

Coagulation of Emulsion Polymers

Margarida Marques, Maria do Rosário Ribeiro¹, Nida Othman², Timothy McKenna³

1 Institute for Biotechnology and Bioengineering (IBB), Instituto Superior Técnico (IST), Universidade de Lisboa; 2 Laboratoire d'Automatique et de Génie des Procédés (LAGEP) UMR 5007; 3 Chemistry, Catalysis, Polymers and Processes (C2P2) UMR 5265

The stability of polystyrene particles produced by emulsion polymerization and stabilized by the anionic surfactant sodium dodecyl sulfate (SDS) was studied by turbidity measurements. Initially were analyzed the influence of latex particle size, solid content and particle size distribution on backscattering of light, using the TurbiscanTMLab and TurbiscanTMOn Line. It was found that the backscattering increases with particle size and solid content and is more sensitive to bigger particles when two latexes with different particle sizes are mixed. The use of TurbiscanTMOn Line with the simple force of gravity to analyze latexes with a high solid content is not advisable, since they do not flow properly. The influence of surfactant concentration, solid content and particle size on Hamaker constant was studied in TurbiscanTMLab with experiments in which coagulation between particles was induced by electrolyte addition. The results show that this constant is sensitive to the slope of the curves of stability in function of electrolyte concentration, $\log W$ vs C_E . To complement this project, it were analyzed two more polystyrene latexes stabilized with a clay, in which the effect of the clay concentration on Hamaker constant was studied. It was observed again the sensitivity of this constant to the slope.

Key words: Emulsion polymerization, sodium dodecyl sulfate, turbidity, coagulation, slope, Hamaker constant.

1. Introduction

Polymer latexes are used for a variety of industrial and scientific purposes, including the manufacture of water-based coatings, inks, packing material in chromatographic columns, and rapid agglutination medical diagnostic tests. ^{[1], [2], [3]}

Conventional emulsion polymerization (EP) is a heterogeneous process used to carry out free-radical polymerization reactions. A classical batch recipe contains: water, monomer(s), surfactant(s) and water soluble initiator(s). This process leads to colloidal polymer particles dispersed in a continuous medium, most often water. These polymeric dispersions are called latexes, emulsion polymers, polymer dispersions or polymer colloids. ^{[1], [4], [5]}

EP was first implemented at an industrial scale during the World War II with the aim to overcome the urgent need for synthetic rubber. From that moment, this kind of polymerization developed rapidly and is nowadays the process of choice to prepare a large variety of synthetic polymers. ^[4]

The chemical composition is one of the factors that affect the form and properties of the final product. The components are added before or during the polymerization. There are two phases in an emulsion, the dispersed (oil) phase containing the

monomers and other monomer-soluble components, and the continuous (aqueous) phase containing water-soluble components, such as surfactant and initiator. ^{[1], [4], [5], [6]} The surfactant, also known as a stabilizer or emulsifier, is an amphiphilic molecule, what means that have a hydrophobic and hydrophilic sections. This characteristic causes the partition between the two phases by adsorbing at the particle interface. When the surfactant is adsorbed at the interface, it keeps the particles separated since they are repelled due the electrostatic and/or steric stabilization mechanisms. This is one of the reasons why the use of surfactant is very important to prepare emulsions more colloidally stable ^{[4], [6]}

Coagulation leads formation of larger particle aggregates from smaller particles and/or individual particles in a colloidal dispersion. Is of major importance understand the factors that influence the coagulation in order to reduce or eliminate the coagulum. Colloidal stability is an important issue to master during an EP process. In the reaction or the plant, undesirable coagulation can be a problem when the latex is sheared through pumping or mixing; when the latex is frozen and then thawed; when additives are introduced into the latex and when the latex is stored for long periods of time at different temperatures. The formation of lumps due to coagulation can lead to reactor shut down, or degrade latex properties, plug

lines and filters, and cost money since they need to be removed (if possible).^{[1], [4], [7], [8]} Currently, the techniques used to detect physical destabilization are the naked eye or analytical methods, which are more accurate and reliable, such as microscopy, spectroscopy, turbidity and particle size analysis.

Particle size distribution

The particle size distribution (PSD) of a latex is one of the main parameters that influences the final quality of a latex. The PSD contributes to the surface aspects of films made from the latex, plays a role in the reaction kinetics, influences reaction stability, and can have an impact downstream on the way in which additives are absorbed, etc. High solid content latexes are an example of a product that requires an accurate control of the PSD, since their formulation usually requires a very well-defined PSD in order to maintain acceptable levels of viscosity. There are three major group techniques that can be used to measure the particle size and PSD. These techniques are based on microscopy (optical microscopy, electron microscopy, flow ultramicroscopy, dark field microscopy), light scattering (dynamic light scattering - DLS, laser diffraction) or on the movement of the particles (fractional creaming, disc centrifuge sedimentation, microfiltration, hydrodynamic chromatography, electrozone sensing). The choice of method to use depends on the size range of interest, the effort required, and the accuracy desired.^[4]

The electrostatic stabilization model and balance populations can be used to describe the distribution of particle size. In this approach, coagulation rate between the particles, β , must be determined for particles of different size. The model must accurately predict the coagulation based on their particle size to well represent the mean diameter, the mean number of particles of the latex and the PSD. For systems where the coagulation of particles is the only phenomenon that affects the density function, the balance populations, or the evolution of the PSD, is determined by^{1, [9]}

$$\frac{\partial f(m_i, t)}{\partial t} = -\frac{f(m_i, t)}{V_T} \int_{m_0}^{m_i} \beta(m_i, m_j) f(m_j, t) dm_j + \frac{1}{2V_T} \int_{m_0}^{m_i - m_0} \beta(m_i - m_j, m_j) f(m_i - m_j, t) f(m_j, t) dm_j \quad (1)$$

Where $f(m, t)dm$, V_T and $\beta(m_i, m_j)$ corresponds to the fraction of particles with mass between m and $m+dm$ (or density function); the reaction volume and the coagulation rate between two particles of masses m_i and m_j , respectively. The best way to determine β is to use the DLVO theory, described below.

¹ Valid only if coagulation occurs through 2-body collisions.

Electrostatic stabilization Model- DLVO theory

The colloidal properties of polymer latexes are determined by interactions between particles. If the latex is stabilized with ionic surfactants or/and charged groups on the surface of the particles (e.g., sulfate groups from initiators), the stabilization mechanism is based on the creation of electrostatic repulsive forces between polymer particles. The ionic species adsorb onto the particle surface, form a charged layer near the surface. The surface charges are in equilibrium with counterions in both inner and diffuse regions of the electrical double layer. These regions are called Stern region and Gouy-Chapman region, respectively. In the Stern region the counterions are strongly adsorbed onto ions of the particle surface. On the other hand, in the Gouy-Chapman region the counterions are freely distributed due to the lower attractive force between surface ions and counterions.^{[9], [10]}

Deryaguin, Landau, Verwey and Oberbeek (DLVO) used the representation described above to establish the DLVO theory with the aim to determine the interaction energy between two charged particles. This theory is applied to electrically charged surfaces submerged in a diluted solution of salts.

According to this theory, the total potential energy of interaction (V) can be determined as the sum of the attraction energy (V_A) and the repulsion energy (V_R):^{[9], [10]}

$$V = V_A + V_R \quad (2)$$

The attractive forces between polymer particles come from the interaction between the temporary dipole on one molecule and the induced on a neighboring one. The attractive energy is proportional to the semiempirical Hamaker constant, A , which depends on the polymer, the polarizability of atoms or molecules and the medium in which the particles are dispersed.^{[9], [10], [11]}

This model can be used for the theoretical description of the coagulation between particles with confidence. The coagulation rate of two particles of size i and j (β_{ij}) is related to Funch's stability ratio (W_{ij}):^{[9], [10]}

$$W_{ij} = 2(r_i + r_j) \int_0^{\infty} \frac{\exp\left(\frac{V}{K_B T}\right)}{R^2} dR \quad (3)$$

$$\beta_{ij} = \beta_{ji} = \frac{2k_B T (r_i + r_j)^2}{3\eta W_{ij} r_i r_j} \quad (4)$$

Where r_i , r_j , K_B , T , R and η correspond to the diameter of particle i in a two-body collision, the diameter of particle j in a two-body collision, the Boltzmann constant, the medium temperature, the center-to-center separation and the viscosity of the medium, respectively.

The Hamaker constant referred before is the only parameter that can be adjustable for the determination of the force balance between the polymer particles and the coagulation rates calculated in the DLVO model. This is why it's possible to use the model and experimental data to fit reasonable values for A. Since the Hamaker constant is related to attractive forces between the polymer particles, low values of this constant correspond to a higher stability of polymer particles due to the decrease of the attractive forces. [9],[10]

Turbidity

The models can be validated with experiments in which coagulation between polymer particles is induced by electrolyte addition. The stability/instability of polymer latexes can be evaluated with turbidity measurements using, for example, the device TurbiscanTMLab, which is the spearhead of the TurbiscanTM range to analyze quickly and accurately the stability of concentrated dispersions such as emulsions, suspensions and foams. [12] The TurbiscanTM uses multiple light scattering (MLS) to characterize concentrated liquid dispersions without dilution. The multiple light scattering consists of sending photons into the sample, using a pulsed near infrared light source (NIR, $\lambda=880$ nm). [12],[13] The most important item in the TurbiscanTMLab is a detection head which moves up and down along a flat-bottom cylindrical glass cell, where the sample is inserted. It is in this head that is located the NIR light source and two synchronous detectors, which can be seen in figure 1. The photons, after being scattered many times by the particles in the dispersion, emerge from the sample and are detected by the two detectors. The transmission detector (0° from light source) receives the light which goes through the sample, and the backscattering detector (135° from light source) receives the light scattered backward by the sample. With the TurbiscanTMLab it's possible to regulate the temperature between 4 and 60°C . [12],[13],[14],[15]

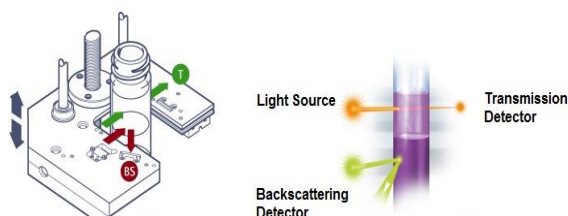


Figure1: Principle of TurbiscanTMLab measurement. [Adapted from [12],[13]]

The backscattered flux measured with TurbiscanTM depends on the penetration distance of the photon into the dispersion, l^* . [13],[14],[17],[18],[19]

$$R = \frac{1}{\sqrt{l^*}} \quad (5)$$

According to Mie theory, l^* is inversely proportional to the particle volume fraction, Φ , and proportional to their average diameter, d : [12],[13],[14],[15],[16]

$$l^*(\Phi, d) = \frac{2d}{3\Phi(1-g)Q_s} \quad (6)$$

The parameters g and Q_s corresponds to the asymmetry and extinction efficiency factors, respectively, and both depend on the average diameter, the wavelength of incident radiation and the refractive index of the dispersed and continuous medium.

Measurement of stability ratio:

The stability ratio, W , in homo-coagulation processes is given by the ratio of the rate of rapid to slow coagulation processes (equation 7), where τ is the turbidity and C_E the electrolyte concentration. The point of separation between the slow and the fast coagulation corresponds to an electrolyte concentration called critical coagulation concentration (CCC). [15],[16],[20]

$$W = \frac{(d\tau/dt)_{0,C_E > CCC}}{(d\tau/dt)_{0,C_E}} \quad (7)$$

If the electrolyte concentration is higher than CCC, the electrostatic repulsive forces are canceled and rapid coagulation occurs due the Brownian motion of the polymer particles. On the other hand, if the electrolyte concentration is below the CCC, coagulation is slower. [9],[10],[17]

According to Reerink and Overbeek [18] and Romero-Cano [22], the slope of the graph $\text{Log}W$ vs $\text{Log}C_E$ allows the calculation of Hamaker constant using the following equation if is used a symmetrical electrolyte:

$$A = \sqrt{\frac{1.73 \times 10^{-57} (\text{dlog}W/\text{dlog}C_E)^2}{r^2 \text{CCC}}} \quad (8)$$

2. Material and equipments

Styrene monomer (with inhibitor) was supplied by Acros Organics with a purity of 99%. Sodium dodecyl sulfate (99%, Acros Organics, and 98,5%, Sigma-Aldrich) was used as surfactant and potassium persulfate (99%, Sigma-Aldrich) as initiator. Sodium chloride (99,5%, Acros Organics) was used for the coagulation studies. To clean the latex was used a Dowex MR-3 (mixed bed ion-exchange resin), supplied by Sigma- Aldrich, and a glass wool used as a filter and

supplied by Roth. The clay used corresponds to Laponite® ($\text{Na}^{+}_{0.7}[(\text{Si}_8\text{Mg}_{5.5}\text{Li}_{0.3})\text{O}_{20}(\text{OH})_4]^{0.7-}$) which is a layered silicate manufactured from naturally occurring inorganic mineral sources and it is used to improve the performance and properties of a wide range of industrial and consumer products, such as surface coatings, household cleaners and personal care products. [23], [24]

Deionized water was used through the work.

All the reactions were carried out in a 1L jacketed glass reactor equipped with a 3-blade impeller. The pre-emulsion was introduced in a glass tank. The temperature of the reactor solution was controlled using a circulating water bath from Huber. In order to keep the emulsion well mixed, a stirrer from Ika. To pump the water from the bath and the pre-emulsion were used two pumps.

To measure the PSD was used the Mastersizer®3000 from Malvern and the average particle sizes were determined using the Zetasizer®Nano ZS from Malvern. The turbidity measures were performed in Turbiscan™Lab and Turbiscan™On Line, both from Formulacion and with the same principle of measure with the difference than in the first one the measurements are performed offline and in the second are performed online. The coagulation studies were performed only in Turbiscan™Lab.

3. Results and Discussion

Latex selection

In order to study the effect of particle size, solid content and particle size distribution on turbidity, four samples of polystyrene latexes were used (NB8, NB9, NB7 and NB10), which were synthesized in other project under a semi-batch process. All the components used to produce these latexes, as well as the particle diameter (D_p) and solid content (SC) of the final latex, are listed in table 1.

To analyze the effect of particle size, the samples to be compared should have the same solid content and different sizes. So, the samples NB8, NB9 and NB7 were selected.

To study the effect of solid content, the sample NB7 at 5, 10, 15 and 20%w/w were analyzed.

In order to study the effect of size distribution, the latex NB9 was mixed with NB10 in the proportions 7:3, 1:1 and 3:7. To perform correctly this study, both the latexes should have the same SC. So, before mixing, the latex NB10 was diluted until 20%w/w, which is the SC of sample NB9.

Table 1: Details of recipes for experiments, which results the samples NB8, NB9, NB7 and NB10, using SDS as surfactant.

Components	NB8	NB9	NB7	NB10
Water (g)	800	800	800	800
SDS (g/L _{water})	10	1.5	1	0.5
Monomer (reactor+pre-emulsion) (g/L _{water})	40+ 160	40+ 160	40+ 160	40+ 160
KPS (g/L _{water})	1.6	1.6	1.6	1.6
D_p (nm)	53	86	276	479
SC (%w/w)	20	20	20	23

During the reactions, different samples (not available to use in this research work) were extracted and the respective diameters and solids content were measured. With these data, the following graph was drawn:

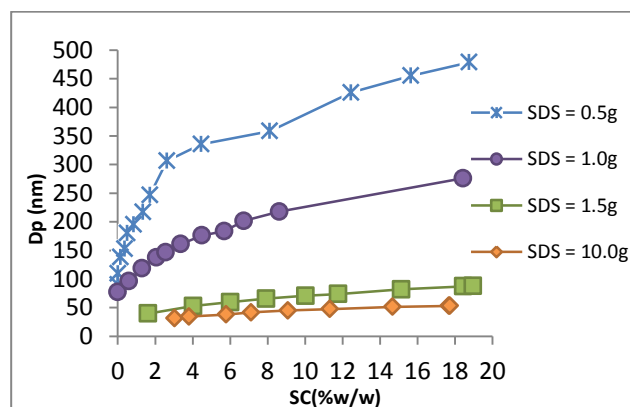


Figure 2: Evolution of particle diameter with solid content (%w/w) at different SDS concentrations.

Figure 2 is very useful to understand which reactions should be taken into account in order to use samples that can be comparable in coagulation studies.

To study the effect of SDS concentration on coagulation, only this parameter should vary between the samples to compare (the particle size and solid

content should be approximately the same). So, there were performed two new reactions, MM1 and MM2, synthesized with 1 and 0.5 g/L_{water} of SDS, respectively, in order to have more latex quantities to use in coagulation studies. During these reactions, different samples were taken. To perform this study the final latex of reaction MM1 (SC=19%w/w and D_p= 286nm), called MM1 final, and the 5th sample taken from the reactor during the reaction MM2 (SC=10%w/w and D_p=264nm), called MM2(5), were used. A certain amount of these latexes (the sufficient to perform all the tests) were diluted until 5% of SC and, then analyzed. In order to enrich this study, about 300ml of MM1 final was diluted until 6%w/w and cleaned² by repeatedly passing it over a mixture of anionic and cationic ion-exchange resins.³ After the washing step, a certain amount of the cleaned latex were transferred for 3 bottles and 1g/L_{water}, 2g/L_{water} and 3 g/L_{water} of SDS were added. Then, these 3 new latexes were studied. It was analyzed the coagulation in two more latex, called LP1 and LP2, which were not synthesized in this project and whose stabilization system was different. Here, instead of SDS was used a clay. The components and their quantities used in the polymerizations are inserted in table 3.

To study the effect of solid content the sample MM2 (5) was analyzed at 10, 5 and 2%w/w.

The influence of particle size was study comparing the MM2 (5) at 2% and the 2nd sample taken from the reactor (SC=2%w/w and D_p=157nm), called MM2 (2).

Table 2: Details of recipes for experiments MM1 and MM2 using SDS as surfactant.

Reaction	MM1	MM2
Water (g)	800	800
SDS (g/L _{water})	1	0.5
Monomer (reactor+pré-emulsion) (g/L _{water})	40+160	40+160
KPS (g/L _{water})	1.6	1.6

² Removal of surfactant, residual initiator and remaining monomer.

³ The withdrawal of the ionic species was monitored by measuring the latex conductivity, and it was assumed that the washing step was complete when the conductivity no longer decreased with successive passes over the resin. At the end of this procedure, the polymer content of the latex was around 5 %w/w.

Table 3: Details of recipes for experiments, which results the samples LP1 and LP2, using a clay as a stabilizer.

Components	LP1	LP2
Water (g)	800	
[clay] (g/L _{water})	1	2
Monomer (reactor+pré-emulsion) (g/L _{water})	40+160	
KPS (g/L _{water})	1.6	
D _p (nm)	251	240
SC(%w/w)	18	18

Effect of particle size and solid content- TurbiscanTMLab and TurbiscanTMOn Line

Relatively to the effect of particle size, the transmission, T, and backscattering, BS, of light were measured with TurbiscanTMLab and TurbiscanTMOn Line. The results are shown in figures 3 and 4, in which the abscissa axis corresponds to the particle size and the ordinate axis to the turbidity signal (percentage of transmission or percentage of backscattering).

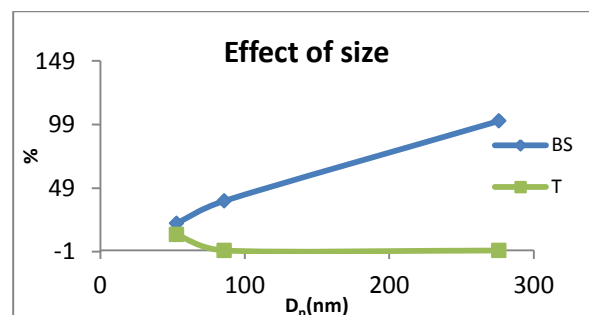


Figure 3: Transmission and backscattering of samples NB8(53nm), NB9(86nm) and NB7(276 nm) at 20%w/w, measured with TurbiscanTMLab.

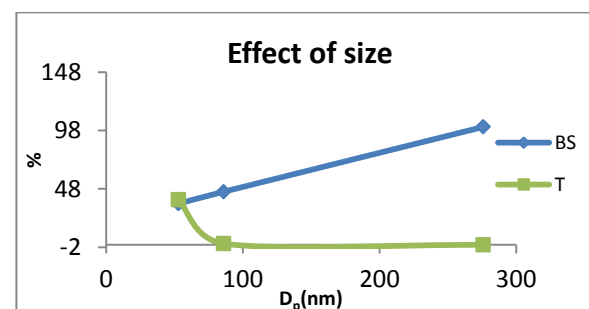


Figure 4: Transmission and backscattering of samples NB8(53nm), NB9(86nm) and NB7(276 nm) at 20%w/w, measured with TurbiscanTMOn Line.

Observing figures 3 and 4, it's concluded that the backscattering increases with the size, what was expected since the particles are smaller than the wavelength of incident light.⁴ It's important to notice that the only sample that transmits is the one with the smaller particles, the NB8. In Turbiscan™ On Line, the sample NB9 transmits around 1% of light.

Figure 5 shows the results for the study of solid content only on backscattering, since the sample NB7 don't transmit light. The abscissa axis corresponds to the solid content and the ordinate axis to the backscattering signal in percentage (%BS).

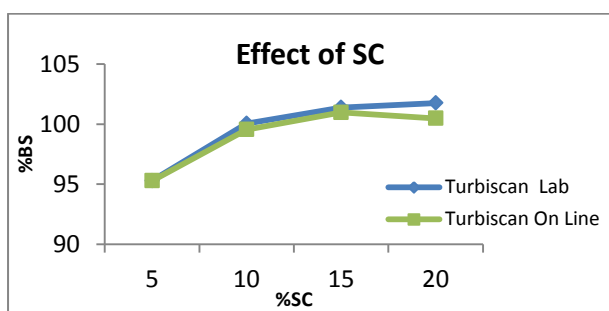


Figure 5: Backscattering of a sample NB7 (276nm) at different SC (%w/w), measured with Turbiscan™ Lab and Turbiscan™ On Line.

According to [12] when the concentration is higher than the critical concentration ($\Phi_c \approx 0.1\%$), there is no transmission signal (opaque product) and the backscattering level increases with an increase of concentration. This statement is clearly confirmed with this study. The values obtained with both devices are very similar. It's important to notice that the sample NB7 becomes saturated for a SC over the 10%. Therefore, the SC should be taken into account when working with these devices, in order to have reliable values.

During the measurements in Turbiscan™ On Line, the mass flow, Q_M , was also measured in order to know how the particle size and solid content affects the flowability of the latex, since wasn't used a pump (the latexes flowed with the force of gravity). The mass flow were determined with the mass obtained in the end (after the sensor), M_{total} , and the time that the latex took to pass through the pipes, t . More than 1 test was

performed for each sample. The mass flows are presented in tables 4 and 5.

Table 4: Mass flow of samples NB8 (53nm), NB9(86nm) and NB7(276 nm).

Sample	Nº of tests	M_{total} (g)	t(s)	Q_M (g/s)
NB8	1 st test	202	41	4.9
	2 nd test	192	25	7.7
	3 rd test	189	42	4.5
NB9	1 st test	205	24	8.5
	2 nd test	196	22	8,9
NB7	1 st test	185	34	5.5
	2 nd test	187	15	12.5
	3 rd test	179	21	8.5

Table 5: Mass flow of sample NB7 (276nm) at different SC (%w/w).

SC(%)	Nº of tests	M_{total} (g)	t(s)	Q_M (g/s)
5	1 st test	244	7	34.8
	2 nd test	209	46	4.5
	3 rd test	239	6	39.8
10	1 st test	248	10	24.8
	2 nd test	247	6	41.1
	3 rd test	215	7	30.6
15	1 st test	221	8	27.7
	2 nd test	219	8	27.3
	3 rd test	217	10	21.7
20	1 st test	202	41	4.9
	2 nd test	192	25	7.7
	3 rd test	189	42	4.5

The mass flow of sample NB9 was consistent in both tests. The same didn't happen with the samples NB8 and NB7. A possible explanation is the fact that there were bubbles of air inside the pipes preventing the good flow of latex. The particle size not affects significantly the flow. On the other hand, the solid content affects the latex flow, i.e., the higher the SC, more difficult it becomes to pass through the pipes and, consequently, more difficult is to analyze it with Turbiscan™ On Line.

Effect of particle size distribution- Turbiscan™ Lab

This study was performed in Turbiscan™ Lab being the results plotted in figure 6.

⁴ According to [7], [8], [9] and [12] an increase in size for particles with a size smaller than the wavelength of incident light (880nm) leads to an increase in backscattering.

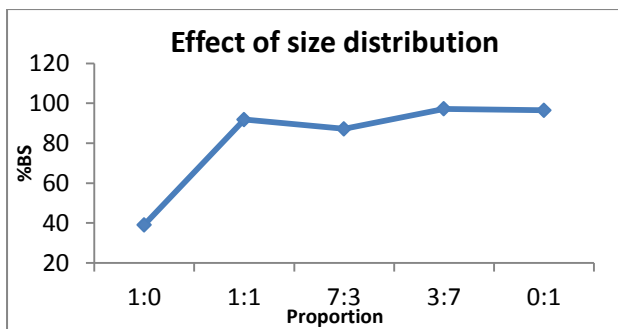


Figure 6: Backscattering values resulting from mixture NB9+NB10 at different proportions, measured with Turbiscan™ Lab.

Whatever the proportion, the backscattering is always closer to the backscattering of sample NB10 (proportion 0:1), what means that the backscattering is more affected by bigger particles.

Effect of SDS, solid content and particle size on Hamaker constant- Turbiscan™ Lab

The estimation of Hamaker constant was made with experiments in which coagulation between polymer particles was provoked by electrolyte addition, in this case NaCl.

Figures 7, 8 and 9 show the experimentally measured stability ratio versus electrolyte concentration (in logarithm) curves corresponding to the effect of SDS concentration, solid content and particle size. In addition to calculating the stability ratio, one can also determine the CCC of each latex sample. This concentration was obtained from the intercept with the abscissa of the logW-LogC_E plots, and the results are given in table 6, 7 and 8, jointly with Hamaker constants, which were calculated using equation (8). In order to enrich this work and to check if the method used to coagulate a latex is effective, it was induced the coagulation in other 2 polystyrene samples, which were stabilized with different amounts of a clay instead of SDS. The results can be seen in figure 10 and are resumed in table 9. Figure 11 shows the experimental curves for a SDS and clay concentration at 1g/L_{water}.

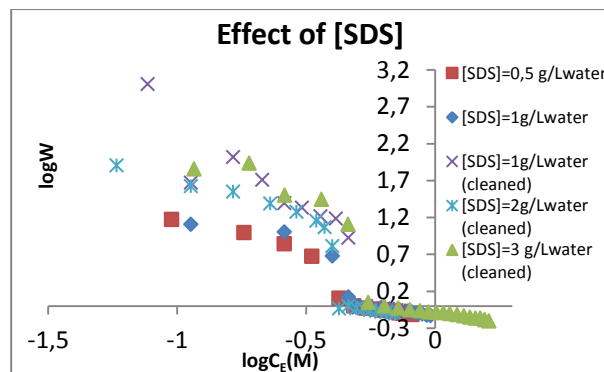


Figure 7: Experimental dependence of LogW on the LogC_E of samples stabilized with different amounts of SDS and with a SC of 5% w/w.

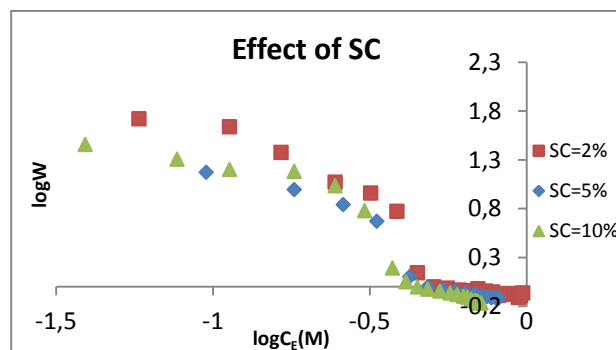


Figure 8: Experimental dependence of LogW on the LogC_E of sample MM2 (5) (D_p=264 nm) at different SC.

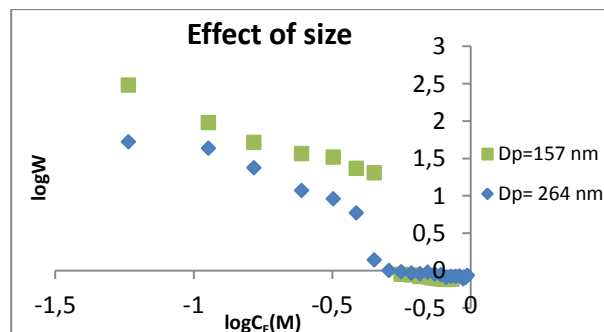


Figure 9: Experimental dependence of LogW on the LogC_E of samples MM2 (2) (D_p=157 nm) and MM2 (5) (D_p=264 nm) at 2%w/w.

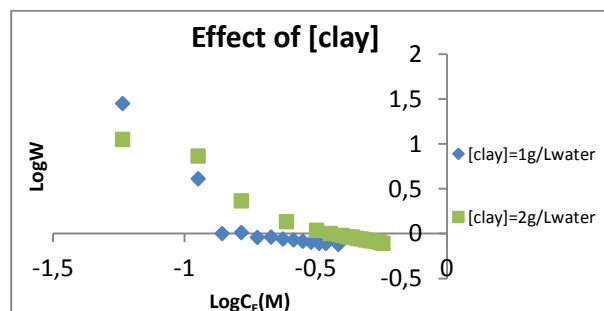


Figure 10: Experimental dependence of LogW on the LogC_E of samples LP1 and LP2 at 5%w/w, which were stabilized with 1 and 2 g/L_{water} of clay, respectively.

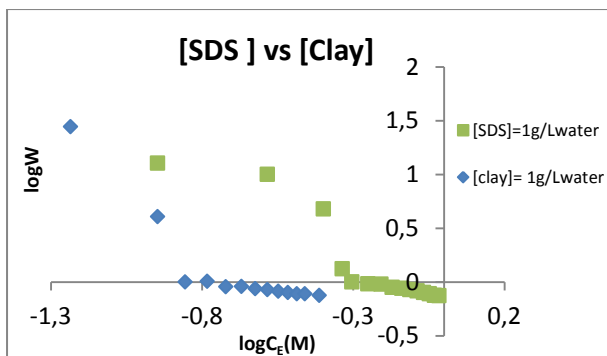


Figure 11: SDS concentration versus clay concentration at 1g/L_{water}.

Before analyze the values of CCC and A, it's important to notice that the 3 latex samples that were cleaned and to which were added surfactant, coagulate in a different way than the others. For 0.5 and 1g/L_{water} of SDS the polymer particles became bigger but remains dispersed. For 1, 2 and 3g/L_{water} (cleaned) the particles increased in size also but in the first two they sedimented and in the third they creamed. When a latex is cleaned, the charges are removed, some from the initiator and a lot from the surfactant. So, after washing a latex, there is very little surfactant and a little of initiator. Then, there is added a control amount of surfactant to the surface. It's expected that the destabilization of the latex that was cleaned to be a little different from those not cleaned, depending on the surface coverage. This could be a reason why the cleaned samples had a different behavior after coagulated. The more surfactant is added, the more different the surface will became and more difficult is to destabilize, and when destabilizes maybe the way that it happened is different. This could be an explanation for the creaming of the sample stabilized with 3g/L_{water} of SDS.

Another aspect that cannot be forgotten is that, according to Mastersizer[®] the cleaned samples didn't coagulate, since the PSD before and after the coagulation is practically the same. The reason why it happened is completely unknown.

Due to what was described above, it was decided to repeat the experiments for the latexes with 2 and 3g/L_{water} of SDS. For 2g/L_{water}, the particles sedimented again and for 3g/L_{water} the particles didn't sediment or creamed but remains dispersed, what means that for the first case, the latex destabilized in the same way but for the second destabilized in a different way, what is

inexplicable. According with PSD, both these samples didn't coagulate.

Table 6 shows that CCC increases with the increase of SDS concentration (except for the two cases of 2g/L_{water}) what was expected since latexes with a higher SDS concentration are more stable, what makes more difficult the coagulation. If the coagulation is more difficult, the CCC will increase. The values of Hamaker constant are more difficult to explain. This constant characterizes the attraction between the polymer particles.^{[10], [22]} Thus, low values of this constant correspond to a higher stability of polymer particles due to the decrease of the attractive forces. However, this trend wasn't observed. The Hamaker increases until 2g/L_{water} and then decreases, what makes difficult to explain how the SDS concentration affects this constant. One possible explanation is the high sensibility of this constant to the determined slope (dlogW/dlogC_E). In order to obtain the expected trend, and since the Hamaker constant is directly proportional to the slope and inversely proportional to the CCC, it should have been observed a decrease in slope or at least it should remain constant when the concentration of SDS increase. In literature there are some theoretical values for polystyrene-water systems determined by different models. These values are comprised between 0.4×10^{-21} and 4.8×10^{-21} J.^{[22], [25]} Except the Hamaker constant for 2g/L_{water} (2nd test), all the other values obtained in this work are within this range of values.

Observing table 7, the CCC decreases with the increase of solid content, what was expected, since the increase of solid content means that there are more polymer particles so, the probability of coalescence and then coagulation is higher. Regarding the Hamaker constant, it should increase with the solid content, since this constant measure the attraction force between polymer particles. So, higher values of this constant correspond to a lower stability. This trend was observed when comparing the values obtained for 5 and 10%. Moreover, all the values for the Hamaker constant are within the range of theoretical values given in [22] and [25].

According to [26], the DLVO approach and the concept of stability ratio, W, predict that the small particles are more easily coagulated than the larger

particles. However, the application of the theory in its kinetics forms (i.e., W criterion) to specific particle size effects has not been successful, since there are evidences in literature that the stability appears to decrease with increasing particle size^{[26], [27], [28]}. In this project, the application of the theory in its kinetics forms wasn't also successful since the stability decreases with the increase of particle size, what can be seen in figure 9. Table 8 shows that the CCC is higher for small particles, what means that the bigger particles coagulate more easily.

Reerink and Overbeek^[29] predicted that the slope of the curves $\log W - \log C_E$ should increase with particle size. However, it wasn't observed. In fact, the slope decrease with increasing particle size (see table 8). In [25], the theory predictions weren't also observed. The polystyrene particles are spherical and monodisperse so that neither the polydispersity or non-spherical shape can be invoked to explain this disagreement, as Reerink and Overbeek did to explain some results.

Ottewill and Shaw^[25] concluded that there is a variation, a decrease, of Hamaker constant with particle size. The same was noticed in this work, what can be seen in table 8. In literature there are some values of experimental Hamaker constant of polystyrene. These values are comprised between 0.5×10^{-21} and 50×10^{-21} J.^{[25], [28], [30] to [38]} The Hamaker constants found in this work are within this range.

The idea is to have more sizes to compare so a sample with a particle size of 425 nm (final sample of reaction MM2, called MM2 final) were coagulated 2 times, being the evolution of backscattering represented in figure 12. Until 0.3 M the backscattering is always increasing, decreasing after this point. A possible explanation for this behavior can be found in figure 4 of reference [12]. When the coagulation is being provoked, the particle size is increasing. Maybe, the 0.3 M

corresponds to the peak of the graph represented in this figure, reason why the backscattering increases and then decreases. With this profile was impossible to calculate the CCC.

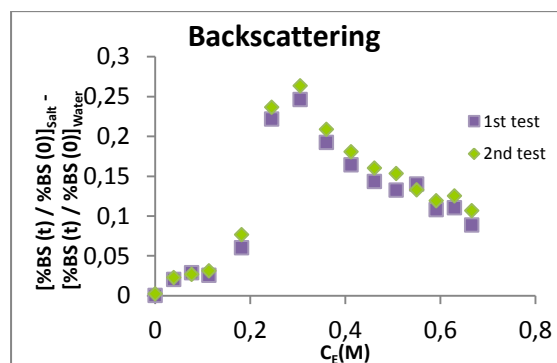


Figure 12: Evolution of backscattering with C_E of sample MM2 final at 2%w/w.

Figure 10 and table 9 shows that the CCC is higher for the sample stabilized with a higher amount of clay, what was expected. The Hamaker constant is in agreement with theory that affirms that this constant should decrease with the increase of surfactant, in this case a clay (notice that the clay is not a surfactant but performs the same function of stabilize the latex). It was also observed a variation in the slope of the curves $\log W - \log C_E$. It wasn't found literature about Hamaker constant with this stabilization system. However, the values obtained are similar to those obtained with SDS as surfactant.

Figure 11 shows that, at the same concentration, the polystyrene latex is more stable with the use of SDS.

Table 6: Values of CCC and A determined by turbidity measurements for the samples stabilized with different SDS concentrations.

[SDS](g/L _{water})	0.5	1	1 (cleaned)	2 (cleaned)	2 (cleaned)-2 nd test	3 (cleaned)	3 (cleaned)-2 nd test
r(nm)	132	143	155				
$-\frac{d \log W}{d \log C_E}$	4.3	7.5	10.4	11.9	18.5	6.0	5.0
CCC(M)	0.48	0.50	0.54	0.46	0.51	0.64	0.64
A(J)	1.9×10^{-21}	3.1×10^{-21}	3.8×10^{-21}	4.7×10^{-21}	7.7×10^{-21}	2.0×10^{-21}	1.7×10^{-21}

Table 7: Values of CCC and A determined by turbidity measurements for sample MM2 (5) at different SC.

SC(%w/w)	2	5	10
$-\frac{d \log W}{d \log C_E}$	6.7	4.3	4.4
CCC(M)	0.51	0.48	0.41
A(J)	3.0×10^{-21}	1.9×10^{-21}	2.2×10^{-21}

Table 8: Values of CCC and A determined by turbidity measurements for samples MM2 (2) (D_p=157 nm) and MM2 (5) (D_p=264 nm) at 2%w/w.

D _p (nm)	157	264
$-\frac{d \log W}{d \log C_E}$	10.2	6.7
CCC(M)	0.56	0.51
A(J)	7.2×10^{-21}	3.0×10^{-21}

Table 9: Values of CCC and A determined by turbidity measurements for samples LP1 and LP2 at 5%w/w.

[clay] (g/L _{water})	1	2
r(nm)	126	120
$-\frac{d \log W}{d \log C_E}$	3.6	1.8
CCC(M)	0.1	0.4
A(J)	3.2×10^{-21}	9.7×10^{-22}

4. Conclusions

The purpose of this research project was to develop experimental protocols with the TurbiscanTM devices to study the latex stability under different conditions and to identify key parameters influencing the results.

It were used four latexes, produced by emulsion polymerization and not synthesized in this project, with

the aim to study the effect of particle size, solid content and particle size distribution of the latex in turbidity, using the TurbiscanTMLab and TurbiscanTMOn Line. The interpretation of data shown that the backscattering is proportional to the particle size and solid content and is much more sensitive to bigger particles when 2 latexes with different sizes, but same solid content, are mixed. The use of TurbiscanTMOn Line with the simple force of gravity to analyze latexes with a high solid content is not advisable since they do not flow properly.

The effect of SDS concentration, of solid content and of particle size was study on coagulation. The main objectives were to determine the CCC and the Hamaker constant, an important parameter in coagulation models. To do so, were performed two styrene polymerizations using different amounts of surfactant. The coagulation was provoked by addition of an electrolyte, in this case NaCl. In order to clarify the effect of SDS on the Hamaker constant, the final polystyrene latex of one of this polymerizations was cleaned and used for coagulation studies upon addition of different concentrations of SDS. To acquire the data of backscattering was used the TurbiscanTMLab.

Latexes stabilized with a higher amount of surfactant should have a higher CCC, what was confirmed. An interesting thing was how the cleaned samples destabilized in a different way than the non cleaned ones when coagulation was induced. Regarding the Hamaker constant, it changes with the amount of SDS used. However is complicated to explain how the SDS concentration affects this constant, because no clear trend was observed. The uncertainty associated to the calculation of the slope of curves logW-logCE can be an explanation for this. Although it's not possible to

conclude how the surfactant affects the Hamaker constant, the order of magnitude of the values obtained is within the range of values found in the literature. Another interesting point was how the cleaned samples destabilized in a different way than the non cleaned ones when coagulation was induced.

Concerning the effect of the solid content on coagulation, a decrease of CCC value with the increase of the latex concentration, was observed. This behavior was the expected since the existence of more polymer particles in the latex leads to a higher probability of coagulation between them. Similarly to what happened with the Hamaker constants determined from the previous study, the values determined here do not follow a clear trend when increasing the solid content but are in the some order of magnitude of the ones found in literature.

In what concerns the effect of particle size on coagulation it could be expected that the particles with smaller sizes will tend to be more easily coagulated than the bigger ones. So, the CCC should be higher for bigger particles. However, this didn't happen. In fact, some authors predict an increase of the slope of the curves $\log W$ against CE with particle size and others show the opposite. In this work, it was observed that the slope is lower for the small particles. About the Hamaker constant, the values found are within the range reported in literature, and decrease with particle size, as already observed by other authors. The ideal will be to have more particle sizes to compare. Thus, a sample with a bigger particle size was coagulated. The results are interesting since during coagulation the backscattering profile increases until a certain electrolyte concentration, but after this point, it starts to decrease, what makes impossible the calculation of CCC and Hamaker constant. of CCC and Hamaker constant.

Finally, it was tested other stabilization system, using a clay instead the well known SDS. In this case, the CCC is proportional to the clay concentration and the Hamaker constant inversely proportional. It was observed that the system using $1\text{g/L}_{\text{water}}$ of SDS produces more stable latex than the one that uses a $1\text{g/L}_{\text{water}}$ of clay.

References:

- [1] Asua, J.M., Polymer Reaction Engineering, Blackwell Publishing Ltd, 2007.
- [2] Vanderhoff, J.W., van den Hul, H.J., Tausk, R.J.M and Overbeek, J.T.G., Clean Surfaces: Their Preparation and Characterization for Interfacial Studies, Marcel Dekker, New York, 1970.
- [3] El-Aasser, M.S., Poehlein, G.W., Ottewill, J.W., Goodwin, J.W., Science and Technology of Polymer Colloids, Vol. II, 1983.
- [4] Anderson, C.D., Daniels, E.S., Emulsion Polymerization and Latex Applications, Vol. 14, Number 4, 2003.
- [5] Vale, H., Population Balance Modeling of Emulsion Polymerization Reactors: Applications of Vinyl Chloride Polymerization, 2007.
- [6] Vieira, C.R., Novas Dispersões Aquosas com Morfologia Controlada para Revestimentos, 2013.
- [7] Mengual, O., Meunier, G., Cayré, I., Puech, K., Snabre, P., Turbiscan MA 2000: multiple light scattering measurement for concentrated emulsion and suspension instability analysis, 1999.
- [8] Mengual, O., Meunier, G., Cayré, I., Puech, K., Snabre, P., Characterization of instability of concentrated dispersions by a new optical analyser : the Turbiscan MA 1000, 1999.
- [9] Heredia, M.F., Modélisation de Procédés pour la synthèse de latex multipopulés, 1992.
- [10] Heredia, M.F., Graillat, C., McKenna, T., Coagulation of Anionically stabilized Polymer Particles, 2004.
- [11] Hamaker, H.C., Physica, 4, 1508, 1937.
- [12] Stability of Pigment Inkjet Inks, Formulacion, 2009.
- [13] Turbiscan Lab, Guide d'utilisation, Formulacion.
- [14] Mengual, O., Meunier, G., Cayré, I., Puech, K., Snabre, P., Turbiscan MA 2000: multiple light scattering measurement for concentrated emulsion and suspension instability analysis, 1999.
- [15] Mengual, O., Meunier, G., Cayré, I., Puech, K., Snabre, P., Characterization of instability of concentrated dispersions by a new optical analyser : the Turbiscan MA 1000, 1999.
- [16] Abismail, B., Canselier, J.P., Wilhelm, A.M., Delmas, H., Gourdon, C., Emulsification processes: on-line study by multiple light scattering measurements, 2000.
- [17] Santos, A., Santos, A.F., Sayer, C., Araújo, P.H. H., Heredia, M. F., Coagulation of Carboxylic Acid-Functionalized Latexes, 2008.
- [18] Verwey, E. J. W., Overbeek, J.Th.G ; Theory of Stability of Lyophobic Colloids, The Interaction of Sol Particles having an Electric Double Layer; 1948.

- [22] Romero-Cano, M.S., Martín-Rodríguez, A., Chauveteau, G., de las Nieves, F.J., Colloidal Stabilization of Polystyrene Particles by Adsorption of Nonionic Surfactant, II. Electrosteric Stability Studies; 1997.
- [23] Dyab, A.K.F., Al-Lohedan, H.A., Essawy, H.A., El-Mageed, A.I.A.A., Taha, F., Fabrication of core/shell hybrid organic-inorganic polymer microspheres via Pickering emulsion polymerization using laponite nanoparticles, 2011.
- [24] BYK Additives & Instruments, Technical Information B-RI 21, Laponite, Performance Additives
- [25] Ottewill, R.H., Shaw, J.N., Stability of Monodisperse Polystyrene Latex Dispersions of Various Sizes, 1966.
- [26] Wiese, G.R., Healy, T.W., Effect of Particle Size on Colloid Stability, 1969.
- [27] Mathews, B.A., Rhodes, C.T., J. Colloid Interface Sci., 1968, 28, 71.
- [28] Watillon, A., Joseph-Petit, A.M., Disc. Faraday Soc., 1966, 42, 143.
- [29] Reerink and Overbeek, Disc. Faraday Soc., 1954, 18, 74.
- [30] Watillon, A., Joseph-Petit, A.M., A. C. S. Symposium on Coagulation Coagulant Aids, 1963, p.61. Abstract
- [31] Curtis, A.S.G., Hocking, L., Trans. Faraday Soc, 1968, 66, 138.
- [32] Kotera, A., Furusawa, K., Kudo, K., Kolloid Z. Z. Polym., 1970, 240, 837.
- [33] Goldstein, B., Zimm, B.H., J. Chem. Phys., 1971, 54, 4408.
- [34] Krapp, H., and Walter, G.J., Colloid Interface Sci., 1972, 39, 421.
- [35] Schild, R.L., El-Aasser, M.S., Pehlein, G.W., Vanderhoff, J.W., "Emulsion lateses and Dispersions", 1978, p.99.
- [36] Bijsterbosch, G.H., Colloid Poly. Sci., 1978, 256, 343.
- [37] Ono, H., Jidai, E., Shibayama, K., Colloid Olym. Sci., 1975, 253, 114.
- [38] Tsaur, S-L., Fitch, R.M., Preparation and properties of Polystyrene Model Colloids, II. Effect of Surface Charge Density on Coagulation Behavior, 1986.