAA functional monomer had better scrub performances than when preparing blends employing AA functional monomer in the synthesis of the latex. Thus, the use of MAA functional monomer, as previously seen (Figure 5.16), resulted in a better polymer-pigment particle interaction. On the other hand, paint-like films prepared with Laternul PD-104 surfactant had better scrub resistance, followed by Dowfax 2A1 and the worst scrub resistance were obtained with Sipomer Pam-200 surfactant. Therefore, it seems that better interaction between polymer particles and calcium carbonate particles is

obtained when the latex is synthesized with Laternul PD-104 surfactant, then with Dowfax 2A1 and last Sipomer Pam-200.

Water uptake

The water uptake of the films obtained from latexes (at the pH of 9, Appendix IV) and paint-like films were measured (immersing them in water for one week). The water uptake of latex films did not follow a specific trend, even if lower water uptake was observed for lower functional monomer amounts.

In Figure 5.17 the water uptake along a week for the paint-like films prepared with latexes synthesized with different amounts of different functional monomers at the PVC values of 30, 40 and 50 can be observed. It has to be pointed out that for water uptake experiments thinner films are need. Due to this, water uptake measurements were possible to be carried out at the PVC value of 50 (although the mechanical properties were not possible to be performed at this PVC).

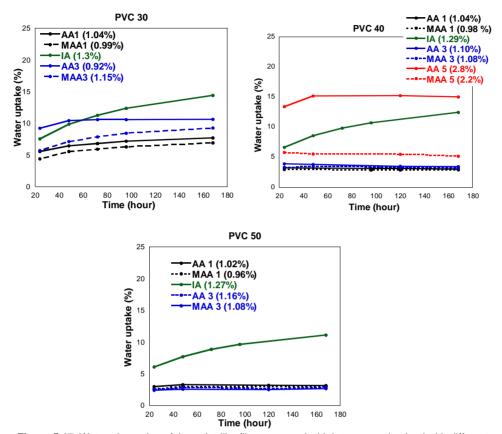


Figure 5.17. Water absorption of the paint-like films prepared with latexes synthesized with different amounts of different functional monomers.

As it can be observed in Figure 5.17, the water uptake is lower when the binder content is decreased; at the PVC value of 30 paint-like films prepared with AA and MAA functional monomers absorbed around 4 and 10% in one week, whereas, at PVC 50 values were below 4%. In the case of IA functional monomer, the water absorption amount was higher, but it was

also noticed that increasing the PVC the paint-like film absorbed less water, passing from 14% (PVC 30) to absorb 10% (PVC 50) in one week. Same results were obtained by Sacide Alsoy Altinkaya et al. in 2010²⁵, where sorption results of films made by the same latexes composition revealed that solubility of water decreases with the decreased binder content in the paint films. At PVC values of 30 and 40, it is clearly seen that increasing the amount of functional monomer in the synthesis of the latex the final paint-like films absorbed more water. This can be attributed to the contribution of two different facts, the increase in hydrophilic nature of the paint-like film structure and a worse interaction between latexes synthesized with high amount of functional monomer and calcium carbonate particles. Regarding the different functional monomer employed along the latex synthesis, an increase in the polarity of these functional monomers turns out to an increase in the water uptake.

As far as the weight loss of the paint films is concerned, not big differences were observed from one to another. However, higher amount of weight lost was detected when IA was used in the synthesis of the latex and when latexes where prepared with 5 wbm% of functional monomer.

The water uptake of the latexes films synthesized with different surfactants can be observed in Appendix IV, where big differences from one to another were not observed. In Figure 5.18, the water uptake during a week for the paint-like films prepared at the PVC value of 40 with latexes synthesized with different surfactants and different functional monomers can be observed.

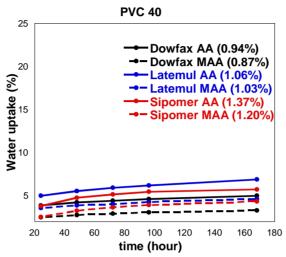


Figure 5.18. Water uptake absorption along a week for paint-like films prepared with different surfactants and functional monomers at the PVC value of 40.

Regarding Figure 5.18, firstly, it can be observed the slight differences between paint-like films prepared with MAA or AA functional monomer. Paint-like films containing MAA instead of AA functional monomer absorbed slightly less amount of water. This can be attributed to a lower polarity of this functional monomer and to a better interaction of this latex with the calcium carbonate particles.

Secondly, the following tendency can be slightly appreciated; Paint-like films prepared with latexes containing Laternul PD-104 absorbed more water, then with Sipomer Pam-200 and lastly with Dowfax 2A1. The high absorption of films prepared with Laternul can be attributed to a higher amount of this surfactant in the films.

To verify this, a latex with a lower amount of Latemul surfactant was synthesized (2.19 mmol/L instead of 6.84 mmol/L) and with MAA functional monomer. A CaCO₃/acrylic latex blend was prepared from this new latex at the PVC value of 40 (as explained in 5.2.3). The water uptake was measured for this new paint-like film and the obtained graph is shown with the previous one for the sake of comparison in Figure 5.19. It can be observed that the water uptake for paint-like film decreased when lower amount of surfactant was employed in the synthesis of the latex.

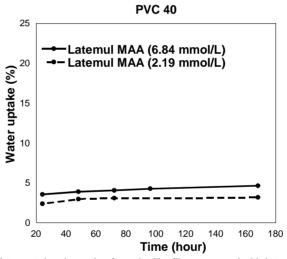


Figure 5.19. Water uptake absorption for paint-like films prepared with latexes synthesized with different amounts of Laternul at the PVC value of 40.

5.3.3 CaCO₃/acrylic latex blends without the use of any additive: after dialyzing the latexes

In the previous results, it has been observed that increasing the amount of functional monomer in the synthesis of the latexes the final paint performances were worse. This can be attributed to the presence of water soluble oligomers that harms the dispersion with CaCO₃ particles. Therefore, some of the latexes were dialyzed in order to remove the possible effect of water soluble species in the final paint-like films properties. As explained in the experimental part (5.2.4), latexes containing different amount of MAA functional monomer (1 wbm% and 5 wbm% more precisely), were cleaned by means of dialysis, blends were prepared from these and final films were characterized. The mechanical properties of the paint-like films prepared with 1 wbm% of MAA after dialyzing the latex and before dialyzing it can be observed in Figure 5.20 (when employing 5 wbm% of MAA, coherent films could not be obtained to perform mechanical properties).

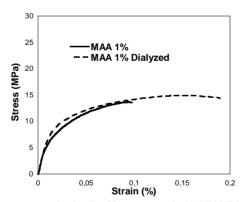


Figure 5.20. Tensile test curves of paint-like films prepared with MMA/BA/MAA (49.5/49./1) latex after dialyzing the latex and without.

As it can be observed in Figure 5.20 thanks to the dialysis of the latex, the obtained paint-like films elongate more (passing from elongating 0.1% to 0.2%). Therefore, removing the water soluble species of the latex the interaction between CaCO₃ particles and polymer particles was enhanced. The water uptake of the obtained paint-like films was also measured and the graph can be observed in Figure 5.21.

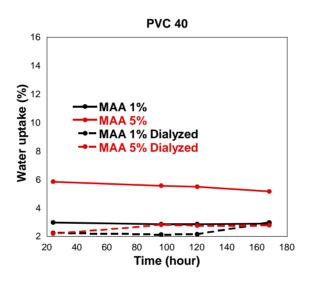


Figure 5.21. Water uptake absorption of paint-like films prepared with latex synthesized with 1 wbm% and 5 wbm% with and without dialyzing the latexes.

As it can be observed in Figure 5.21, when paint-like films were prepared after cleaning the latexes, the water absorption of the films was lower. This can be attributed both to a lower amount of hydrophilic species and to a better interaction between polymer particles and CaCO₃ particles, when no water soluble species were present in the medium.

The final properties of the paint-like films regarding the contact angle values, gloss values and scrub resistance were also measured and are shown in Table 5.11. Paint-like films properties prepared without the dialysis of the latexes are also shown for the sake of comparison.

Table 5.11. Contact angle, gloss and scrub values for paint-like films prepared after dialyzing the latex and without.

PVC 40	Contact angle	Gloss	Scrub
MMA/BA/MAA 1 wbm% (Dialyzed)	75±1	57±2	1400
MMA/BA/MAA 5 wbm% (Dialyzed)	82±2	53±2	-
MMA/BA/MAA 1 wbm%	78±3	52±1	1175
MMA/BA/MAA 5 wbm%	85±2	48±2	-

As it can be observed in Table 5.11 all the final paint-like films properties were better (lower contact angle values, higher gloss, and higher scrub resistance) when preparing blends after cleaning the latexes, which means that the presence of water soluble species harms the dispersion of the filler particles inside the paint-like film. However, it was expected to reach better properties when employing higher amount of the functional monomer in the synthesis of the latex, due to a higher incorporation of this on the surface of the polymer particles, which will enhance the interaction with CaCO₃ filler. This was not the case, and the reason might be the high Tg that the latex synthesized with MAA 5 wbm% present, which can cause a more difficult film formation process.

5.3.4 Study of the interaction of acrylic polymer-CaCO₃ particles by NMR

NMR measurements were carried out in order to study the interaction between latex of different natures and calcium carbonate particles. This was done by investigating the absorption of polymer particles on the surface of CaCO₃ particles. When preparing low solids content CaCO₃/acrylic polymer blends, polymer particles will absorb onto CaCO₃ particles and they will precipitate with filler particles in the medium. Therefore, the signal of polymer proton of the supernatant in ¹H-NMR spectrums will be decreased or completely lost. This means that a quantification of the polymer signals in the supernatant can lead to direct measurement of the absorption (by substraction from the total). Latexes of different natures, in this case in terms of functional monomer and surfactant type, should interact different with CaCO₃ particles, therefore, the absorption profile will be different and it will be possible to conclude which latex interacts best with the filler particles. To carry out these analysis a CaCO₃ sample from Sigma-Aldrich was used (purity of <99.99%).

Latex/CaCO₃ blends were prepared at different polymer-CaCO₃ ratios. Blends were mixed at high speed and were let for two days in order to obtain a complete adsorption and sedimentation of polymer particles on calcium carbonate particles. Afterwards, the supernatants were taken and directly added in the NMR tubes. From the NMR spectrum of the supernatant, the polymer protons in the region between 1-0.5 ppm were integrated and normalized. The obtained final results are shown in Figure 5.22. The absorption profiles for blends prepared with latexes containing different amounts of different functional monomers are depicted at the top part of the graph, whereas blends prepared with latexes containing different surfactants at the bottom.

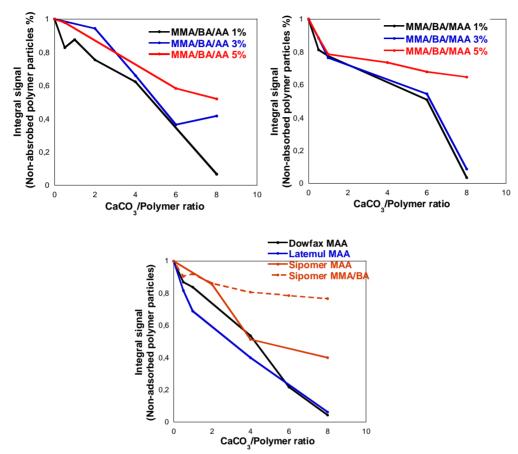


Figure 5.22. Normalized polymer protons integration between 1-0.5 ppm as a function of the CaCO₃/polymer ratio. At the top for blends prepared with different amounts of different functional monomers and at the bottom part blends prepared with different surfactants.

In Figure 5.22 it can be seen that when no CaCO₃ is added the total signal of the polymer is one, and after the addition of different of CaCO₃ ratios the signals of the polymer decrease, which prove the absorption of polymer particles onto CaCO₃ particles. Moreover, the

absorption profile was different depending on the latex used. First, it has to be said that when using lower amounts of the functional monomer, the polymer signal is completely lost at the 8:1 CaCO₃/polymer ratio, which was not the case for higher amounts of functional monomers (AA 3%, AA 5% and MAA 5%). In those cases, the polymer signals were not completely lost, which means that not all polymer particles were absorbed onto the surface of the filler particles. These results demonstrate that the increase of the amount of the functional monomers in the synthesis of the latex leads to a worse interaction between polymer-CaCO₃ particles.

At the bottom graph, the absorption profile with latexes synthesized with different surfactants can be observed. When preparing the blends with the latex synthesized with Sipomer Pam-200 and without the functional monomer the polymer signals remained practically constant at the whole CaCO₃/polymer ratio, which means a weak interaction between the polymer particles and the filler particles, due to the absence of the functional monomer. Moreover, different absorption profiles were observed between the different surfactant employed. At the 8:1 CaCO₃/polymer ratio the polymer signals are completely lost when using Laternul PD-104 and Dowfax 2A1 surfactant, while the signal for Sipomer Pam-200 still remained. This means a lower affinity of the polymer particles to CaCO₃ particles when Sipomer surfactant is used. Moreover, at lower CaCO₃ to polymer ratios (2:1), it can be observed that the absorption with Laternul is more significant, as the remaining polymer signal is lower in comparison with Dowfax. Therefore, the interaction between polymer particles and CaCO₃ particles is enhanced when employing Laternul PD-104 surfactant.

In order to study the effect of the water soluble oligomeric species of the latexes on the interaction with CaCO₃ particles, the absorption of the polymer particles on the surface of CaCO₃ particles was studied after dialyzing the latexes. The obtained results when using dialyzed and non-dialyzed latexes are shown in Figure 5.23.

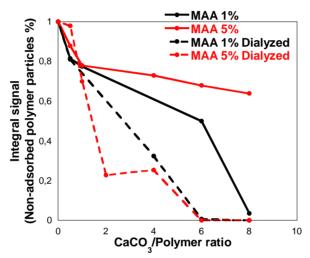


Figure 5.23. Normalized polymer protons integration between 1-0.5 ppm as a function of the CaCO₃ /polymer ratio when using dialyzed and non-dialyzed latexes.

As it can be observed in Figure 5.23, after the latexes were dialyzed the signal of the non absorbed polymer particles is lower for all the CaCO₃/Polymer ratios. This means that higher amount of polymer particles are absorbed onto CaCO₃ filler particles after the latexes were dialyzed. Therefore, this proves again that the water soluble species interfere with the interaction between acrylic polymer particles and CaCO₃ polymer particles.

5.3.5 Study of the interaction of surfactant-CaCO₃ particles by NMR

It has been already seen that the presence of different surfactants in the latexes affect the interaction of binders and CaCO₃, and as a consequence the final properties of paint-like blends. However, in order to shed more light on this effect, the adsorption of pure surfactants on CaCO₃ was also studied. Following the same procedure that in the section before (5.3.4), the absorption capacity of the different surfactants on CaCO₃ filler particles was checked by ¹H-NMR studies. The obtained results can be observed in Figure 5.24.

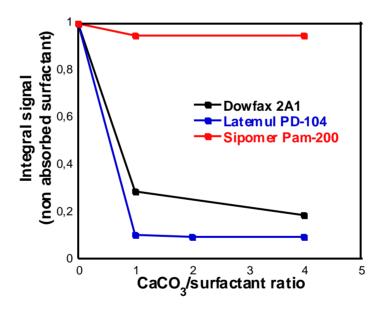


Figure 5.24. Normalized surfactant protons integration as a function of the ratio CaCO₃/surfactant for different surfactants.

As it can be observed in Figure 5.24, when preparing the blends with Sipomer Pam-200 surfactant, the proton signal of the surfactant remained practically constant at the whole CaCO₃/polymer ratio, which means a weak interaction between this surfactant and the CaCO₃ filler. However, when employing Dowfax 2A1 or Laternul PD 104 surfactant, the surfactant signals are almost lost at the 4:1 CaCO₃/surfactant ratio, which means a high affinity of these surfactants for CaCO₃ filler. Moreover, the signal loss is more significantly with Laternul PD 104 surfactant, which proves that the best interaction with CaCO₃ is achieved with Laternul PD-104 surfactant.

5.4 Summary and conclusions

Different latexes were synthesized with different amounts of different functional monomer and with different surfactant types. Waterborne-like paints were prepared without the use of any additive, only blending these latexes with CaCO₃ filler at different PVC values. This was possible thanks to the strategy employed, in which a mill base was not prepared and CaCO₃ powder was directly added to diluted latexes. Stable blends and good rheology profiles were obtained. It is worthy to mention that removing NaPA, some CaCO₃ agglomerates can be obtained in the paint-like films, but the elimination of this component allows to better see the interaction between different latexes nature and calcium carbonate filler particles. For example, when paint like-films were prepared with latexes synthesized without the functional monomer, blends coagulated. This incompatibility was not possible to be detected before due to presence of NaPA.

From waterborne-like paints prepared with different amounts of different functional monomers different conclusions were achieved. The rheology of the final paint-like blends

increased with increasing the amount of functional monomer (due to the increase of oligomers in the aqueous phase), and when IA was used as functional monomer, the viscosity increased sharply.

AFM images showed that the dispersion of calcium carbonate particles was better with low amount of functional. The contact angle values were lower with lower amounts of functional monomer and for MAA functional monomers, and the gloss was higher in these cases. Moreover, the mechanical properties were more elastic with lower amount of functional monomer and slightly higher maximum elongation and higher toughness values were achieved when the paint-like films were prepared with latex synthesized with MAA functional monomer. Regarding the water uptake measurements, paint-like films prepared with low amount of functional monomer and with MAA absorbed less water and the scrub resistance was better.

In order to sum up all the paint-like properties described above, a 3D graph was designed in which all the final properties were taken into consideration in order to conclude which amount and which functional monomer gives the best performances. To carry out this, for each property the maximum punctuation was given to the paint-like film with the best performances, and the lowest punctuation to the worse blend. Afterwards, the scores were summed up and the obtained results are showed in Figure 5.25.

In that 3D it can be clearly seen that better final paint-like film properties were obtained with low amount of functional monomers and for MAA functional monomer. On the contrary, worse performances were obtained with high amount of functional monomers and for IA functional monomer.

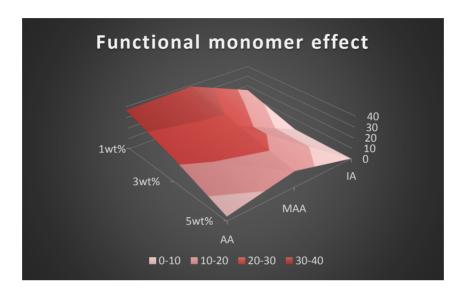


Figure 5.25. Effect of the different amounts and different functional monomer in paint-like films properties.

In order to eliminate the possible effect of water-soluble species of the latexes in the final paint-like films properties, latexes were dialyzed and blends were prepared from them. With the removal of these water soluble species better final properties were achieved, which means that water-soluble species are able to harm the dispersion of the CaCO₃ filler particles. Unfortunately, this water-soluble oligomers are not able to disperse CaCO₃ filler particles, because the molar mass of the water-soluble oligomer is too low.

Regarding blends prepared with latex synthesized with different surfactants, slightly lower contact angles values and slightly higher gloss values were obtained when employing Laternul PD-104 surfactant. Moreover, the mechanical properties for paint-like films prepared with latex synthesized with Laternul PD-104 were more elastic and better scrub resistances were achieved. A 3D graph was also done (Figure 5.26) for paint-like films prepared with latexes synthesized

with different surfactants and different functional monomers, in order to be able to visually see which latex gives the best properties.

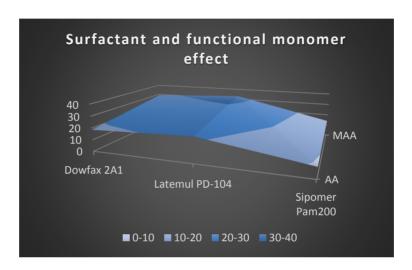


Figure 5.26. Effect of surfactant and functional monomer type on paint-like films properties.

As it can be seen in Figure 5.26, better final paint-like performances were achieved when employing Laternul PD-104 surfactant, which means that when employing this surfactant polymer particle-CaCO₃ interaction is enhanced. Unfortunately, paints prepared with this latex absorb more water, due to the high amount of this surfactant in the synthesis of the latex in comparison with latexes prepared with Sipomer Pam-200 and Dowfax 2A1. The worse paint-like film properties were obtained when employing Sipomer Pam-200.

The interaction between different latexes and calcium carbonate particles was also studied by ¹H-NMR studies. By this technique it was possible to conclude what previously was showed;

Calcium carbonate filler interacts better with latexes synthesized with Laternul PD-104 surfactant, using MAA as functional monomer and with low amount of functional monomers. Moreover, the interaction between polymer-filler particles is better without the presence of water soluble components.

5.5 References

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Chapter 6. Conclusions

The main objective of this thesis was to study the main parameters affecting the interaction between CaCO₃ filler and acrylic polymer, in order to improve the final performances of coatings and to be able to add as much filler as possible without losing the final properties. The great challenge of this work has been to prepare CaCO₃/acrylic latex blends with applicable rheology, using as less additive as possible, to completely isolate the study of the interaction between both components.

Along this work, different poly (methyl methacrylate-co butyl acrylate) P(MMA/BA) (50/50) latexes were synthesized by seeded semi-batch emulsion polymerization to afterwards prepare the paints or paint-like blends with CaCO₃.

After measuring the zeta potential of both polymer particles and CaCO₃ particles, it was decided to prepare blends at pH of 9, because at that pH both particles showed the same surface charge, which provides repulsive forces between both particles and the achievement of colloidally stable blends. Initially NaPA was used as a reference CaCO₃ dispersing agent in order to produce blends with the acrylic latexes. The optimum amount of NaPA needed to stabilize CaCO₃ particles was calculated by measuring the viscosity, zeta potential and particle size as

function of different amounts of NaPA added to the CaCO₃ dispersion. According to these measurements, it was concluded that 0.4 wt% of NaPA based on the weight of calcium carbonate was needed to well disperse filler particles.

Different approaches were developed to prepare stable CaCO₃/acrylic latex blends and with applicable rheology. First, blends were prepared by dispersing the pigment, the NaPA and the thickener in water, the so-called mill base and afterwards blending the mill base with the latex at pH 9. Blends were prepared at different PVC ratios and with two different thickeners; a non associative thickener (HEC) and an associative one (HASE). The final paint-like properties were highly affected by the use of the thickener type; even the nature of the thickener played an important role on the CPVC value. Therefore, it was decide to remove the use of thickener in CaCO₃/acrylic latex blends.

The preparation of CaCO₃/acrylic latex blends without any thickener was possible thanks to the increase of solids content of both the latex and the mill base. Blends were prepared at different PVC values and with different nature of acrylic binder, in terms of different particle sizes (120 nm, 300 nm and 600 nm), functional monomer (with or without functional monomer) and surface coverage by carboxylic acid moieties (different synthesis pH). It was seen that paint-like films prepared with the acrylic acid functional monomer showed slightly better properties than those prepared without any functional monomer. It was also seen that better properties were achieved when synthesizing the latex under acidic conditions rather than basic conditions, due to a higher incorporation of the carboxylic acid functional group in the surface of the polymer particles. Moreover, better final properties were achieved when using the acrylic latex of the smallest particle size (120 nm). Paint-like films with higher PVC values without complete loosing

of the properties were achieved in this case. Polymer particle with smaller particle size, present a higher surface area, which turned out to enhance the interaction with CaCO₃ filler.

In the next step, the effect of different functional monomers and different surfactants in the synthesis of the latex on final paint properties was studied. With the aim to prepare the less amount of paints possible, waterborne paints were prepared with the combination of a design of experiment (DOE) and high throughput experiments (HTE).

Fully formulated waterborne paints were prepared with latexes synthesized with 1 wbm% of AA, MAA, and acrylamide and one latex synthesized with both AA and Acrylamide adding 1 wbm% of each one in the synthesis. The surfactant employed (at the same concentration in water) were a conventional surfactant Dowfax 2A1, and two polymerizable surfactants, Latemul PD-104 and Sipomer Pam-200.

Although waterborne paints prepared with the acrylamide functional monomer showed slightly worse final paint properties, no big differences were observed from one to another. Taking into account these results it was concluded that NaPA has high affinity for CaCO₃ particle surface and it hinders the effect of the different functional monomers of the latex. Moreover, some flocculation problems were observed, and it was concluded that it was because of the depletion flocculation caused by EHEC thickener.

In the case of waterborne paints prepared with latexes synthesized with different surfactants, the flocculation problem was solved by changing the thickener employed. Unfortunately, big differences were neither observed from one surfactant to another, and the reason was the same as previous; the use of the NaPA hindered the possible effects.

In order to see the effect of the different functional monomer and surfactant type used in the synthesis of the latexes on the final properties, paint-like blends were prepared without the use of NaPA dispersing agent. This was possible thanks to the direct addition of CaCO₃ powder to diluted latexes, instead of preparing a mill base before. In this case, latexes were prepared at acidic pH with MAA, AA and IA functional monomers at 1, 3 and 5 wbm%. Furthermore, latexes with the different surfactants were prepared with the same surfactants previously described.

Thanks to the preparation of blends without the use of NaPA it was seen that better final paint properties were obtained with the use of MAA functional monomer, and with low amount of functional monomers. This was seen by a higher gloss, a smoothness surface, more elastic mechanical properties and a higher resistance for the scrub measurements. On the other hand, the worse performances were achieved when using IA functional monomer and at high amounts of functional monomers. Moreover, some latexes were dialyzed in order to remove all the water soluble species and blends were prepared from these. With the removal of water soluble species better final performances were achieved, which means that these species harm the dispersion of CaCO₃ filler particles.

Regarding the differences given by latexes synthesized with different surfactants, best properties were obtained by those blends prepared with the latex synthesized with Laternul PD-104 surfactant and the worst performances for Sipomer Pam-200 surfactant.

The interaction between these latexes and calcium carbonate particles were also measured by ¹H-NMR studies. By this technique, the absorption capacity of the different latexes on the calcium carbonate surface was calculated. According to these NMR studies, calcium carbonate filler interacts better with latexes synthesized with Latemul PD-104 surfactant, using MAA

functional monomer and with low amount of functional monomers. Moreover, it was double checked that the interaction between polymer-filler particles is better without the presence of water soluble components.

Overall, it can be concluded saying that the interaction between CaCO₃ and acrylic polymers is enhanced when synthesizing the acrylic polymers at acidic conditions, with small particle size, with MAA functional monomer and at low amounts of functional monomers and with Laternul PD-104 surfactant.

List of publications and conference presentations

"Polimero akrilikoen eta kaltzio karbonatoaren arteko elkarrekintza pinturetan". Verónica Alvarez eta Maria Paulis. Materialen Zientzia eta Teknologia IV.Kongresuko lanen bilduma. Donostia, 2018ko Uztailak 2-3. ISBN 978-84-8081-608-3

"Effect of Acrylic Binder Type and Calcium Carbonate Filler Amount on the Properties of Paint-like Blends". Verónica Alvarez, Maria Paulis. Progress in Organic Coating, **2017**, 112, 210–218.

Effect of different amounts of different functional monomers on the final paint-like properties. Verónica Alvarez, Maria Paulis. To be submitted.

Effect of the surfactant type on the final paint-like properties Verónica Alvarez, Maria Paulis. To be submitted.

Erreologi modifikatzaileen eragina uretan disolbatutako pinturen propietateetan. Verónica Alvarez, Maria Paulis. To be submitted.

Oral presentations

"Effect of acrylic binder type and calcium carbonate amount on paint properties" V.Alvarez, M.Paulis. European Coating Technology. Berlin, October 2018.

"Effect of acrylic binder type and calcium carbonate amount on paint properties" V.Alvarez, M.Paulis.International Polymer Colloids Conference (IPCG). Arantzazu, June 2017.

"Effect of acrylic binder type and calcium carbonate amount on paint properties" V.Alvarez, M.Paulis. European Coating Show Conference. Nuremberg, March 2017.

Poster presentations

"Polimero akrilikoen eta kaltzio karbonatoaren arteko elkarrekintza pinturetan" V.Alvarez, M.Paulis. Materialen Zientzia eta teknologia IV. Donostia, July 2018.

"Effect of acrylic binder type and calcium carbonate amount on paint properties" V.Alvarez, M.Paulis. European Techical Coatings Congress (ETCC). Amsterdam, June 2018.

"Effect of acrylic binder type and calcium carbonate amount on paint properties" V.Alvarez, M.Paulis.International Polymer Colloids Conference (IPCG). Arantzazu, June 2017.

"Polimero akrilikoen eta kaltzio karbonatoaren arteko elkarrekintza pinturetan" V.Alvarez, M.Paulis, J.C. de la Cal. Materialen Zientzia eta teknologia III. Kongresua, Markina-Xemein, July 2016.

Laburpena eta ondorioak

1970garren hamarkadan erabilitako pinturen %90a disolbatzaile organikoetan disolbatutako pinturak ziren. Disolbatzaile organikoak bai ingurunerako bai giza gorputzarako toxikoak dira, beraz, gobernuek konposatu hauen erabilpena murrizteko edo guztiz eliminatzeko lege zorrotzak finkatu dituzte. Hori dela eta, gaur egungo sozietatean, uretan disolbatutako pinturek gero eta interes handia sortzen dute. Pinturak osagai asko nahasiz prestatzen dira, baina pigmentuak (ingurunean disolbaezinak diren partikula solidoak), latexa (uretan dauden partikula polimerikoen dispertsioa) eta ura, dira osagai nagusienak.

Pigmentuak bi kategoria desberdinetan bana daitezke: funtzionalak edo betegarriak. Funtzionalek (titanio dioxidoa, esate baterako), film propietateak hobetzen edo propietate berriak eskaintzen dituzte. Betegarriak, berriz, merkeagoak dira eta orokorrean formulazioaren balioa murrizteko erabiltzen dira. Europan gehien erabiltzen den betegarria kaltzio karbonatoa (CaCO₃) da.

Latexak emultsio-polimerizazioaren bidez sintetizatzen diren partikula polimerikoen dispertsioa uretan dira. Pinturen formulazioan latex akrilikoak erabilgarrienak dira, eta polimero akriliko zehatz baten hautaketa, pinturaren ezaugarri fisikoak zehazten du, bereziki gogortasunarekin erlazionatutakoak. Pinturen gutxi gorabeherakoen konposizioa hurrengoa da: % 64a butil akrilatoa (BA), % 35a metil metakrilatoa (MMA) eta %1a azido akrilikoa (AA). Konposizio honekin 0 °C-ko beira-trantsiziozko tenperatura lortzen da.

Konposatu hauetaz gain, pinturei aditibo desberdinak gehitzen zaizkie (hala nola: emulsifikatzaileak, biozidak, dispertsaileak, erreologi modifikatzaileak eta hezegarriak). Osagai hauek kantitate txikietan gehitzen dira, baina pinturen propietateetan eragin handia dute. Aditiboen artean bi dira aipagarrienak. Alde batetik, agente dispertsailea, zeina pigmentu partikulak ondo sakabanatzeko erabiltzen dena. Adibidez, CaCO₃ pigmenturako sodio poliakrilatoa (NaPA) oso ohikoa den dispertsatzailea da eta partikulen aglomerazioa saihesten du. Bestetik, erreologi modifikatzaileak oso garrantzitsuak dira baita, behar den aplikazioetarako erreologi profila egokia izateko. Bi erreologi modifikatzaile mota daude, asoziatiboak eta ezasoziatiboak. Ez asoziatiboak uretan disolbatzen dira eta bertan hedatuz pinturen ur fase librea murrizten dute. Asoziatiboak, berriz, talde hidrofoboak dituzten polimeroak dira eta pigmentu eta latexarekin interakzionatzen dute hiru dimentsiotako sare bat sortuz.

Pinturen formulazioan, pigmentu bolumen kontzentrazio parametroa (PVC) oso garrantzitsua da. PVC parametroak, sisteman dagoen pigmentu kantitatea nahaste osoarekin konparatuta adierazten du. Beraz, pintura baten PVC-aren balioa gero eta altuagoa izan, gero eta pigmentu ehuneko gehiago izango du eta polimero kantitate gutxiago.

$$PVC = \frac{\textit{Pigmentu bolumena}}{\textit{Pigmentu boluma+latex bolumena}} x \ 100$$

PVC balioak biziki eragingo du pinturaren propietateak, hala nola; uraren absortzioan eta propietate mekanikoetan. Beraz, aplikazio baterako, behar diren propietateen arabera PVC balioa egokitu daiteke. Gainera, pigmentu bolumen kontzentrazio kritiko (CPVC) jakin bat dago,

eta bertan, polimeroen gaitasuna pigmentu partikulak elkarren artean lotzeko gainkargatzen da. CPVC baliotik gora, pinturaren film propietateak okertzen dira.

Lan honen **helburua**, kaltzio karbonato (CaCO₃) betegarria eta latex akrilikoen arteko elkarrekintzan eragiten duten faktore nagusiak ikertzea da, pinturen prezioa murriztu ahal izateko. Horretarako, poli(metil metakrilato-butil akrilato) P(MMA/BA) latex desberdinak sintetizatu dira. Latex desberdinekin pigmentu/latex nahaste fisiko desberdinak prestatu dira, osagaien proportzioak aldatuz eta filmen propietateak (AFMko irudiak, propietate mekanikoak eta urradurarekiko erresistentzia) karakterizatu egin dira.

P(MMA/BA/AA) (49.5%/49.5%/1%) latex akrilikoa sintetizatu zen, emultsio polimerizazio erdi-jarraitu baten bitartez, 50-ko solido edukiaz eta 300 nm-ko partikula tamainaz. CaCO₃/P(MMA/BA/AA) nahasteak bi erreologi modifikatzaile desberdinekin prestatu ziren, berain arteko desberdintasunak aztertzeko, PVC balio desberdinetan. Horretarako, mill-base bat prestatu zen, %70ko solido edukiarekin. Mill-basea CaCO₃ partikulen dispertsioa uretan da, gehi NaPA (%0.4 CaCO₃ pisuan oinarrituta) eta gehi erreologi modifikatzaile (ez asoziatiboa, HEC edo asoziatiboa, HASE) gehituz. Pinturak mill-basea latexari (pH 9) gehituz lortu ziren eta pinturen propietateak karakterizatu egin ziren. Erreologi modifikatzaile batetik bestera pinturen propietateak oso desberdinak zirela ikusi zen. Gainera, HEC erabili zenean CPVC balioa PVC 50 eta 60 artean zegoela ikusi zen eta HASE erabiltzean PVC 40 eta 50 artean. Emaitzak hauek ikusita eta CaCO₃ eta polimero akrilikoen arteko elkarrekintza ikusi ahal izateko, erreologi modifikatzaileak nahasketetatik kentzea erabaki zen.

Beraz, CaCO₃/P(MMA/BA/AA) nahasteak erreologi modifikatzaileak erabili barik prestatu ziren. Hau posible izan zen latexaren solido edukina % 60-ra igotzen eta mill baseren solido edukina % 75-ra igoz. CaCO₃/polimero akriliko nahasketak latex desberdinekin prestatu ziren. Horretarako, latexak pH desberdinetan sintetizatutako ziren, polimeroen partikulen tamaina desberdinekin (120 nm. 300 nm eta 600 nm), eta AA monomero funtzionalaren presentziarekin eta erabili gabe ere. Pinturen azkenengo propietateak hobeak aurkitu ziren hurrengo kasuetan: latexak ingurune azidoan sintetizatu zirenean, polimeroen partikula tamaina txikia zenean eta monomero funtzionalaren presentziarekin. Hiru kasu hauetan pinturen filmeek distira hobeagoa, uraren absortzio eskasagoa eta propietate mekaniko elastikoagoak erakutsi zituzten.

Hurrengo atalean, latexak monomero funtzional desberdinekin eta emultsionatzaile desberdinekin sintetizatu ziren, hauek pinturen propietateetan duten eragina aztertzeko. Latexak, lehenik, azido akrilikoarekin, azido metakrilikoaren, eta akrilamida monomero funtzionalekin sintetizatu ziren (%1 monomeroekiko), eta latex bat bai azido akrilikoa eta bai akrilamida gehitzen (%1 monomeroekiko bakoitzeko). Bestetik, emultsionatzaile konbentzional bat (Dowfax 2A1) erabili zen eta bi emultsionatzaile polimerizagarri (Latemul PD-104 eta Sipomer Pam-200), kontzentrazioa berdinetan 6.84 mmol/L. Latex desberdin hauekin, denbora laburrean pintura gehien prestatu ahal izareko, esperimentuen diseinua, goi-mailako esperimentuekin konbinatu zen. Gainera, pintura hauek industrian formulatzen diren pinturak bezala prestatu ziren, hau da, aditibo guztiekin.

Akrilamida monomero funtzionalarekin prestatutako ur-pinturek propietate ez zirela hain onak ikusi zen, hala ere, ez ziren desberdintasun handirik ikusi ez monomero funtzional batetik bestera

ezta emultsionatzaile desberdinen artean ere. Emaitzak hauek kontutan hartuta, NaPA konposatuak CaCO₃ partikulen azalerekiko afinitate handia zuela eta, beraz, latex desberdinen izaera ikustea galarazten zuela postulatu zen.

Aurreko emaitzak direla eta, NaPA konposatua pinturetatik kentzea erabaki zen. Hau posiblea izan zen CaCO₃ hautsa latex diluituari zuzenean gehitzen, mill-base bat aurretik prestatu barik. Kasu honetan, latexak pH azidoan prestatu ziren, % 1, 3 eta 5 monomeroekiko, azido akrilikoa, azido metakrilikoa eta azido itakonikoarekin. Latexak ere prestatu ziren lehen aipatutako hiru emultsionatzaile der berdinekin.

Beraz, CaCO₃/ latex nahasteak inolako aditibo barik prestatu ziren eta honi esker latex batetik bestera diferentziak ikusi ziren. Propietate hobeak lortu ziren MAA monomero funtzionala erabiltzean eta monomero funtzional kantitate gutxirekin. Pintura hauek, distira handiagoa, gainazala leunago, propietate mekanikoak elastikoagoak eta urradurarekiko erresistentzia handiagoa erakutsi zuten. Bestalde, azido itakoniko monomero funtzionala erabiliz eta monomero funtzionalen kopuru handietan pinturen propietateak okerragoak izan ziren.

Latex batzuk dializatu egin ziren, uretan disolbagarriak diren espezie guztiak kentzeko. Eta, ondoren, nahasketak berriro prestatu ziren hauekin. Uretan disolbagarriak ziren espeziak kentzean, pinturen propietateak hobetu ziren. Horrek esan nahi du espezie horiek CaCO₃ betegarri partikulen dispertsioa kaltetzen dutela.

Bestetik, Latemul PD-104 emultsionatzaile erabiliz pinturen propietate hoberenak lortu ziren, eta aldiz Sipomer Pam-200 erabiliz propietate txarrenak.

Polimero akrilikoen eta kaltzio karbonato partikulen arteko elkarrekintzak ere ¹H-RMN bidez ikertu zen. Ikerketen hauen arabera, kaltzio karbonatoak afinitate gehiago zuela Latemul PD-104 emultsionatzailearekin sintetizatutako latexekin, MAA monomero funtzionalarekin eta monomero funtzional gutxi dutenekin latexekin ikusi zen. Gainera, polimeroen eta pigmentu partikulen arteko elkarrekintza uretan disolbagarriak dauden osagairik gabe, hobeagoa zela egiaztatu zen.

Ondorio nagusi bezala, esan daiteke, CaCO₃-aren eta polimero akrilikoaren arteko elkarrekintza hobetzen dela, latexa ingurune azidoan izanik, partikulen tamaina txikiarekin, MAA monomero funtzionalarekin eta monomero kantitate gutxi eta Latemul PD-104 emultsionatzailea erabiliz.

Appendix I. Latex characterization methods

I.1. Solids content and conversion

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

$$SC = \frac{Weight of the solid material}{Weight of the latex}$$
 (I.1)

The instantaneous conversion (X) was determined by the following equation,

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

Where, SC_i is the solids content, SW_1 is the fraction of initiator plus surfactant in the reactor and MW_1 is the fraction of monomer plus polymer in the reactor at the sample time.

I.2. Particle size and particle size distribution

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

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

I.3. Glass transition temperature (Tg)

The glass transition temperature of the polymers was analyzed by Differential Scanning Calorimetry, DSC (Q200, TA Instruments). The sample was cooled to -50 °C and then the analysis started by heating up to 200°C at 10°C/min.

I.4. Gel content

The gel content is considered as the fraction of polymer that is not soluble in a good common solvent such as tetrahydrofuran (THF). The gel fraction was determined by Soxhlet extraction.

To measure the gel content glass fiber square pads (CEM) were used as backing. A few drops of latex were placed on the filter (filter weight= W_1) and dried in the oven at 60 $^{\circ}$ C overnight. The filter together with the dried polymer was weighed (W_2) and a continuous extraction with

THF under reflux in the Soxhlet for 24 hours was done afterwards (I.1). After this period of time, the wet filter was dried in the oven and the weight of the dry sample was taken (W₃). Gel content was calculated as the ratio between the weight of the insoluble polymer fraction and that of the initial sample, as Equation I.3 shows.

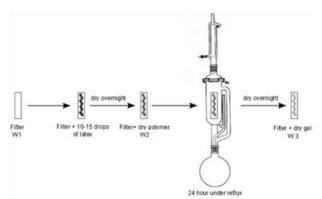


Figure I.1. Scheme of Soxhlet extraction method for gel content measurements.

Gel content (%) =
$$\frac{w_3 - w_1}{w_2 - w_1} \times 100$$
 (1.3)

I.5 Molecular weight

The molecular weight of the soluble polymer fraction (obtained by Soxhlet extraction) was determined by Size Exclusion Chromatography/ Gel Permeation Chromatography (SEC/GPC). The samples taken out from the Soxhlet were first dried, redissolved in THF to achieve a

concentration of about 0.1 % (g/mL) and filtered (polyamide Φ =45 µm) before injection into the SEC instrument. The set up consisted of a pump (LC-20A, Shimadzu), an autosampler (Waters 717), a differential refractometer (Waters 2410) and three columns in series (Styragel HR2, HR4 and HR6, with pore sizes ranging from 10^2 to 10^6 Å). Chromatograms were obtained at 35 °C using THF flow rate of 1 mL/min. The equipment was calibrated using polystyrene standards (5th order universal calibration) and therefore, the molecular weight was referred to PS.

The molar mass of the water-soluble oligomers in the latex synthesis were analysed by aqueous SEC/MALS/RI. The equipment was composed by a LC20 pump (Shimadzu) coupled to a miniDAWN Treos multiangle (3 angles) light scattering laser photometer equipped with an He-Ne laser (I¼658 nm) and an Optilab T-Rex differential refractometer (I¼658 nm) (all from Wyatt Technology Corp., USA). Separation was carried out using two columns in series (Ultrahydrogel 120 and 250, with pore sizes of 120 and 250 A°, respectively, Waters, Barcelona, Spain). The analyses were carried out at 35 °C and using 0.01 M NaNO3 solution as the mobile phase at a flow rate of 0.6 mL min.The dried polymers were dissolved in the mixed eluent at 1.0 mg/mL (0.01 M NaNO3) concentration and afterward there were filtered and injected (100 IL) into the equipment. The SEC/MALS/RI data was analysed by using the ASTRA software version 6.1. (Wyatt technology, USA). The relative molar masses were obtained from the calibration of the columns using water-soluble polyethylene glycol (PEG) standards with molecular weights in the range 2000-21 000 g/mol.

I.6 Partitioning of the carboxylic acid group

The carboxylic groups of the acid monomers can be present in the different phases of a latex: aqueous phase, surface of the particles and in the core of the particles. Therefore, the quantification of the acid groups was done in two parts.

I.6.1 Carboxylic group in the surface of the particles.

In order to measure the carboxylic acid groups present in the surface of the particles, titration was carried out. Previously to the titration the latexes were diluted (5 wt%) and cleaned by means of dialysis tubes (Spectra/Por®, MWCO: 12 000- 14 000). The entire dialysate volume was changed for fresh water at least once a day. Dialysis was allowed to run until the conductivity of the dialysate was close to that of the DDI water (2 µS/cm).

Afterwards, the acidity of the medium was adjusted to pH 3 by adding an aqueous solution of HCI to protonate all the acidic groups. The samples were then titrated with NaOH (0.015 M). As an example, the graphic obtained by titration of the MMA/BA/AA 300 nm latex synthesized at basic pH is shown in Figure I.2.

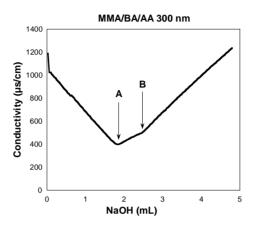


Figure I.2 Titration with NaOH (0.015 M) of MMA/BA/AA 300 nm latex synthesized at basic conditions.

During the titration (Figure I.2), NaOH reacts first with the strong acid groups (excess of hydrochloric acid). The concentration of H⁺ decreases by reaction with NaOH while the concentration of Na⁺ increases (conductivity decreases). When all the strong acid groups are consumed (A point), NaOH reacts with the carboxylic acid groups immediately accessible (carboxylic acid groups on the surface of the polymer particles). After all the carboxylic groups are neutralized (B point) the conductance increases due to the excess of OH⁻. Therefore, the carboxylic groups in the surface of the particles can be calculated, as the equivalent NaOH moles consumed between A and B.

I.6.2 Carboxylic groups in the water phase.

In order to calculate the carboxylic groups in the water phase, first the aqueous phase was separated from the polymer particles by ultracentrifugation. For this, latexes were introduced

in appropriate tubes and put into the ultracentrifuge (Cetrikon T-2190) with operation conditions of 60 min, 4 °C and 20000 rpm. This condition was enough to get clear serum. The amount of carboxylic acid groups in the water phase were calculated gravimetrically. First, the latex synthesized without the functional monomer was centrifuged, the water phase was taken and let to dry, in order to calculate the amount of water soluble species (such as remaining Dowfax and NaPS amounts). Afterwards, the rest of the latexes were centrifuged and they were left to dry in the same way in order to determine the acid monomer oligomers in the water phase. To the obtained value, the amount of soluble species in the latex synthesized without the use of any functional monomer was removed, and therefore the obtained values were the corresponding to the oligomers containing carboxylic acid groups in the water phase.

Appendix II. CaCO₃/acrylic latex blends characterization

II.1 Rheology measurments

The viscosity vs. shear rate of the latexes and CaCO₃/acrylic latex blends paints were measured using a rheometer from TA instruments (AR 1500 model). Measurements were carried out at 25 0 C by continuous increasing of shear rate from 0.1 to 10⁴ s⁻¹. A 40 mm flat plate of 50 micron gap was applied.

II.2 Blends stability

Blends stability was followed by studying the evolution of the backscattered light using the Turbiscan LAb^{expert} equipment. The reading head of this device consists of a pulsed near infrared light source (λ =880 nm) and two synchronous detectors. The transmission detector receives the light flux transmitted through the sample while the backscattering detector measures the backscattered light. The detection head scans the entire length of the sample (55 mm) acquiring transmission and backscattering data every 40 μ m. A representation of the equipment is presented in Figure I.1. The curves that are obtained provide the transmitted and

backscattered light flux in percentage relative to standards (suspension of monodisperse spheres and silicon oil) as a function of sample height (in mm).

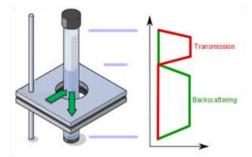


Figure I.1. Representation of the Turbiscan LAbexpert detection principle.

This technique allows very early visualization of creaming, sedimentation and coalescence/flocculation. Creaming takes place when the dispersed phase has a lower density than the continuous phase. It can be easily detected because the backscattering flux decreases at the bottom of the sample and increases at the top due to the increase in the dispersed phase concentration. Sedimentation takes place when the density of the disperse phase is greater than the continuous one. In this case, the backscattering increases at the bottom of the sample due to an increase in the sample concentration. Coalescence/flocculation leads to the fusion of interfaces increasing the droplet size. The particle size variation leads to a variation (usually a decrease) of the backscattering over the whole height of the sample.

II.3 Drying kinetics

The drying kinetics was followed with Adaptive Speckle Imaging Interferometry (ASII) with Horus® (formulaction). The principle of the measurements consists of sending laser light into the drying film. Part of the incident coherent light is adsorbed by the sample and the other part is scattered back and detected by the video camera through an interference image, also called Speckle image. During film formation, the sample udergoes some changes such as particle movement or refractive index changes; this activity causes temporal fluctuations in the scattered light and, consequently, random changes of light intensity on the Speckle image. The speed of light fluctuations (the Speckle rate) during the drying process is directly related to the motion of the scatteres inside the sample. The morion of the particles is strongly dependent on the viscosity of the film in the way that as water evaporates, viscosity rises and the scatters motion (Speckle rate) slows down. The main stages during film formation can therefore be associated with changes in the Speckle rate. To study the effect of the thickener type, samples were drawn on a glass substrate with a wet thickness of 150 μ m. In all the cases measurements were done at a relative humidity of 55 % and a temperature of 22 $^{\circ}$ C.

Appendix III. Waterborne film characterization

III.1 Characterization of waterborne paint-like films

III.1.1.AFM

AFM pictures were obtained using an atomic force microscope Veeco Nanoscope IV multimode in tapping mode with a tapping silicon cantilever equipped with a rotated monolithic silicon tio. The nominal resonant frequency of the cantilever was 150 kHz and the spring constant was 5 N/m. Films were formed by casting the blends onto a round silicon mould. In order to analyse the cross-section of the waterborne-like films, they were cut using a diamond knife by cryosection The roughness profiles of the films were extracted from the height images of the AFM micrographs.

III.1.2. Gloss

Relative surface gloss of the paints films was measured with a Glossmeter (micro-TRI-gloss) at incident angle of 85°. The measurement results of the glossmeter are related to the amount of reflected light from a black standard with a defined refractive index, and not to the amount of incident light. Films were cast in black substrates with 350 µm thickness. Each film was measured at three points on the film surface, and at least two films were measured for each sample in order to obtain an average gloss value and the standard deviation. Films were dried at 50 °C and 55% of humidity.

III.1.3 Water static contact angle

For the measurements of the water static contact angle, 150 µm wet thick films were cast onto glass substrate, and dried at 50 0 C and 55% relative humidity for one day. The measurements were carried out in a Contact Angle System OCA (Daraphysics) equipment, taking an average value from 20 measurements.

III.1.4. Water uptake

To measure the water uptake, latex films were cast into silicone moulds and dried at 50 $^{\circ}$ C and 55% relative humidity for a week. All the resulting films had the same weight. The obtained films were weight (m_o) and they were placed into different flasks full of distilled water. Then, they were removed from the flasks at given times, they were dried with paper and weighted (m₁). After weighting the films, they were placed again in their respective flasks.

$$Water uptake = \frac{m_t - m_o}{m_o} \times 100$$
 (III.1)

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

III.1.5. Mechanical properties

Tensile-testing

In order to assess the mechanical properties of the waterborne-like films, tensile tests were carried out. Films were first dried in Teflon moulds at 50 °C and 55 % relative humidity. Afterwards, films were cut in the dimensions given in Figure III.1.

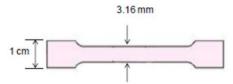


Figure III.1. Dimensions for the probe employed for the tensile test measurements.

Tensile tests were performed in a universal testing machine, TA.HD.plus texture analyser applying a crosshead speed of 25 mm/min to an approximate 0.5 mm thick film. At least five specimens of each film were tested, and the results were averaged.

Hardness

The hardness of the paint films were measured by Persoz pendulum hardness. This method evaluates the hardness by measuring the damping time of an oscillation pendulum. The measurements provide information about the coating film resistance to dampen vibrations. The paint films with a wet thickness of 350 μ m were applied to a metal substrate and dried for a week at 50 °C and 55% humidity.

Scrub measurements

The scrub resistance of the paint films was determined by washability according to the ASTM D2486 standard method. The paint films (wet thickness = $350 \, \mu m$) were applied to black plastic panels and dried for a week at 25 0 C and 55 % humidity. The coated panel was then scrubbed with a nylon bristle brush in an abrasive scrub medium until the paint film was removed in one continuous thin line. The number of back-and-forth strokes (cycles) required to remove the film was determined.

III.2 Characterization of waterborne paint-like films (AkzoNobel)

III.2.1Atomic Force Microscopy (AFM)

AFM pictures were obtained using an atomic force microscope Veeco Nanoscope V multimode in peak force tapping mode. The nominal resonant frequency of the cantilever was 300 kHz and the spring constant was 40 N/m. The roughness profiles of the films were extracted from the height images of the AFM micrographs.

III.2.2 Profilometer

The roughness of the surfaces were measured by an optical non-contact µscan explorer surface profilometer (nanofocus), which has the capability to capture 3D surface topographies.

The sensor employed was a CLA-1000 chromatic sensor, which is based on a confocal method. A light source sheds light on a very small point of the surface, and the sensor detects heightened light intensity when the object is in focus; on the contrary, it detects no light intensity when the object is out of focus. A spectrometer measures the heights through colour differences. The paints were prepared at 75 μ m thickness and the measurement speed was 500 μ m/s.

III.2.3 Gloss

Relative surface gloss of the paints films was measured with a Glossmeter (micro-TRI-gloss) at incident angle of 85° . The measurement results of the glossmeter are related to the amount of reflected light from a black standard with a defined refractive index, and not to the amount of incident light. Films were cast in black substrates with 6 mil ($152 \, \mu m$) thickness. Each film was measured at three points on the film surface, and at least two films were measured for each sample in order to obtain an average gloss value and the standard deviationRelative surface gloss of the paints films was measured with a Glossmeter (micro-TRI-gloss) at incident angle of 85° . The measurement results of the glossmeter are related to the amount of reflected light from a black standard with a defined refractive index, and not to the amount of incident light. Films were cast in black substrates with 6 mil ($152 \, \mu m$) thickness. Each film was measured at three points on the film surface, and at least two films were measured for each sample in order to obtain an average gloss value and the standard deviation

III.2.4 Spreading rate at 98%

Spreading rate is given in m²/L *i.e.* the area covered with a litre of paint. The Contrast Ratio is a ratio of the film's reflectance and absorbance over black and its reflectance and absorbance

over white. For this, four drawdowns were performed at different thicknesses and their individual spreading rates are calculated and plotted against their contrast ratios. The obtained graph (Figure 3) is used to determine the spreading rate at a given contrast ratio.

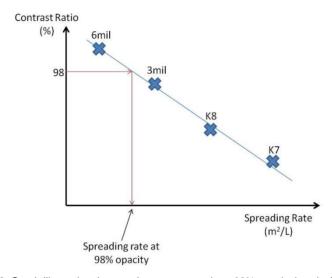


Figure III.2. Graph illustrating the way the constrast ratio at 98% opacity is calculated.

III.2.5 Weight loss after 200 cycles

Paints were drawn down on black panels, which are placed in a scrub machine (Figure 4), with abrasive pads and surfactant solution. After the panels are subjected to 200 scrub cycles the amount of paint lost is measured by weight.

Appendix IV. Supporting information of Chapter 5

IV.1 13C-NMR

¹³C-NMR measurements were carried out of the pure polymerizable surfactants (Latemul PD-104 and Sipomer Pam-200) and of the latexes after polymerization in order to assess the polymerization of the surfactants by monitoring in NMR the double signal intensity. The NMR spectra of the pure surfactants and at the end of the reaction are displayed for both Latemul PD-104 and Sipomer Pam-200 surfactants.

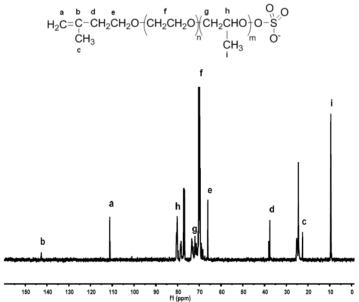


Figure IV.1. ¹³C-NMR spectra of Laternul PD-104 surfactant in D₂O.

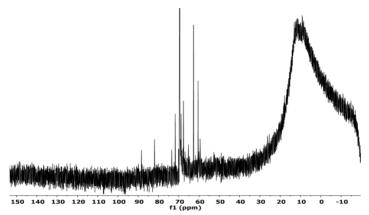
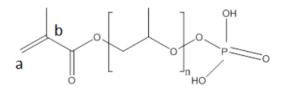


Figure IV.2. $^{\rm 13}\text{C-NMR}$ spectra of P(MMA/BA/MAA) polymerize with Laternul PD-104 surfactant in D_2O .



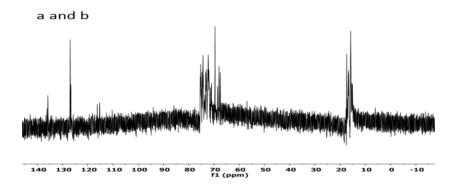


Figure IV.3. ¹³C-NMR spectra of Sipomer Pam-200.

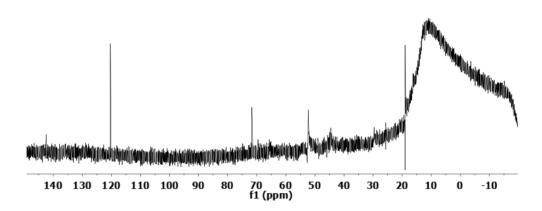


Figure IV.4- ¹³C-NMR spectra of P(MMA/BA/MAA) polymerized with Sipomer Pam-200 surfactant.

It could be clearly observed that the signal corresponding to the unsaturated carbon C, the ones appeared around 140 ppm for Laternul PD-104 and the ones around 124 and 135 ppm for Sipomer Pam-200 completely disappeared. This means that both surfactants have complete polymerized. Moreover, the "e" signal of the Laternul PD-104 surfactant can be observed in the final latex, which proves that the surfactant was chemically incorporated into the polymer particles during the polymerization process. In the case of the latex polymerized with Sipomer Pam-200 the NMR has to be repeated (at higher concentration), due to the low signal of peaks that can be observed. It has to been mentioned that the technical data sheet warms that Sipomer Pam-200 could rapidly homopolymerize when it is mixed with an initiator solution even without heating. Therefore, the disappearance of the unsaturated carbon can be due to the homopolymerization of the surfactant in the water phase.

IV.2 Rheology of the latexes

The latexes synthesized in Chapter 5 were neutralized with ammonium hydroxide and the rheological behaviour was analysed.

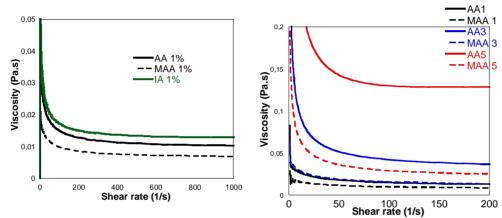


Figure IV.5 Viscosity profiles for the different latexes synthesized with different amounts of different functional monomers.

From Figure IV.5 it can be observed that latexes with AA functional monomer present higher viscosity profiles than MAA, but lower than IA. Moreover, when increasing the amount of functional monomer, the viscosity of the latex also increased. For all the latexes the particle size and the polydispersity was similar, therefore, the differences in viscosity is coming from the amount of acidic oligomers in the water phase. The more oligomers present in the aqueous phase, the higher the viscosity (IA>AA>MAA). Therefore, it can be concluded that the oligomers present in the water phase can act as thickeners for the latexes.

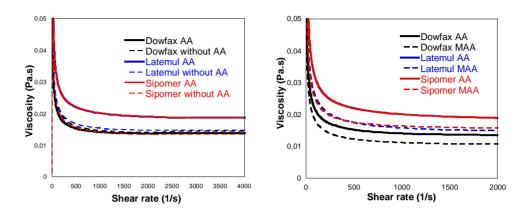


Figure IV.6. Viscosity profile of the latexes synthesized with different surfactant types and functional monomers.

In Figure IV.6 it can be observed that those latexes synthesized without any functional monomer have lower viscosity profiles. At basic conditions the acid groups present in the surface of the particles can be ionized and the layer expands from the particle surface. This expansion has a significant contribution on the hydrodynamic diameter of the polymer particles, leading to an effective increase in the volume fraction of the particles. That is the reason why latexes without functional monomers showed lower viscosity profiles. Moreover, it can be seen that those latexes synthesized with the polymerizable surfactants (Latemul and Sipomer) presented higher viscosity than latexes synthesized with the convectional one (Dowfax). A possible reason, can be that both polymerizable surfactants can homopolimerize in the aqueous phase, and these homopolymers would increase the viscosity. Latexes synthesized with the AA functional

monomer presented higher viscosity profiles than the latexes synthesized with MAA, tendency also observed in Figure IV.5.

IV.3 Mechanical properties of the latexes

The stress-strain curves of the latex films with different amount of different functional monomer are depicted in Figure IV.7.

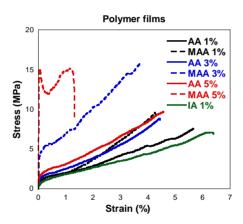


Figure IV.7 Mechanical properties of the latexes film synthesized with different amounts of different functional monomers.

As it can be observed in Figure IV.7, latex films were more brittle when increasing the amount of functional monomers in the synthesis. Moreover, latexes containing MAA were more brittle than latexes with AA and IA, but more tough. This fact was also observed with the high

increase in the glass transition temperature (Table 5.3) when MAA was used as functional monomer.

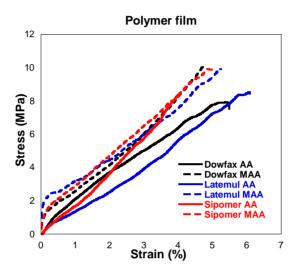


Figure IV.8. Mechanical properties for latexes synthesized with different surfactants.

It can be seen in Figure IV.8 that the mechanical properties were more or less the same independently on the surfactant type used during the polymerization process. Moreover, latexes prepared with the MAA functional monomer were more brittle, as it can be observed by the increase in the Young's modulus value.

IV.4 Water uptake of the latexes films

The evolution of water uptake for films obtained from latexes with different functional monomers can be observed in Figure IV.9 and the weight loss of the films after water uptake experiment is shown in the legend of the graph. The water uptake evolution of the latexes containing AA 1% and MAA 1% can not be distinguished because they were identically the same.

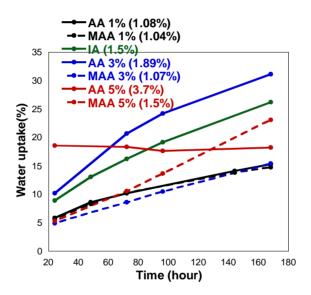


Figure IV.9. Water uptake of the polymer films synthesized with different amounts of different functional monomers.

In Figure IV.9 it can be observed that films presented an increasing water absorption along time, with the exception of AA 5% which presented a very fast initial absorption but afterwards the absorption did not continue and even a slight desorption was observed. The amount of water absorbed at the end of the experiment varied significantly depending on the functional monomer and amount employed during the synthesis. Increasing both the polarity (IA>AA>MAA) and the amount of functional monomers latexes, films turned to absorb more water.

In order to shed more light on these results, the weight loss of the films after the water uptake experiment was analysed (drying the films in the oven until a constant weight of the film was obtained). After water uptake experiments all the films lost weight. The fact that the films lose weight in water implies that water-soluble species (oligomers, salt and surfactant) diffused to the water phase during the water uptake experiment. As all the latexes were synthesized at acidic pH, the formation of water-soluble oligomers during the synthesis depends on the hydrophobicity of the functional monomer. The more hydrophilic functional monomer (IA > AA> MAA) would polymerize preferentially in the aqueous phase producing water-soluble oligomers, therefore more weight is lost from the films at the end of these experiments.

Figure IV.10 represents the evolution of water uptake for films obtained from latexes synthesized with different surfactant with acrylic acid and methacrylic acid functional monomers. Synthesis were carried out under acidic conditions (except for Sipomer).

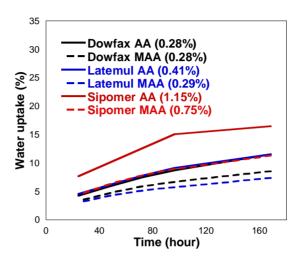


Figure IV.10. Water uptake for latexes synthesized with different surfactant types.

As it can be observed in Figure IV.10, the behaviour of the films was similar, namely, high amount of water was absorbed at the beginning of the experiment and during the rest of the days a slower increase was observed. It is worth to mention that although the amount of surfactant used during the polymerization was equivalent in moles (6.84 mmol/L), the weight percent (wt%) of surfactant in the films was not the same because the molecular weight of the surfactants differs from one to another (Latemul> Dowfax> Sipomer). Previous studies showed that the water uptake of the films at the end of the experiments were proportional to the surfactant amount used during the polymerization; namely the higher the surfactant amount, the higher the final water uptake, which was attributed to the presence of more hydrophilic groups into the film¹. According to this theory, latexes prepared with Sipomer Pam-200 should absorb less water, however, the

opposite effect was observed. To explain this it has to been taken into consideration that latexes synthesized with Sipomer Pam-200 were synthesized under neutral conditions.

Sipomer Pam-200 has a phosphate group in the structure and at very acidic or basic conditions the hydrolysis of the ester linkage and the phosphate group might occur. Due to the different pH during the synthesis, the formation of water-soluble species were favoured for latexes containing Sipomer PAM-200, therefore, polymer film obtained from these latexes are able to absorb more water.

Regarding the latexes synthesized with Laternul PD-104 and Dowfax 2A1 similar water absorption tendencies were observed. Once again it has been observed that latexes containing MAA absorbed less water than latexes containing AA, due to its lower polarity.

The weight loss of the films after the water uptake experiment was analysed, and the results are shown in legends of Figure IV.10. For latexes synthesized with different surfactants the weight loss of the films was lower than the surfactant weight, suggesting that independently of the surfactant type used, part of the surfactant remained in the film after water uptake experiments. However, higher amount was lost when employing Sipomer Pam-200 in the synthesis of the latex. This might suggest that Sipomer Pam-200 homopolymerize in the aqueous phase and after immersing the latex films into water these homopolymers diffuse to the aqueous phase. This could also explain the high water uptake of the latex films containing Sipomer Pam-200. It can also be observed that those latexes prepared with AA functional monomer lost more

water than those latexes prepared with MAA, demonstrating than when AA is used more water soluble oligomers are formed.

IV.5 Reference

 Ulrich, K., Centeno, S. A., Arslanoglu, J. & Del Federico, E. Absorption and diffusion measurements of water in acrylic paint films by single-sided NMR. *Prog. Org. Coatings* 71, 283–289 (2011).

Acronyms list

AA	Acrylic acid
AFM	Atomic Force Microscopy
BA	Butyl acrylate
CA	Contact angle
CPVC	Critical pigment volume concentration
DLS	Dynamic Light Scattering
DSC	Differential scanning Calorimetry
Dowfax 2A1	Dodecyl diphenyloxide disulfonate
Dp	Particle diameter
EHEC	Ethoxylated hydroxyethlycellulose
HEC	Hydroxylethylcellulose
HASE	Hydrophobically modified alkali soluble emulsion polymer
GCC	Ground calcium carbonate
GPC	Gel Permeation Chromatography
IA	Itaconic acid
kp	Propagation rate coefficient
MAA	Methacrylic acid
MMA	Methyl Methacrylate
Mw	Weight average molar mass
NMR	Nuclear Magnetic Resonance
NaPS	Sodium persulfate
Np	Number of particles
Np _{seed}	Number of particles in the seed
ñ	Average number of radicals per particle
PCC	Precipitated calcium carbonate
PMMA	Poly(methyl methacrylate)
PS	Polystyrene
PVC	Pigment volume concentration
S	Styrene
SC	Solids Content

SEM SR T	Scanning electron microscopy Spreading rate Temperature
TEM	Transmission Electron Microscopy
Tg	Glass transition temperature
THF	Tetrahydrofuran
TT	Tensile test
VOC	Volatile organic compounds
W	Whiteness
wbm	Weight based in monomer
wt	Total weight
Zp	Zeta potential