Colloidal and Rheological Properties of Natural Rubber Latex (NRL) Concentrated with Hydroxyethyl cellulose (HEC) and Sodium Dodecyl Sulphate (SDS)

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ABSTRACT

Natural Rubber Latex (NRL) is a complex colloidal system composed of rubber particles surrounded by a layer of phospholipids and proteins maintaining its colloidal stability. NRL creaming is a non-robust concentration method, and its colloidal and rheological properties can be altered due to the presence of creaming agents and surfactants. Both properties must remain stable over time after creaming to ensure conditions for subsequent manufacturing processes. These properties have been evaluated for synthetic latex but not for NRL in which phenological factors make system being always different. In this research, a creaming agent and surfactant selection was made allowing to choose HEC and SDS to concentrate NRL. Design of Experiments (DoE) with a response surface methodology was used to establish the optimal HEC and SDS concentration to obtain the more stable system and the rheological properties of creamed NRL. Flocculation and stabilization by depletion are involved on NRL concentration depending on HEC and SDS concentration. Those agents modify NRL colloidal stability in a range of -78 mV and -63 mV, and viscosity increases more than 10 times the raw NRL value. SDS plays a key role on enhancement of creaming process and in electrostatic stability because its anionic nature. Physicochemical interactions between NRL, HEC and SDS are proposed.

KEYWORDS

Natural rubber latex, creaming agent, surfactant, colloidal stability, rheology, depletion

OBJECTIVES

MAIN OBJECTIVE

To analyze the creaming agents and surfactants effect in colloidal and rheological properties to concentrate natural rubber latex from Bajo Cauca Antioqueño.

SPECIFIC OBJECTVES

OE1. To select a creaming agent and a surfactant that presents a high increase in Total Solid Content (TSC) of natural rubber latex.

OE2. To Analyze the changes over time in colloidal properties of concentrated natural rubber latex with creaming agent and surfactant addition by means of z-potential analysis.

OE3. To analyze the rheological properties of concentrated natural rubber latex with creaming agent and surfactant addition by means of rotational and oscillatory measurements.

1. INTRODUCTION

1.1. Natural Rubber Latex (NRL)

NRL is a colloidal suspension that emerges from laticiferous cells of the rubber tree *Hevea brasiliensis.* The continuous phase is water, also called serum (~50-60%) and the dispersed phase is mainly *cis-1-4,* poly isoprene chain (~35%) and small non-rubber species (~5%) that are proteins (~1,5%), phospholipids (~1,3%), carbohydrates (~1,5%) and minerals (~0,7%) [1]–[4]. The most widely accepted model for rubber particles is that are pear or sphere shaped with polymeric chain surrounded by a monolayer conformed by phospholipids and proteins [2], [5]–[8] as shown in **Figure 1.** Rubber molecules are arranged in a way that have their nonpolar chains packed together to form the rubber core and their polar ends pointing outward, forming an interface with serum. This minimized polar-nonpolar interaction makes the rubber particle spherical and causes it to be covered with the monolayer of phospholipids and proteins [7]. Due to the negative charge of long chain fatty acids, the ionization of carboxylic groups and positive charges from amino groups of proteins, the whole systems have a negative net charge [2], [9], [10]. The non- rubber particles also contribute significantly to system colloidal stability [3], [11] due to the presence of 'lutoids' in a 12-22% weight fraction in rubber latex and 'Frey-Wyssling' particles, and are present in a 2-3%. Colloidal stability on NRL can be measured by means of z-potential due to its electrostatic repulsions of their negative net charge. Normally, a colloidal system as NRL particles has a stability range between -30 mV and -70mV [12], being the most negative the most stable value. Moreover, ammonia is added to the fresh dispersion to avoid spontaneous coagulation in field, this component increase alkalinity and also anionic repulsions between particles and its presence affect stabilization on time [7]. NRL is a complex colloidal system because environment factors as the phenological stage, clones and soil nutrients can influence the colloidal stability and also, properties as thermal, rheological, size and yield rate measured by dry rubber content (DRC) [2].

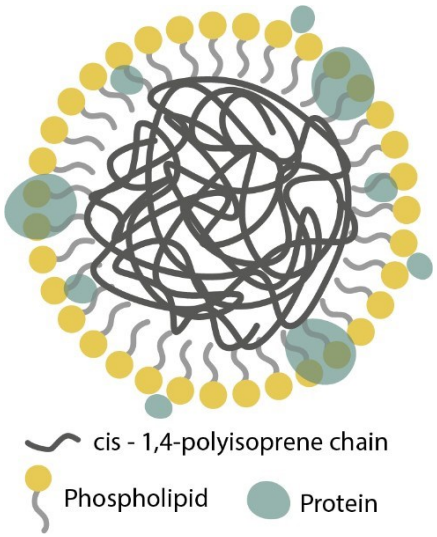

Figure 1. Rubber particle proposal conformation based on [3].

1.2. Creaming process in NRL

NRL concentration or creaming is a typical process used to enhance rubber content on latex batches to form final products, and also make sustainable transportation [13]. Despite this, concentration method affects NRL properties. In this method the physical and chemical phenomena allows to concentrate latex particles by the movement of rubber particles under gravity to form a concentrated layer at the top of the dispersion [14]. Creaming velocity depends on gravity (g), particle density (ρ) and continuous phase density ($\rho_!$), viscosity of aqueous medium (ɲ) and size of particles (a) and it is represented by Stokes law Equation (1) and is enhanced if particle size is increased, density difference between phases is large and viscosity of continuous phase is low, allowing free movement of particles. Creaming is also enhanced by flocculation, flocs conformation causes a faster movement than individual particles because of their greater effective size [14].

$$v = 2a''(\rho_! - \rho)g/9\eta_! \qquad \text{Equation (1)}$$

NRL particles density is slightly minor (ρ ≈ 0.97 g/ml) than the continuous phase (i.e., water) ($\rho_!$ =1 g/ml) [13]. Creaming is not a spontaneous phenomenon into NRL system. To promote creaming and weak-flocculation in NRL, water-soluble and high- molecular polysaccharides, also called **'creaming agents'**, as celluloses, alginates, arabic gums, etc. are added into NRL system. Polysaccharides are predominantly hydrophilic and therefore are not particularly surface-active, the presence of this

non-adsorbing species in system causes a depletion flocculation phenomenon [15]–[18]. This effect is associated with an osmotic pressure difference between the rubber interparticle region depleted of polysaccharide molecules and the continuous phase [14], [19]. Therefore, polysaccharides can inhibit Brownian motion on NRL particles due to weak chemical bonds as hydrogen bonds forming a network of NRL particles promoting creaming; and also allowing depletion flocculation on particles [18], [20]–[23].

Different creaming agents have been studied, and its effect on rubber content and some properties were evaluated. Some of those creaming agents are: Arabic gum (AG), sodium alginate (SA), methylcellulose (MC), hydroxyethtyl cellulose (HEC), tamarind seed powder (TSP), carboxymethyl cellulose (CMC), poly vinyl alcohol (PVA) [24]–[27] the studies were focused only on increasing the rubber concentration by measurements in Total Solid Content (TSC) and Dry Rubber Content (DRC).

Surfactants are also added to a latex dispersion to enhance creaming velocity and impart stability on particles, they have an amphiphilic structure that adsorbs onto NRL particles improving stability due to its chemical nature, surfactants can bind its hydrophilic side with proteins of rubber particle or its hydrophobic side with hydrophobic groups of protein rubber [28], [13], [29] most of studies were realized to analyze the effect of surfactants on the adsorption and stability of latex system. K. Silva and S. Walpalage [30] found that adding little quantities ($0.5x10^{\#\$}$mol 100g^{-1}) of Ammonium Laureate (ALS) into NRL particles enhances mechanical stability of latex from 100 sec to 1000 sec, and decreases viscosity. H. Lim and M. Misni [31] shows that Sodium Dodecyl Sulphate (SDS) adsorbed and impart stability more than Polyoxyethylene Dodecyl Ether (Brijj 35) in NRL particles by Langmuir isotherms and zeta potential measurements from -49 to -60 mV at different SDS concentrations. Triton X-100 and SDS were tested on positively and negatively charged polystyrene latex particles by a sequential adsorption, results shows that both surfactants adsorbed into particles and enhance colloidal stability [32]. Specially with Triton X-100 the maximum amount of surfactant depend mainly on the hydrophobic characteristics of the particles surface [33].

Studies were attempting to understand the effect of adding creaming agents on latex dispersions and its combination with surfactants. Peethambaran [34] studied the effects of surface active agents on the viscosity of centrifuged and creamed NRL under different shear rates and temperature. Latex was creamed with Carboxymethyl cellulose (NaCMC), Polyvinyl alcohol (PVA), casein, sodium alginate (SA). Found that latex concentrated with NaCMC showed more viscosity than other agents. Also, found that creamed rubber latex has more pseudoplastic behavior, and a higher viscosity than

centrifugated. Yumae et al. [24] showed that hydroxyethyl cellulose (HEC) was a good creaming agent for NRL, and compare centrifugated latex with creamed latex properties. A 0.4 parts hundred rubber (phr) of HEC was mixed with 0.3 phr of ammonium laureate (ALS). It was found that HEC provided good efficiency to separate rubber particles from the aqueous phase with a DRC close to 64%. Also, it was found that mechanical stability was improved due to the addition of ALS (1362 sec) compared with centrifugated latex (190 sec). Big differences on viscosity were found between creamed (114.2 cP) and centrifugated latex (58.7 cP) due to the HEC addition. Properties as alkalinity (0.68%), volatile fatty acid (0.0131) KOH number (0.39), pH (11.12), magnesium content (29 ppm) were evaluated according to ASTM D1076. No more in-depth analysis was found on the effect of ALS and HEC into creamed latex properties. Singh et al. [35] evaluated the effect of adding different concentrations of Inulin in the viscoelastic properties of a concentrated latex, the adsorbed layer thickness were calculated by a semiempirical method based on the linear dependence of intrinsic viscosity and with the maximum volume fraction, this value (2.8 nm) was confirmed by dynamic light scattering (DLS). It was found that Inulin concentration increases G' due to repulsion between particles, also maximum volume fraction decreases with the increase of inulin concentration, this is attributed to the formation of an adsorbed surfactant layer on the particle surface that reduces effective volume fraction.

1.3. Interactions between creaming agent and surfactant in NRL

When different concentrations of creaming agent are added into a colloidal system, depletion phenomena are developed. Depletion is divided into two main terms: depletion stabilization and depletion flocculation. Semenov [36], [37] elucidated the term of **"depletion stabilization**" and propose a quantitative theory of this phenomenon. The theory predicts that colloidal particles in a semi dilute solution may be kinetically stabilized by a long-range of polysaccharide concentration that induce repulsion due to a depletion of the chain. Kim et al [38] studied the mechanism of depletion stabilization of nanoparticles with poly vinyl alcohol (PVA) and found that as PVA concentration increases, the microstructure evolves from flocculation by bridging to depletion stabilization reaching a stabilization on particles. Above a certain polysaccharide concentration, the repulsive energy barrier becomes high enough to allow particles kinetically stabilized. Depletion stabilization does not require a specific binding or adsorption with polymers to impart stabilization between particles [38] which is the main difference with an steric stabilization where adsorption always occurs [14], [39]. The presence of low to medium concentrations of non-adsorbing

polysaccharides leads to **depletion flocculation**, microscopic phase separation and macroscopic serum separation [14]. Depletion flocculation can have an enormous effect on creaming stability. Due to their large excluded volumes, polysaccharides with stiff extended backbones (e.g., xanthan gum) are especially effective at inducing depletion flocculation [13],[15]. Moschakis et al. [19] show that moderately low levels of xanthan addition leads to depletion flocculation and gravity-induced phase separation, and increasing the polysaccharide concentration causes immobilization of the microstructure of the emulsion due to an increase in the local viscoelasticity. Kiratzis et al. [40] studied by rheology the depletion flocculation process with HEC in different aqueous colloidal dispersion: alumina and two polystyrene dispersions. It was identified that 0.2% (w/v) was the critical concentration required to induce flocculation. At higher concentrations of HEC, G' becomes larger than G'' because the formation of a three-dimensional network that indicates flocculation in systems. Tagliaro [41] studied the electrostatic depletion effects on colloidal dispersions stability of negative charged sepiolite fibers in NRL, it was found the existence of a depletion attraction enhanced by the electrostatic repulsion between sepiolite and NRL at volume fractions Φ = 0.038. Depletion phenomenon has not been widely studied in NRL systems with water-soluble polysaccharides as HEC.

HEC is an attractive non-ionic, water-soluble, biocompatible, biodegradable, non-toxic, and highly polar due to its high content of hydroxyl groups, as is showed in **Figure 2**. It is also a low-cost polymer with the capability of be a thickener, protective colloid, binder, suspending, stabilizer, and flocculating agent [42], [43]. HEC is mainly hydrophilic, but some authors identified that hydrophobic groups on HEC chain represent areas of high affinity when they are mixed with some surfactant. SDS is an anionic and amphiphilic surfactant used in polystyrene latex with HEC with an adsorption surface capability [44]–[47].

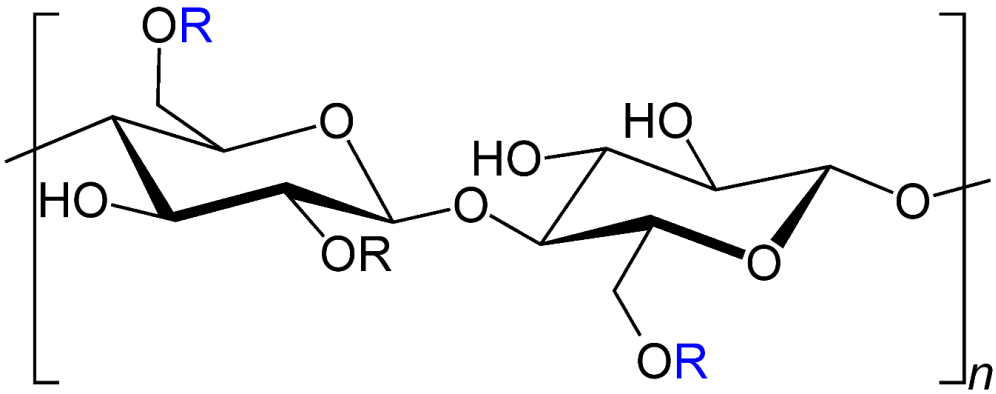

Figure 2. HEC chemical structure. Source: PubChem

In polymer and surfactant systems four adsorption cases can be present [48] : I) Competitive adsorption, both species have affinity for surface but not for each other, II) complex formation, both species have affinity to the surface but not for each other, III) competitive adsorption with complex formation**,** both species have the affinity to the surface and to each other, and IV) no competitive adsorption and no complex formation, only one of these two substances has the affinity to the surface, but they cannot bind to each other. A parameter that influences complex formation is the critical aggregation concentration (CAC). Defined as surfactant concentration where the first association between them and the water-soluble polymer to form complexes occurs. CAC is generally lower than the critical micellar concentration (c.m.c) of the surfactant in absence of polymer [49], [50]. Generally, there are two alternative pictures of complex surfactant/water-soluble polymer solutions: one describing the interaction in terms of a strongly co-operative association or binding of the surfactant to the polymer chain and one in terms of a micellization of surfactant on or in the vicinity of the polymer chain [17]. According to Tadros [50] the CAC/c.m.c. depends weakly only on wide ranges of polymer concentration; CAC/c.m.c. is independent of polymer molecular weight; anionic surfactants show a marked interaction with homopolymers as PEO and PVP and cationic surfactants show a weaker interaction; several uncharged polymers as PEO, PVP, PVA, interact with charged surfactant due to its high hydrophobical groups on its polymer structure. Experimental methods for investigating polymer-surfactant interactions depends on each system [20]. In surfaces as alumina and graphite, HEC-SDS interactions are shown to increases adsorption due to complex formation [51]. It was found that HEC can stabilize alumina particles if it is added big quantities (~500 ppm) to reach a stabilization, or a little quantity of HEC (~100 ppm) if a combination with surfactant as SDS or CTAB is made reaching an electrostatic stabilization [42]. The authors modified HEC chain with hydrophobic groups to increase interactions with surfactant.

Pisárcik et al. [47] studied the effect of the adsorption of HEC and HM-HEC onto polystyrene latex and its combination with SDS. HM-HEC adsorbed 2-3 times greater than HEC. Tanaka et al. [52] and Tadros et al. [53] added HEC and Hydrophobically modified HEC (HM-HEC) to a polystyrene latex, rheological tests were taken and results showed that HEC modifies elastic moduli (G') that tends to increase with a higher molecular weight of HEC and an exponential increase was found with HM-HEC. Despite this, the interaction with unmodified HEC and SDS at different concentration has not been studied in creaming NRL system or its effect on colloidal and rheological properties.

The aim of this work is to analyze the effect of adding creaming agents and surfactants to a concentrate NRL by creaming. A creaming agent and surfactant selection were made between HEC, carboxymethyl cellulose (CMC), and Tamarind Seed Powder (TSP); SDS, Triton X-100 and ammonium

laureate (ALS) by a design of experiments (DoE) to concentrate NRL based on high TSC. Then, a second DoE was carried out to analyze the effect of different concentrations of HEC-SDS on colloidal and rheological properties of NRL on different creaming times. With response surface methodology, optimal HEC and SDS concentration was identified to obtain the highest DRC and colloidal stability (z-potential). Also, physicochemical interactions between NRL, HEC and SDS are presented.

2. EXPERIMENTAL

2.1. Materials

NRL stabilized with ammonia at 0.6% w/w were tapped from *Hevea brasiliensis* trees located in Bajo Cauca, Antioquia, Colombia. The extracted latex was a mixture of clones and were tapped during phenological states filling of fruit and foliation. With an initial DRC of 36,10% and 28,70 % respectively.

2.1.1. *Creaming agents*

Hydroxyethyl cellulose (HEC) commercial grade was purchased in Protokimica. This is a cellulose derivative polysaccharide, water-soluble and non-ionic polymer, its molecular weight is 806.9 $g\ mol^{\#\%}$.

Carboxymethyl cellulose (CMC) commercial grade was purchased in Protokimica. This is a cellulose derivative polysaccharide, water-soluble and anionic polymer, its molecular weight is 263.20 $g\ mol^{\#\%}$.

Tamarind seed powder (PST) was obtained by milling. Tamarind seeds were purchased in Recolsemillas Colombia, with a 90% of tamarind purity. Seeds were washed, dried, roasted, milled and finally sieved with 40, 50 and 100 meshes to obtain a powder with a size ≤ 3 mm, (see Supporting information). PST has low solubility in water and Xyloglucan polysaccharide needs to be extracted as described in methodology section [54]

2.1.2. *Surfactants*

Sodium Dodecyl Sulphate (SDS) PanReac analytical grained pure 96% was purchased. This is an anionic surfactant with a c.m.c of 8 mM, has a good solubility in water at room temperature (25°C), its molecular weight is 288.38 $g\ mol^{\#\%}$. Its physicochemical properties are fully described on [55].

Triton ® X-100 PanReac molecular biology grade was purchased. This is a no-ionic surfactant with a c.m.c of 0.24 mM, has a good solubility in water at room temperature (25°C), its molecular weight is 646.85 $g\ mol^{\#\%}$.

Ammonium laureate (ALS) commercial grade was purchased. This is an anionic surfactant, has a good solubility in water at room temperature (25°C), its molecular weight is 217.35 $g\ mol^{\#\%}$.

All solutions were performed with deionized water.

2.2. Methodology

Creaming agents CMC and HEC were solubilized in water, stirring 1 hour at 500 rpm at room temperature, a 3.0 % w/w gel solution was prepared. The solubilization of CMC and HEC in water allows the polymer chain expansion and therefore a better interaction through hydrogen bonding [56].

Creaming agent TSP were solubilized in water, stirring 2 hours at 500 rpm and at 70°C, a 5% w/w solution was prepared.

Surfactants SDS, Triton x-100 and ALS were solubilized in water, stirring 15 minutes at 500 rpm and at 22°C, a 10% w/w solution was produced.

A Factorial $4^{"}$ and completely randomized Design of Experiments (DoE) was carried out for each creaming agent HEC, CMC and PST to select the creaming agent and the surfactant that increase the TSC. The factors for creaming agent concentration on latex (0.5,1.0,1.5,2.0) % v/v, and type of surfactant (SDS, triton x-100, ALS, and none). Surfactant concentration on latex was fixed in 0.5 % v/v. All TSC measurements were made continuously at creaming days 2,5,10 and 15 to observe the evolution of rubber concentration on time.

After creaming agent selection, a factorial $3^{"}$ and completely randomized DoE was carried out using a wide range of the creaming selected, volume concentration on latex 2, 5, 8 %v/v (0.75mM, 1.85mM and 3mM respectively into NRL dispersion) and surfactant SDS volume concentration on latex 0, 0.5, 0.8 %v/v (0.0 mM, 1.5mM and 2.5mM respectively into NRL dispersion) to analyze the behavior of latex in concentration by DRC, colloidal stability by zeta potential (z-potential). Optimal point for selected creaming agent and surfactant were identified for these properties by a surface response methodology. Also, rheological measurements were made for each run of DoE. All measurements were made continuously at creaming day 2, 15 and 30 to observe the evolution of each property on time

2.2.1. Determination of rubber concentration

In rubber industry, yield is measured by two important parameters that at the same time represents the concentration of a latex batch: TSC % and DRC %. In order to identify the effect of creaming agent and surfactant concentrations on rubber yield, a DRC % measurement was carried out with

the Equation (2) according to ASTM D1076-15 [57]. 2.0% v/v of acid acetic solution was added to 10.0 ± 1.0 g of latex with 25.0% of TSC until the coagulation. This solid was laminated until reach 1 mm thick and washed with enough water. This thin sheet was dried at 70°C for 16 h. TSC% was quantified with the Eq. 2 according to ASTM D1076-15. Rubber mass was obtained drying 2.5 ± 0.1 g of latex at 100°C in an oven with circulating air for 2 h. All measurements were made continuously at day 2, 15 and 30 of creaming process to see the evolution on time. Each test was repeated twice, under controlled atmospheric temperature 22°C and relative humidity 65% with a 95% confidence limit.

$$DRC = \frac{Dry\ coagulum\ mass}{Initial\ latex\ mass} * 100 \qquad \text{Equation (2)}$$

$$TSC = \frac{Dry\ rubber\ mass}{Initial\ latex\ mass} * 100 \qquad \text{Equation (3)}$$

2.2.2. Determination of colloidal stability

Potential zeta measurements were carried out for each sample using a NanoplusHD-Zeta/nano particle analyzer by Particulate Systems. The latex was diluted to 0.2% TSC with deionized water and then the sample was agitated during 5 minutes at 400 rpm. Samples were measured continuously at day 2, 15 and 30 of creaming process. Each test was repeated twice under controlled atmospheric temperature (22°C) and relative humidity (50%) with a 95% confidence limit.

2.2.3. Determination of rheological properties

A rheological analysis was carried out using a Haake Mars III from Thermo Scientific equipped with DIN coaxial cylinders geometry, inner cylinder was a titanium rotor with radium 10 ± 0.002 mm and length 30.0± 0.003 mm, the outer cylinder was a steel cup with radium 10.850 mm, and sample volume was 8.2 ml with a gap of 4.2 mm. Two types of measurements were carried out. First, a rotational type to obtain flow curves, all samples were presheared for 1 minute and left in repose for 2 minutes. Then, tests were carried out at room temperature in a shear rate range from 10 to 1000 $s^{\#\%}$. Second, oscillatory measurements to know the viscoelastic behave under time. A fixed frequency at 1 Hz and the sweep strain amplitude was gradually increased from 0.01 to 100%. This allows to obtain linear viscoelastic zone and analyze viscoelasticity changes. Samples were measured continuously at day 2, 15 and 30 of creaming process, at each DRC sample ($0.27 < \Phi <$

0.55). Each test was repeated twice under controlled atmospheric temperature (22°C) and relative humidity (65%) with a 95% confidence limit.

3. RESULTS AND DISCUSSION

3.1. Creaming agent selection

Creaming agents are known to be low-cost and natural-based. Surfactants were chosen to analyze the effect of its interaction with creaming agent. Selection criteria are: no coagulation and concentrations above TSC[1] of 50 %. This initial concentration was measured before the concentration with each creaming agent as presented on Table 1.

Table 1. TSC % of raw latex for each creaming agent experiment

Creaming agent	Total solid content (%)
Hydroxyethyl cellulose (HEC)	39.72 ± 0.05
Tamarind seed powder (TSP)	34.74 ± 0.04
Carboxymethyl cellulose (CMC)	42.72 ± 0.04

3.1.1. HEC

As **Figure 3** shows, HEC 0.5% v/v concentration is not enough to reach high concentrations of NRL. At this point, HEC concentration is low to flocculate system. However as HEC concentration increases, the NRL concentration gets higher. Also, it takes less time to reach concentrations above 50 %. The results suggest that surfactant has an influence on NRL concentration allowing higher TSC with less quantity of creaming agent, and also showing the existence of an interaction between surfactant-HEC system and rubber particles. The interactions between anionic surfactant (SDS) and no ionic surfactant (Triton X-100) with HEC is by Van der Vaals interaction. It is important to take into account that surfactant concentration was fixed in 0.5 %v/v, and an increase on this concentration would represent more interaction between surfactant and creaming agent. Complexes between Triton X-100 and HEC may be more likely due to low c.m.c. of Triton X-100. SDS has an effect on NRL concentration attribuited in this case to its surface active capability onto NRL particles and the interactions by ion-dipole with HEC. ALS surfactant does not show any enhancement of NRL concentration because its forces are not strong enough to stablish a visible

[1] Each batch of NRL have different initial TSC, because its natural origin.

interaction with HEC. When 1.5% v/v of HEC and ALS is added, some atypical data are found. This is attributed to a rubber particle stabilization due to interaction between surfactant and HEC at this concentration point.

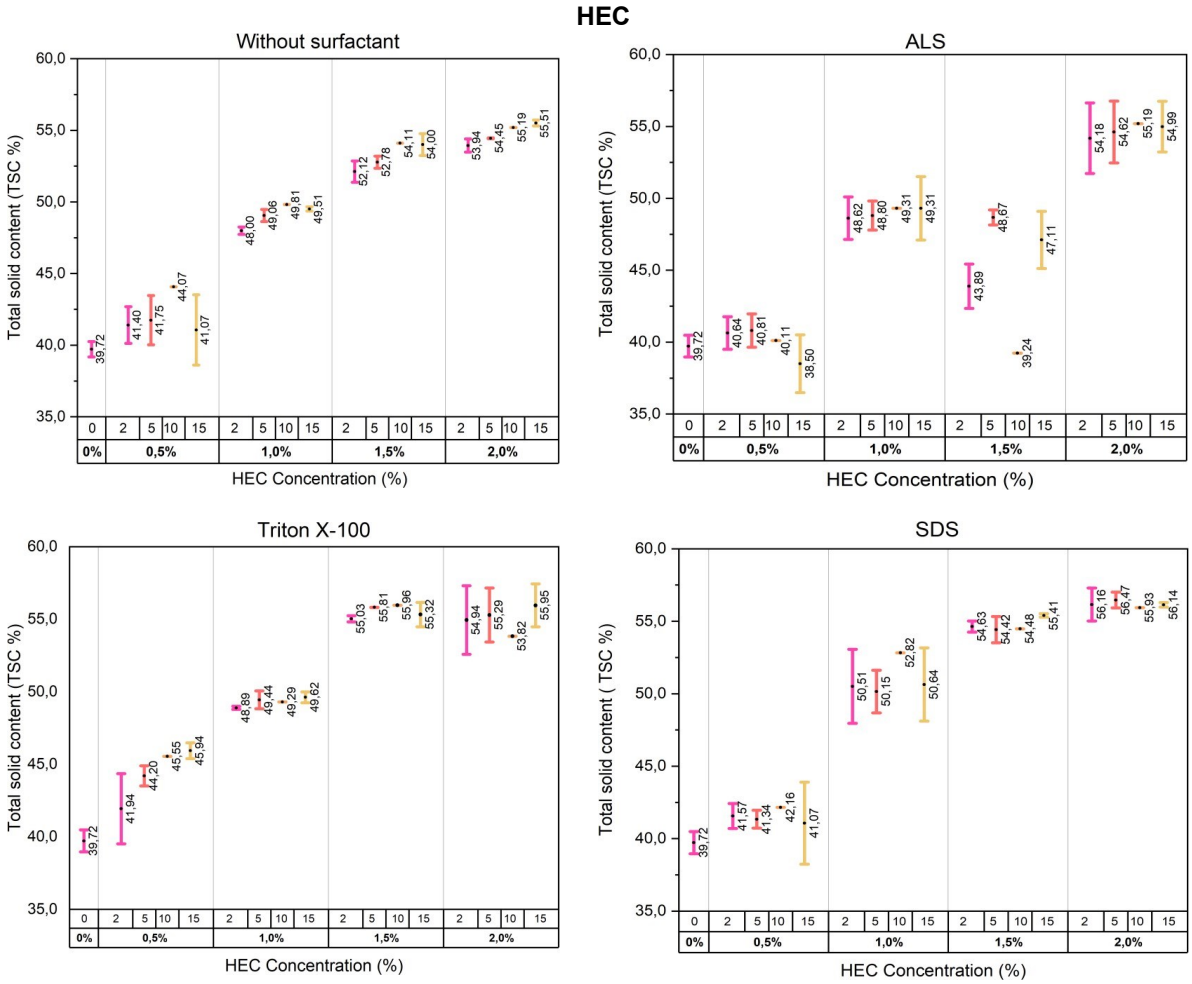

Figure 3. Effect of HEC creaming agent and surfactant on NRL- TSC (%). Pink: day 2; orange: day 5; yellow: day 10 and 15. The standard deviation of measurements is represented by each line amplitude.

3.1.2. TSP

The interaction between TSP polysaccharide (i.e., Xyloglucan) and surfactant polar groups that causes a NRL concentrations is above 1.5% v/v TSP and its combination with SDS and Triton x-100 as shown in **Figure 4**. Nevertheless, the interaction between ALS-TSP does not enhance the creaming, this is attributed to low or non-attractive forces between chemical groups of ALS and Xyloglucan and rubber. During the experiment was observed a sedimentation of TSP particles in latex, this suggests that this creaming agent is not completely soluble on NRL, and the particle

size of powder affects the enhancement of NRL concentration. This is reflected on the wide deviation between TSC of each surfactant and TSP concentration above 1.5% v/v and suggest that it is necessary a deep study to know the effect of particle size and solubility of TSP into NRL concentration and that is out of scope in this research. The NRL concentration is very similar from initial in concentrations lower than 1.5% v/v, the effect is extended over time that in this case is not playing a role on concentration enhancement. According to this, TSP is discarded for NRL concentration.

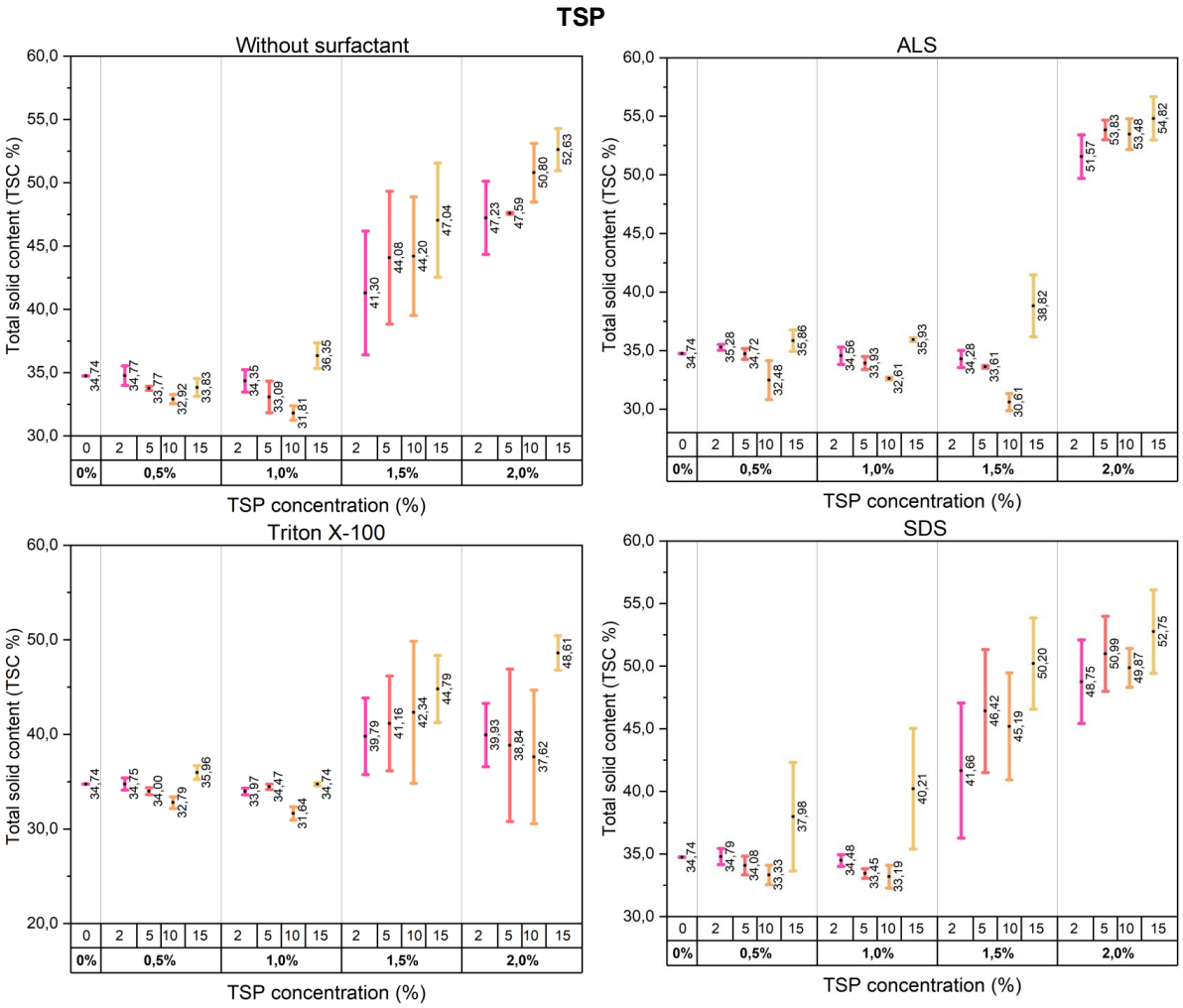

Figure 4. Effect of TSP creaming agent and surfactant on NRL- TSC (%). Pink: day 2; orange: day 5; yellow: day 10 and 15. The standard deviation of measurements is represented by each line amplitude.

3.1.3. CMC

As shown in **Figure 5**, a tendency of TSC increasing with CMC concentration is observed and this is enhanced with the addition of surfactant. The concentration of CMC at 0.5% v/v is not enough to reach high concentrations of NRL. However, from 1.0% v/v higher values of TSC data are reached, with a plateau establishment also in the other concentrations (i.e., 1.5% v/v and 2.0%v/v). The addition of surfactant allows to obtain greater concentrations with time, especially at CMC concentration of 2.0% v/v. This leads to suggest that the interactions developed by CMC-surfactant are mandatory for enhance creaming, results in **Figure 5** shows this. The interaction between surfactants and CMC are attributed to chemical nature of both species. CMC is an anionic creaming agent with a high number of hydrophobic and hydroxyl groups in its chain, this increases the probability of binding with surfactant, especially with SDS and ALS that are also anionic by forming complexes. Moreover, it is feasible that the strong interactions between CMC and NRL particle give rise to an adsorption of this creaming agent on NRL surface and therefore a competitive adsorption between the creaming agent and surfactant for the NRL surface. Nevertheless, these interactions become so strong that rubber particles get closer between them causing an irreversible flocculation on NRL particles and hence a loss in its stability.

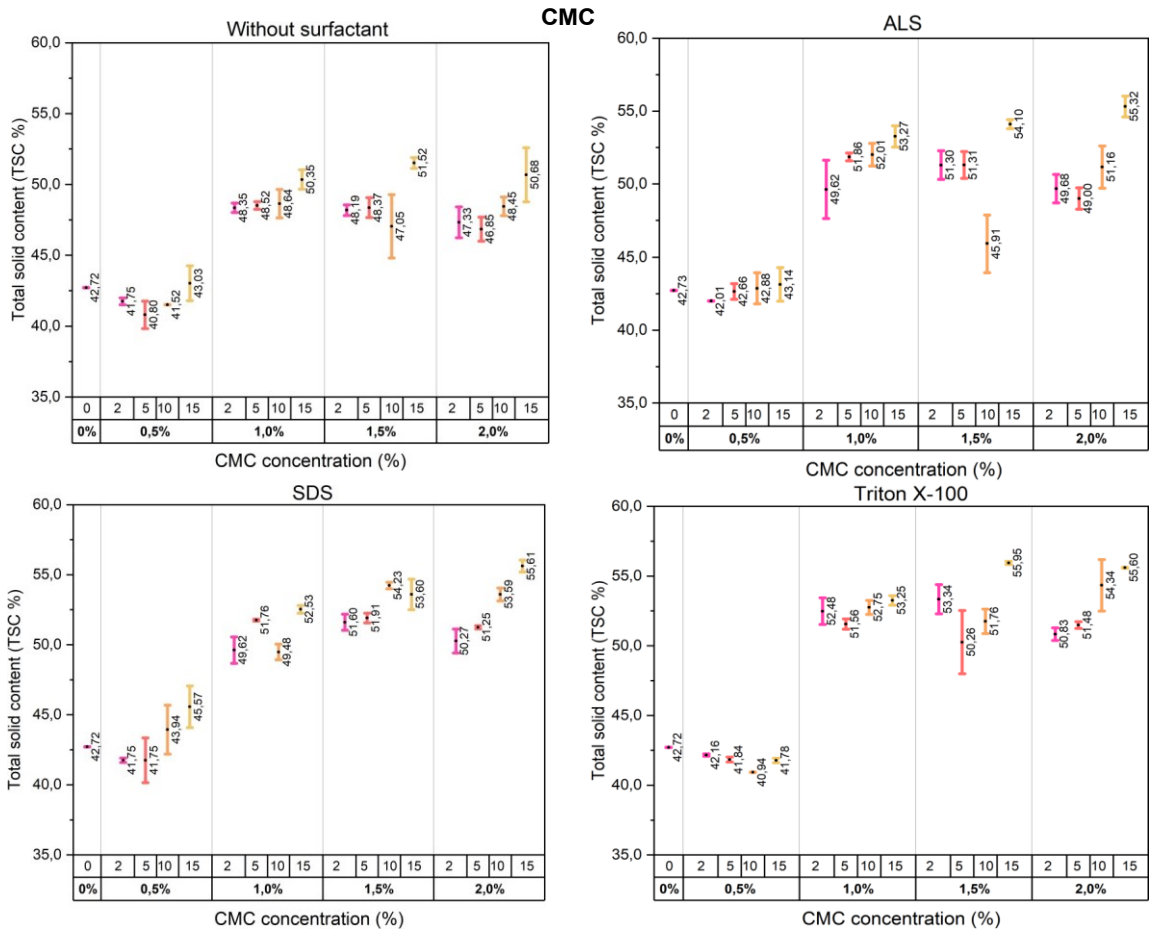

Figure 5. Effect of CMC creaming agent and surfactant on NRL- TSC (%). Pink: day 2; orange: day 5; yellow: day 10 and 15. The standard deviation of measurements is represented by each line amplitude.

In this way, creaming agents CMC and HEC concentrate NRL above 50%. The surfactants SDS and triton x-100 shows a satisfactory behavior increasing NRL concentration, especially on the system CMC. **Figure 6** shows a comparative between NRL concentration with those creaming agents and surfactants SDS and Triton x-100. The results suggest that NRL concentration gets higher with HEC than CMC without surfactant. Moreover, NRL-HEC system has an uniform trend according to **Figure 6A and B.** Then, with surfactant addition, the NRL- CMC system shows a clear tendency to NRL concentration increasing, especially with SDS, attributed to strong chemical interactions as mentioned before. Nevertheless, these systems does not stabilize at a single value after 15 days, which means that it takes longer time to reach constant values of concentration, otherwise in the NRL-HEC system, it is get the NRL concentration and also stabilizes in a single value in less time, even with surfactant addition as shown in **Figure 6C-F.**

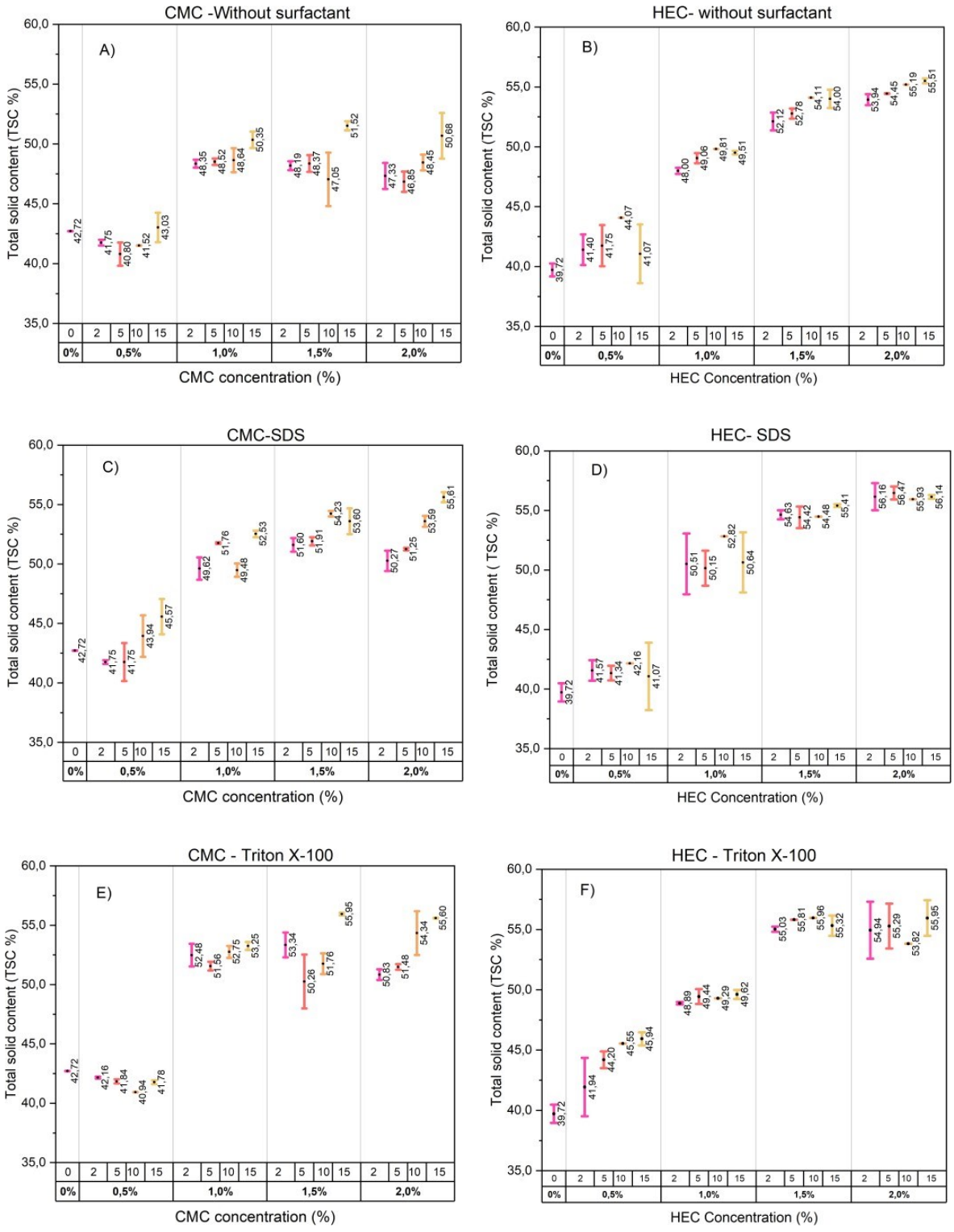

Figure 6. Comparative between CMC and HEC with SDS and triton x-100 surfactants. A), C) and D) are associated to CMC and B), E), and F) are associated to HEC

The rheological behavior in systems is also an outstanding criterion to determine if NRL system coagulates over time. In this way, viscosity measurements were carried out after 27 creaming days to evaluate the rheological behavior of NRL concentrated with HEC and CMC. **Figure 7 and 8** shows the flow curves for HEC and CMC without surfactant.

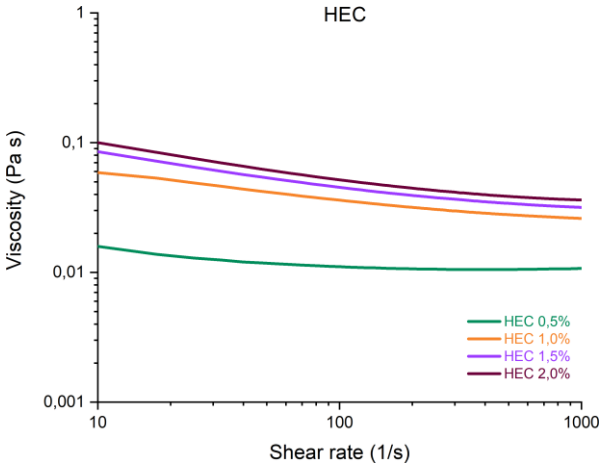

Figure 7. Curve flows of NRL concentrated with HEC at 27 days of creaming

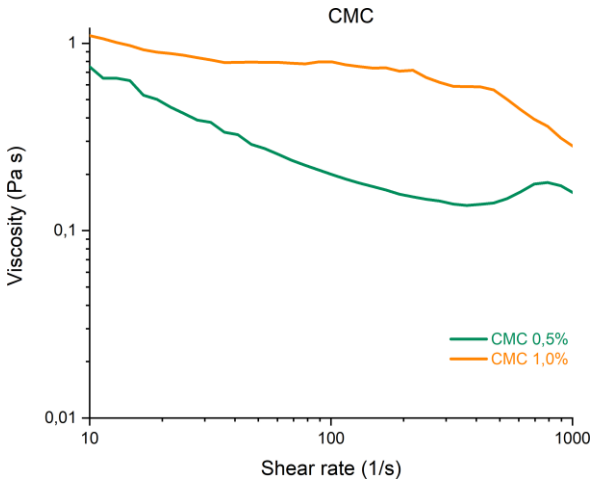

Figure 8. Curve flows of NRL concentrated with CMC at 27 days of creaming

The NRL concentrated with CMC is not rheologically stable even at lower concentrations, for higher concentrations no measurements were carried out because they were coagulated. This can be attributed to the strong interaction between rubber particles and this creaming agent. In opposite, HEC shows a clear behavior of fluidity. This allows to suggest that the NRL concentrated with HEC keep its rheological stability for more time than the NRL concentrated with CMC, since the measurements were made at the same creaming day. In addition to this, NRL viscosity values with CMC and HEC are quite different between them being the NRL- CMC greater than NRL- HEC. This important finding allows to select HEC as creaming agent for optimization DoE. In terms of surfactant effect, Triton x-100 shows to be a good surfactant but was discarded due to its toxicological properties. Also, SDS surfactant has the capability to form electrostatic interactions with NRL particles, that is valuable for the colloidal stability analysis through z- potential. According to the above analysis, supporting information presents the ANOVA for the selected creaming HEC.

After creaming agent selection, a widening of HEC concentration was made to define the levels for this factor in optimization DoE. The range was fixed 1% v/v to 8%v/v without surfactant as present in **Figure 9**. It was found that 1%v/v allows to concentrate latex, but the TSC growing is slow and limited, the same trend was observed for 1.5%v/v. While in the ranges 2%v/v to 5%v/v, the NRL concentration increases. Simultaneously a plateau of concentrations is reached, and a minimum on NRL concentration is identified at 8%v/v HEC and can be attributed to HEC saturation on rubber particles. An enhancement of colloidal and rheological properties of creamed NRL can be attributed to the SDS and HEC interaction at this concentration values. Levels 2 %v/v (low), 5%v/v (medium), and 8 % v/v (high) were fixed for the optimization DoE, with different SDS concentrations (0.0%v/v, 0.5%v/v and 0.8%v/v) into NRL.

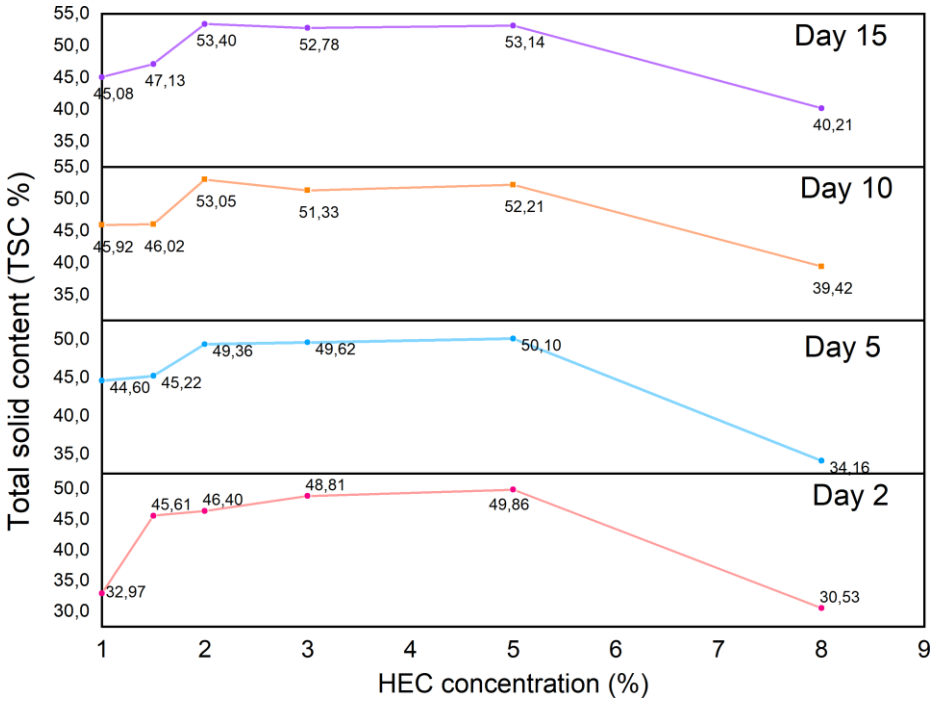

Figure 9. DRC vs HEC concentration without surfactant.

3.2. HEC-SDS interaction in DRC and colloidal properties of NRL system

A DoE with HEC and SDS were carried out to concentrate NRL with an initial DRC of 28,70% and z-potential of -72 mV. HEC act as a thickener of continuous phase in NRL (i.e., water) because of the hydrogen bonding interactions between hydroxyl groups of its chain and the hydroxyl groups of water giving rise to physical creaming of NRL by a reduction of Brownian motion of rubber particles.

HEC and rubber particles polar groups interact together by hydrogen bonding giving rise to a flocculation effect driving by depletion phenomena without adsorption of HEC onto NRL particles. However, this phenomenon changes depending on HEC concentration and SDS addition **Figure 10**. shows the effect of creaming NRL with different concentrations of HEC and SDS for DRC and **Figure 11** display the effect of creaming into colloidal stability by z-potential and its evolution with time.

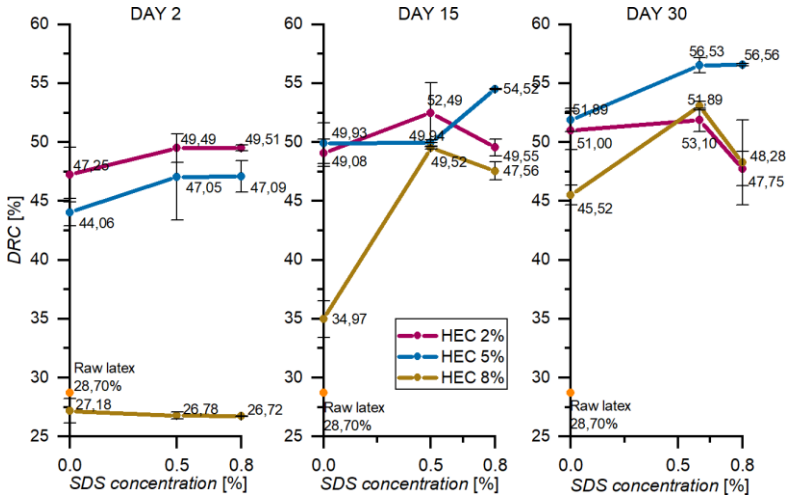

Figure 10. Effect of HEC and SDS on DRC after 2, 15, and 30 days of creaming. Pink line: low HEC concentration, blue line: medium HEC concentration and yellow line: High HEC concentration.

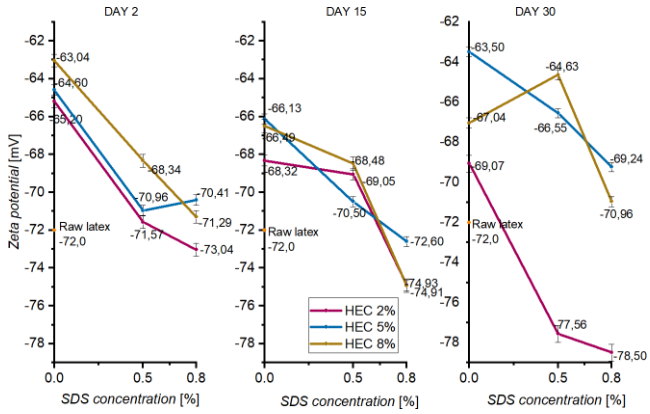

Figure 11.Effect of HEC and SDS on colloidal stability after 2, 15, and 30 days of creaming. Pink line: low HEC concentration, blue line: medium HEC concentration and yellow line: High HEC concentration.

3.2.1. Effect of low HEC concentration and SDS

NRL concentration is reached when 2% v/v (0.75mM) of HEC is added into system. The interactions between HEC and NRL particles give rise to depletion flocculation between particles allowing the concentration. For this low quantity of HEC on NRL system, the rubber particle agglomeration gets faster and hence DRC gets higher in less creaming time. This is shown in **Figure 10** (pink line) where the DRC increases for HEC 2%v/v and 0.0 SDS system in a percentage of 18.55% at first 2 days from the initial DRC. This creaming day represents a critical point called induction period [13] this is the required time for phase separation. At day 15 and 30 concentration increases slowly until reach a plateau and therefore time is not a significative factor (see supporting information). When SDS is added into NRL-HEC system, concentration gets higher than without surfactant. This suggest that SDS and HEC are cooperating between them by Van der Waals interactions to enhance creaming velocity. Therefore, SDS concentration influences in DRC value. When 0.5% v/v of SDS are added into system, DRC increases in a percentage of 20% from the initial DRC, small increasing is also observed at day 15 and 30. Nevertheless, when 0.8% v/v of SDS is added, DRC concentration increases only at day 2 and then stablish a plateau where the value does not change. This suggest that at the concentration of 0.8% v/v of SDS the system is controlled mainly by charge repulsions, especially because at this point the SDS concentration is much higher than the HEC concentration (i.e., 2.5 mM vs 0.75 mM). The effect of SDS concentration on low HEC-NRL systems is more noticeable in colloidal stability by z-potential as presented in **Figure 11** (pink line). Where z-potential of the system with SDS 0.8 %v/v is higher than the others. Therefore, if SDS increases, a growth of repulsive forces due to the electrostatic nature of surfactant is developed and hence the low HEC concentration cannot counteract to keep the flocs on the system, producing a decrease on NRL concentration and an increase on electrostatic-repulsive potential. It is important to mention that stability tends to increase with time, especially after 30 days, where smaller amounts of HEC and higher of SDS keeps enabling predominancy of repulsive interactions making system more stable.

3.2.2. Effect of medium HEC concentration and SDS

When 5% v/v (1.85 mM) of HEC is added into the system, the phenomena are the same that with 2% v/v. Nevertheless, creaming velocity is slow because this HEC concentration addition causes an increase on viscosity that inhibit free movement of NRL particles, delaying flocculation. This suggests a beginning of saturation on HEC-NRL system. It is presumed that interactions by hydrogen bonding

between HEC and NRL particles are slower than the effect of viscosity on particles and that is why depletion flocculation gets higher with time. This is shown in **Figure 10** (blue line) where DRC increases for HEC 5%v/v and 0.0 SDS system in a percentage of 15.36 % at first 2 days from the initial DRC and less that when HEC 2% v/v is added. At day 15 and 30 concentration continue increasing a 5.87 and 7.83% with respect to 2 days. When SDS is added into NRL-HEC system, concentration gets higher. In this case, Van der Waals interactions between HEC -SDS- NRL are predominant allowing weak flocculation. For SDS 0.5% and 0.8 % v/v, the DRC increases proportionally over time (i.e., 10% and 11% from day 2 to 30 respectively). These results suggest that HEC concentration and SDS (i.e., 1.85 mM and 1.5mM, 2.5mM respectively) allows to obtain a remarkable DRC increase, especially when concentrations between HEC and SDS are in the same proportion in NRL dispersion giving place to an equal cooperation between species. In addition to this, repulsion interactions are also present in system because of the SDS and NRL anionic nature. As **Figure 11** (blue line) shows, z-potential of 5 %v/v HEC system is lower than 2 %v/v HEC and do not increase over time unless the SDS addition, that contributes to enhance potential by the repulsive interactions, especially at 0.8%v/v.

3.2.3. Effect of high HEC concentration and SDS

The saturation effect gets higher when HEC 8% v/v (3 mM) is added into NRL system, viscosity increasing causes a particle immobilization and hence a bigger delay on flocculation. At first creaming days, this effect leads to a temporary stabilization of NRL particles, it is proposed a depletion stabilization phenomenon since HEC does not adsorb onto NRL particle, but is acting as a particle stabilizer due to its concentration value. [37], [38] Over time, the phenomena slowly become into depletion flocculation due to the initiation of chemical interactions between HEC and NRL particles. This proves that interactions by hydrogen bonding between HEC and NRL particles are slower than the effect of viscosity on continuous phase. The above mentioned is showed in **Figure 10** (yellow line), where DRC does not increase at first 2 days for HEC 8%v/v system even if SDS is added. However, at 15 and 30 days the HEC 8%v/v and SDS 0.0 system is observed to slowly increase its DRC in a 5.95% from day 2 to 15, and in a 11.05% from day 15 to 30 as showed in **Figure 12A.** This also means that induction period begins at 15 days, and clearly time effect is taking importance at this HEC concentration. When SDS 0.5% v/v is added into this HEC- NRL system, a rapid increase of 15.57% is observed only since day 15, when depletion flocculation starts to take place on the system, as showed in **Figure 12B**. The behavior is similar for SDS 0.8% v/v. Nevertheless, highest values are reached with 0.5%v/v of SDS. This suggest that the concentration of 0.8% v/v of

SDS controls system by electrostatic repulsions despite HEC concentration is higher than SDS (i.e., 3 mM vs 2.5mM).

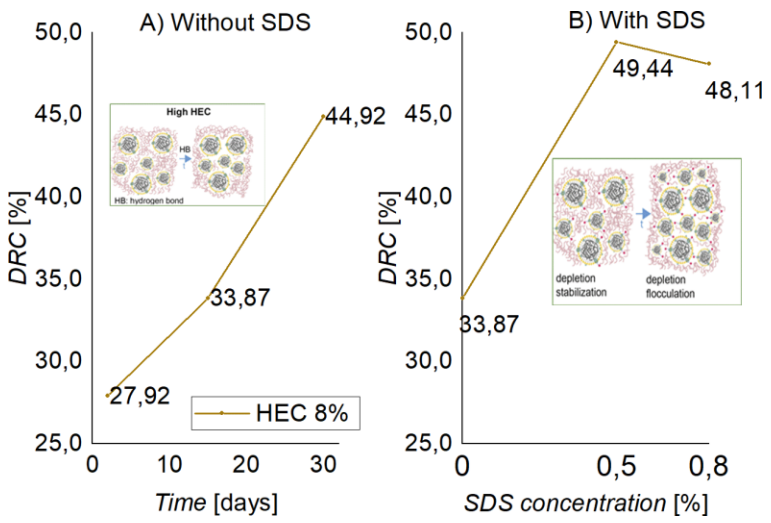

Figure 12. Evolution of high HEC- NRL system A) without SDS over time and B) with SDS concentration at 15 day.

The depletion stabilization effect cannot be measured by z-potential because current techniques as z-potential only measures electrostatic forces between charged particles. Nevertheless, tendency showed in **Figure 11** (yellow line) indicates that presence of high HEC concentration leads to less potential compared to the other HEC systems, and SDS addition causes a rapid increase on stability even from day 2, where no creaming effect is developed yet. This behavior is replicated over time. It is also important to note that even when flocculation has initiated at day 15, the electrostatic stability remains without any changes. This allows to say that even at high HEC concentration electrostatic effects uppermost the depletion flocculation giving rise to colloidal stabilization.

3.3. Response surface analysis for NRL concentration by dry rubber content and colloidal stability by z-potential

Response surface (RS) methodology were implemented to identify optimal points for HEC and SDS concentrations. **Figure 13A and B** shows the RS for DRC obtained after 30 creaming days (see supporting information for the other days). It is showed that NRL gets concentrated with any combination of HEC and SDS. Nevertheless, if we zoom in the graph (see **Figure 13B**), values below 50% DRC concentration were obtained on extreme points HEC 2% v/v -SDS 0.0% v/v, HEC 2%-SDS 0.8% v/v, HEC 8% v/v -SDS 0.0% v/v. The RS validates the behavior already explained, DRC presents

an increase over time especially in system HEC 5% v/v. Concentrations by DRC can be more than 50% if SDS is added into the system. By contour plot analysis the optimal concentrations of HEC and SDS were HEC 5% v/v and 0.4% v/v of SDS. Also, *nlminb* function in RStudio was used to predict the optimal concentration of HEC and SDS: 4.83 %v/v and 0.43 %v/v respectively with a predicted DRC value of 57.55%. (See supporting information). The optimal ranges of HEC concentration 2% v/v to 6% v/v and SDS concentration 0.0 to 0.6% v/v are proposed as the main operation points to get concentration on latex system. With the aim to calculate the HEC and SDS concentrations for a required DRC, *rsm* package in RStudio was used to calculate the DRC model (Equation 4)

$$DRC = 5.2127[HEC] + 13.6454[SDS] - 0.6006[HEC]^2 - 23.3278[SDS]^2 + 1.3517\,[HEC][SDS] + 42.0233 \quad \text{Equation (4)}$$

Where [HEC] represents the HEC concentration, [SDS] represents the SDS concentration and DRC dry rubber content. The quadratic model with curvature effects presents an R-squared and adjusted R-squared of 81.33% and 73.55% respectively, and a p-value of 0.0004, this means that the model is significative for NRL concentration, and it is adjustable for the representation of DRC behavior. In addition to this, the coefficients of the model allow to understand the significance of each factor on the response variable, in this case all factors and its interactions are significative for the presented model. HEC and SDS concentration has a strong influence on DRC behavior especially, SDS concentration is the controlling factor in this model.

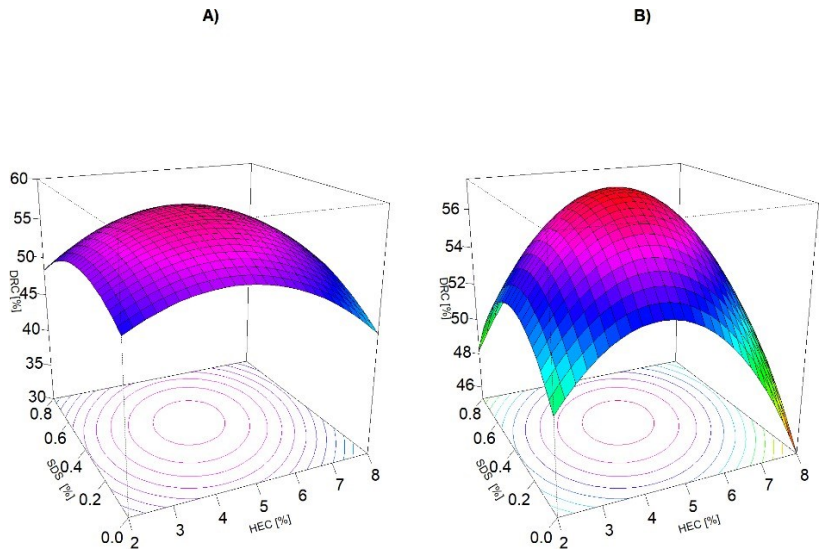

Figure 13. RS for DRC at HEC and SDS concentrations for 30 days of creaming.

Figure 14 shows the z-potential RS obtained after 30 creaming days. The surface predicts the behavior of z-potential with HEC and SDS concentrations and validate that all NRL-HEC-SDS systems are stable. The results suggest that lower concentrations of HEC (e.g., HEC 2% v/v) allows an enhance of electrostatic repulsion between NRL particles and SDS, reaching maximum z-potential values. By contour plot analysis, optimal HEC and SDS concentrations were HEC 2% v/v and SDS 0.8% v/v. Optimal ranges in HEC concentrations 2 to 6% v/v and SDS concentration 0.0 to 0.6% v/v are proposed to ensure colloidal stability during concentration process. Z-potential model was obtained using *rsm* package in RStudio to predict its behavior in NRL systems with HEC and SDS concentrations. z-potential behavior indicated that NRL system will be more stable if low concentrations of HEC are used.

$$ZP= 6.0506\,[HEC]- 9.9862\,[SDS]- 0.5407\,[HEC]^2-6.2166[SDS]^2+1.4002[HEC][SDS]-80.0235 \quad \text{Equation (5)}$$

Equation (5) Represents Z-potential model, [HEC] the HEC concentration and [SDS] is the SDS concentration. The quadratic model with curvature effects presents an R-squared and adjusted R-squared of 80.96% and 73.02% respectively, and p-value of 0.0005, this means that model is significative for the variable, and it is adjustable for the representation of DRC behavior. In addition to this, the model coefficients allow to understand the significance of each factor on the response variable, in this case only HEC factor and its quadratic interactions are significative for the z-potential prediction. This is attributed to the influence of HEC concentration on depletion flocculation and therefore on stability. (For additional information see supporting information).

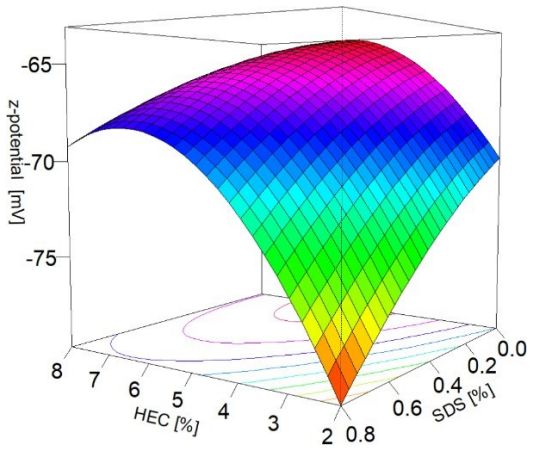

Figure 14. RS for Z-potential at HEC and SDS concentrations after 30 creaming days

4. Rheological properties of NRL concentrated with HEC and SDS

NRL behaves as pseudoplastic fluid, and its viscosity is nearly close to water ~ 1cP. **Figure 15** shows the effect of HEC and SDS on relative viscosity at 2 and 30 days after creaming at a shear rate of 100 $s^{-1.}$ An increasing of viscosity by HEC addition is noticeable even at 2 days. When system reaches 30 days, for high HEC concentration, viscosity is higher because the NRL system is saturated, but for low and medium HEC concentration, viscosity decrease because HEC has reorganized its chain over time, and this reorganization is enhanced due to SDS presence allowing a viscosity reduction. This is attributed to charge repulsions between particles, and the effect is visible since day 2. This allows a better HEC distribution among NRL system, facilitating interactions for NRL concentration.

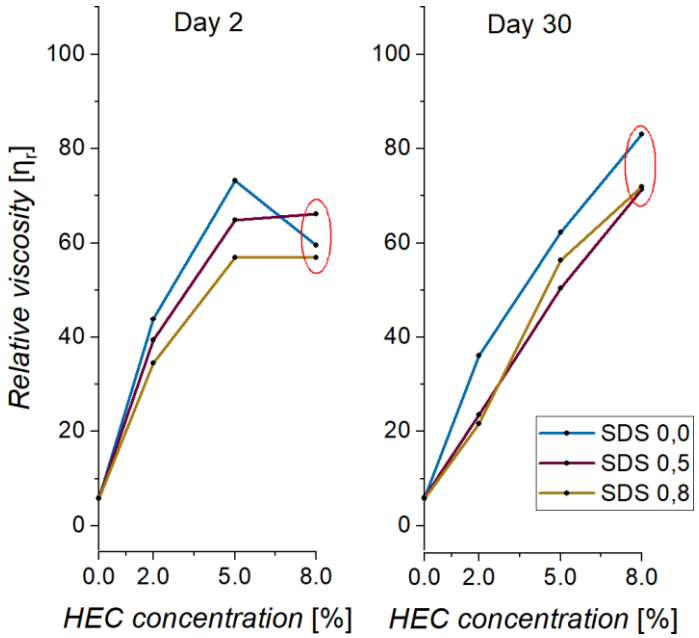

Figure 15. Effect of HEC concentration in relative viscosity after 2 and 30 days. Blue line: NO SDS, pink line: 0,5 SDS, yellow line: 0,8 SDS

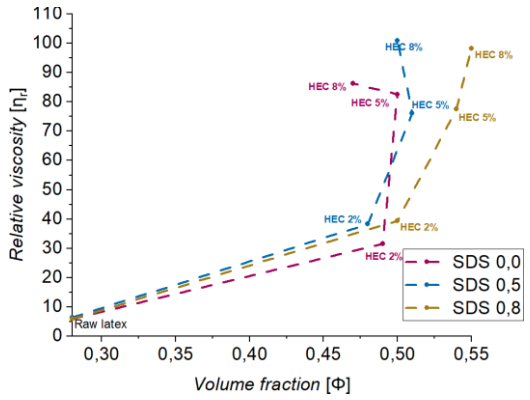

Figure 16. Relative viscosity (η_r)of HEC and SDS systems for its corresponding volume fractions at 30 days

Figure 16 shows the relative viscosity η_r as function of Φ for each HEC and SDS system for a constant shear rate of 100 s^{-1}. Only at day 30, the trend is clearer and a tendency of re-organization of systems is observed. At this point, volume fraction of systems is similar, but viscosity η_r stills changing due to higher HEC concentrations. In this case, HEC 8% v/v system presents higher values of viscosity due to the flocculation effect of creaming agent on particles causing agglomerations and further coagulation. The use of SDS at this HEC concentration is almost mandatory, since at this creaming time, the surfactant-free system is already highly flocculated, and the shear promotes the binding of irreversible agglomerates (coagulation). Decreasing on η_r is followed by HEC 5% v/v and HEC 2% v/v, being the last one with lower η_r, this is attributed to the adsorption of HEC presented over time on NRL particles.

In raw NRL, the particles always present an elastic behavior as showed in **Figure 17** . When HEC and SDS are added the system changes to a viscoelastic. For storage moduli (G'), lost moduli (G'') and complex viscosity (|η*|), oscillatory measurements were carried out with fixed frequency at 1 Hz and strain from 0.1-100%, after 30 days. According to the results, addition of HEC increases G', G''and |η*|. In the viscoelastic linear zone (VLZ), G' predominates over G'' that means that system keeps its elasticity over time and increased proportionally with HEC concentration. In systems with medium and high HEC concentration (i.e., 5% and 8% v/v) the elastic response has a significant increase, 10 and 100 times higher, than low HEC (2% v/v) system. This also means that HEC give a reversible deformation at high strains (%) until reach the cross over point or critical strain (γ_c). The behavior is represented by the red line in **Figure 17**, as HEC concentration grows the cross over point

displaced to the right at strain axis. Nevertheless, when SDS is added into HEC-NRL systems, a loss in the elasticity is identified, leading to a prompt irreversible deformation at less strains (%) compared to the systems without surfactant. This suggest that SDS promote rheological instability by the absorbing of energy from NRL particle withdrawing its elasticity capability, getting the system more viscous and less elastic.

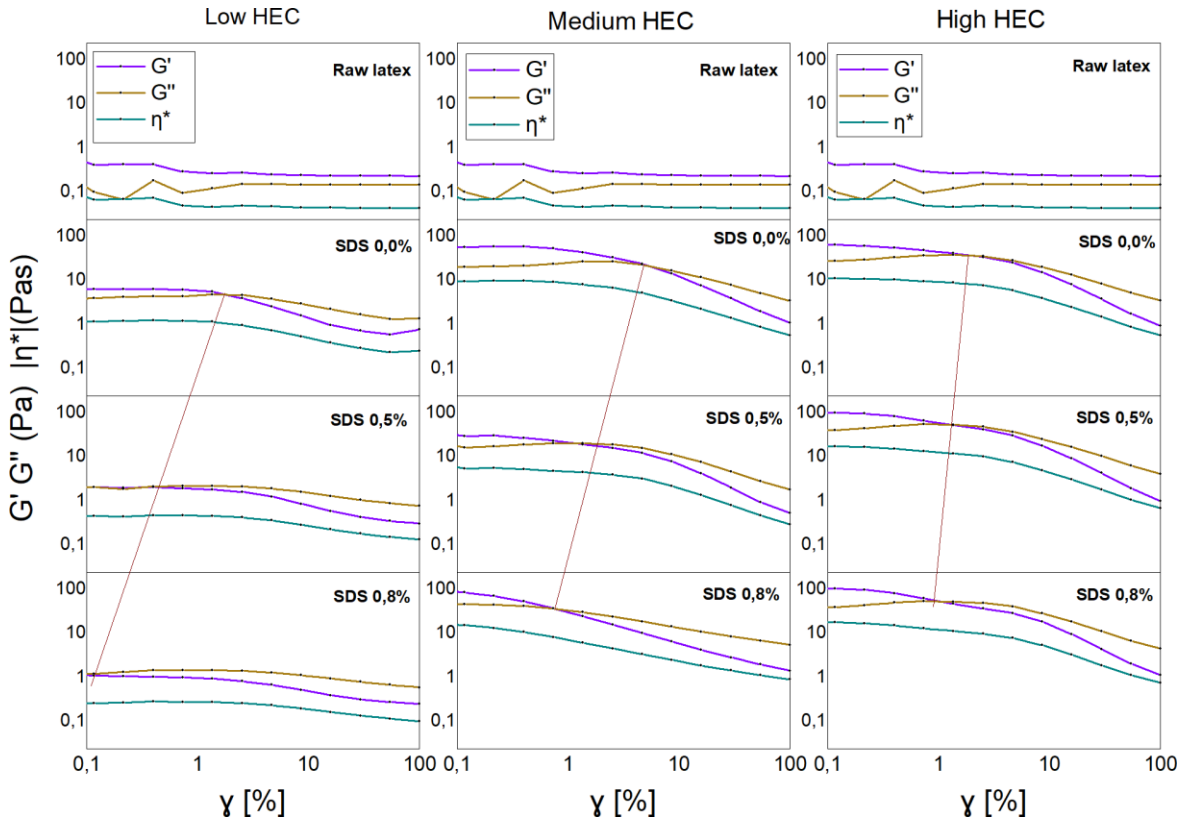

Figure 17. Log G', G'' (Pa) and |η*| (Pas) vs γ (%) for NRL concentrated with HEC and SDS at creaming day 30.

Figure 18 clearly shows that γ_c in NRL concentrated with HEC and SDS tends to decrease when SDS is added into systems. Values shows that system with HEC 5% v/v presents high critical strain values and hence lower loses on elasticity when SDS is added. In this way, higher HEC values promote more particle elasticity, but SDS repulsions restrict system fluency, hence at lower HEC concentrations the effect of SDS is more noticeable on systems.

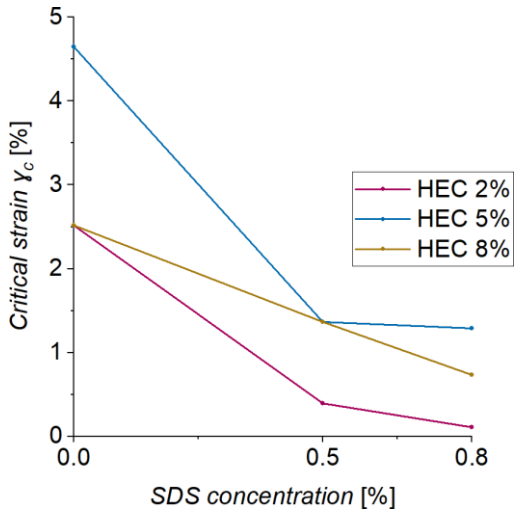

Figure 18. Critical strain vs. SDS concentration for each HEC system on NRL.

4. Proposal of NRL-HEC-SDS interactions in NRL

NRL particles are mainly anionic, therefore its natural state is to be dispersed by means of repulsions forces. HEC and SDS are both species with different chemical nature: non-ionic and anionic, respectively. The role of adding HEC in NRL dispersion is primarily to thicken phases, promoting flocculation (creaming), by weak interaction. When SDS is added, the effect of NRL concentration gets enhanced. As HEC is a non-ionic polysaccharide, no adsorption is present onto NRL particles. However, it is important to note that SDS is an amphiphilic surfactant, and the hydrophobic tail or hydrophilic head can strongly interact with functional groups of NRL proteins giving rise to an adsorption. In this way, three possible adsorption cases can occur as displayed in **Figure 19**:

1. **Hydrophobic SDS tail adsorbs onto NRL particle:** hydrophobic tail is attached by hydrophobic interactions to protein non-polar groups (e.g., allyl and dimethyl allyl groups) repealing water and leaving exposed its hydrophilic head.
2. **Hydrophilic SDS head adsorbs onto NRL particle:** hydrophilic head is attached to amine groups of protein by ion-dipole interactions. Nevertheless, in this case hydrophobic tail will remain exposed in a polar and hydrophilic medium.
3. **Combined hydrophobic tail and hydrophilic head onto NRL particle:** hydrophilic head of some SDS molecules get attached into NRL surface by amine groups and hydrophobic tail of some SDS molecules get attached into NRL surface by hydrophobic groups of proteins.

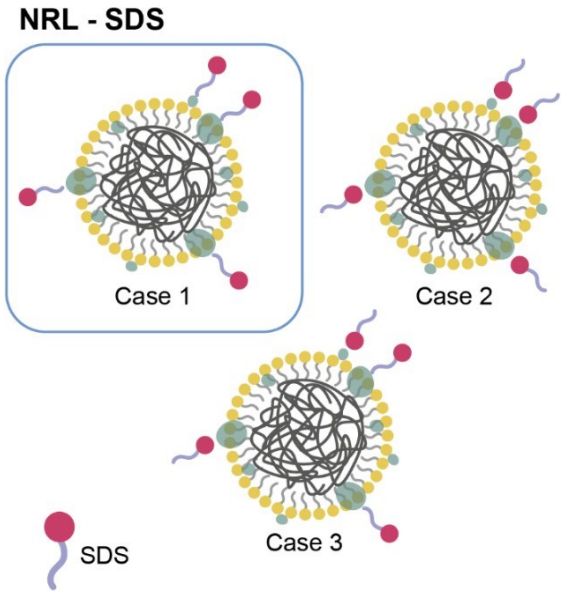

Figure 19. SDS adsorption onto NRL particles. SDS conformation: hydrophilic SDS head (red). hydrophobic SDS tail (blue) and Rubber particle: composed of a layer of proteins (green) and phospholipids (yellow)

According to SDS nature, case 1 is the most probably to occur because when SDS molecules interacts with NRL dispersion the whole medium is polar (i.e., water and net NRL particle layer), this causes that hydrophobic tail to remain "unprotected" and looking for any hydrophobic section to bind until it attaches to non-polar groups on NRL particles.

According to DRC results, hydroxyl groups of HEC and hydrophilic head of SDS interact between them by weak Van der Waals forces (i.e., ion-dipole). Only SDS adsorbs onto NRL protein, and HEC and SDS interacts between them without any adsorption allowing that HEC attract more NRL particles. In addition to this, in the NRL-SDS system, repulsion is also present by electrostatic forces, opening the interparticle space for HEC, as represented in **Figure 20**.

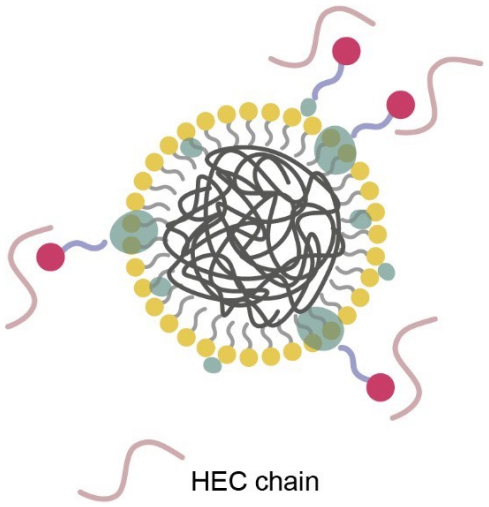

Figure 20. Representation of interaction between NRL-HEC-SDS

HEC and SDS concentrations (see Table 2) used are lower than c.m.c. and CAC. Both c.m.c. and CAC concentrations depend on surfactant. Micellization of SDS is at 8 mM, and the CAC between SDS and HEC is 6 mM [44] . So, in this system is presumed that no complex formation is present because there is not a strong binding between SDS and HEC chain.

Table 2. Equivalences of HEC and SDS concentrations in mM

HEC concentration in [%v/v]	HEC concentration in [mM]	SDS concentration in [%v/v]	SDS concentration in [mM]
2	0.75	0	0
5	1.85	0.5	1.5
8	3.00	0.8	2.5

According to results and the presented relation between HEC-SDS, five co-existing interactions are possible for the NRL-HEC-SDS system: 1) **Chemical interaction between HEC and NRL continuous phase,** by hydrogen bonding that increases continuous phase viscosity giving rise to an initial physical creaming in NRL system. This interaction is present at low, medium, and high HEC concentration and this is presumed to be the first interaction to appear. 2) **Chemical interaction between HEC and NRL particles,** also by hydrogen bonding interaction between polar groups of HEC and NRL particle (especially with the α-terminal groups) [10] this give rise to a depletion flocculation

phenomena due to weak attractions in particles that increases creaming velocity. Flocculation grade depends on low, medium, or high HEC concentration. At high HEC concentration, flocculation begins to appear after 15 days because the immobilization effect caused on NRL particles, also proposed as a depletion stabilization. When SDS is added into NRL-HEC system, 3) **Hydrophobic interactions between SDS and NRL,** appears through hydrophobic tail attachment to NRL protein hydrophobic groups leading into an adsorption. Then, SDS and HEC begins to interact by 4) **Van der Waals forces,** by means of ion-dipole, without complex formation. This behavior is observed for each NRL-HEC system where SDS addition causes a DRC enhancement according to SDS concentration. As it was showed, 0.5 % v/v of SDS represent the concentration where NRL creaming is more noticeable. There is also present 5) **electrostatic repulsions between SDS-NRL particles,** each SDS molecule adsorbed onto NRL particles causes repulsion between other particles, especially when SDS increases (e.g., at SDS 0.8%v/v). The repulsion can allow that HEC distribute among some NRL interparticle spaces facilitating interactions between HEC and SDS. Nevertheless, at lower concentrations of HEC, it becomes more difficult to keep interactions and hence to keep flocculated the NRL particles. The above description is represented in **Figure 21** for each system.

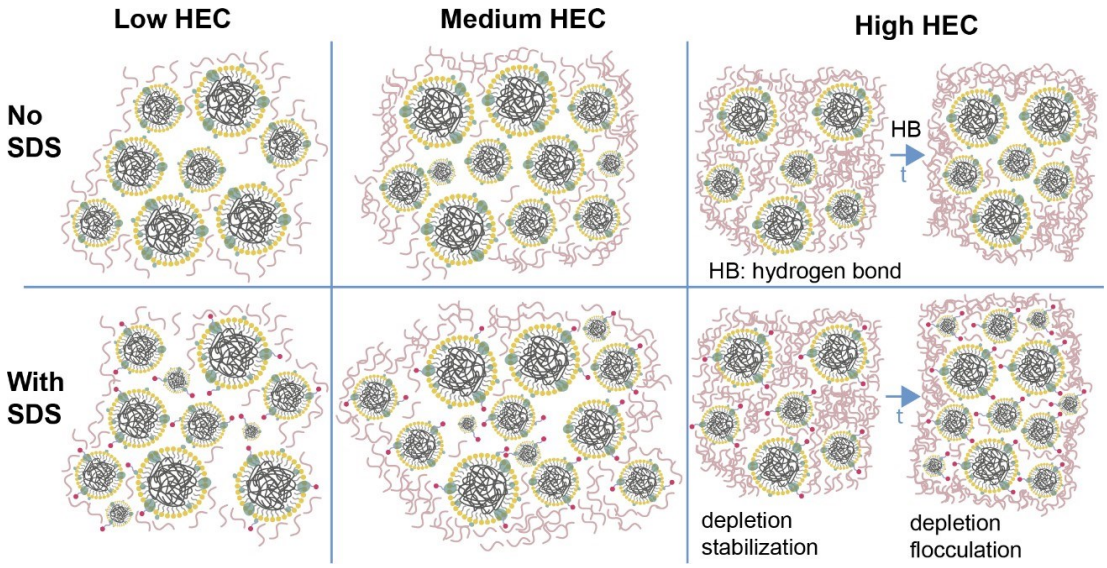

Figure 21. Proposal of behavior of NRL-SDS-HEC systems in creaming at low, medium and high HEC concentrations. t=time

CONCLUSION

This research allowed to select HEC and SDS as creaming agent and surfactant as the main agents for enhancement of concentration in NRL system. Then, the effect of different concentrations of those agents were evaluated in NRL system to get an improvement in the use of this natural resource in field. Therefore, an analysis of the effect of different concentrations of HEC and SDS in NRL system is presented. HEC addition causes an increase on viscosity giving rise to an initial physical creaming and subsequently to chemical interactions leading to depletion flocculation phenomena that also promote creaming. When SDS is added, concentration and stability get enhanced by the HEC-SDS interaction by means of Van der Waals forces and electrostatic repulsions. In this way, NRL system can stand different HEC concentrations to enhance rubber concentration without affecting its colloidal stability because z-potential values are in the range of -78 to -63 mV. SDS addition increase z-potential because of its anionic nature. Due to the saturation effect at high HEC concentration systems, that presents slow concentration process, a depletion stabilization phenomenon starts at 2 days. Therefore, at 15 or more creaming days the systems begin to develop the depletion flocculation effects due to the interactions between HEC and NRL. According to response surface, optimal DRC can be obtained with 4.87% v/v for HEC and 0.43% v/v for SDS and higher z-potential with 2%v/v HEC and 0.8%v/v SDS. Nevertheless, any concentration of HEC and SDS allows to obtain high colloidal stability. Rheological properties of NRL dispersion increases with HEC addition where G' and $|\eta^*|$ gets 10, 100 and 1000 times higher than original raw latex. Nevertheless, SDS addition bring forward the viscous behavior getting the system rheologically instable.

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Supporting Information

S1. Clarifications about the analysis of variance (ANOVA).

In the tests where statistical analysis was used, an ANOVA was developed for the variablesanswer. The hypotheses that were raised were:

Null hypothesis (H0): all factors have the same mean.

Alternative hypothesis (Ha): There are at least one pair of means that are different from each other.

If the p-value is less than the 0.05 level of significance, H0 is rejected.

The assumptions of the ANOVA were validated on the residuals, these are normal distribution and homoscedasticity of the data. The normal distribution was validated graphically with box plots, histograms of frequencies and quartiles. The same was done with homoscedasticity (variance constant). In all cases, the hypotheses were evaluated and normality and homoscedasticity of the data.

S2. Tamarind seed powder preparation

Tamarind seed peeling

1. Weight 200 g of tamarind seeds and wash them with water removing broken seeds. Let the seeds 24 h into water.
2. Remove kernel from the shell with the hands and introduce them in a bag. Repeat steps 1 and 2 until all shells be removed.
3. Weight the seeds in a balance and introduce them into a dryer or oven at 140 °C during 4h.
4. Weight the dry seeds and calculate humidity as follows:

$$\%\text{Humedad} = \frac{W_i - W_f}{W_i} \times 100 \qquad \text{Equation S1}$$

Wi: Initial weight before drying

Wf: Final weight after drying

5. Seed's humidity must have a %humidity between 5%-8%. If this humidity is not reached introduce them into dryer.

6. Keep the seeds into a bag and dehumifider.

Milling and sieving

1. Mill the seeds in a blade mill 5 times until obtain a fine powder.
2. Sieve the powder in 4 different meshes 40,50 and 100. Powder must have an approximately size of 3 mm
3. Keep the seeds into a bag.

S3. ANOVA for TSC (%) in creaming agent selection: HEC -selected agent

This ANOVA were carried out in STATGRAPHICS software. The factors with p-value less than 0.05 (marked as 0.0000) have statistically significant effect on TSC variable for the HEC creaming agent. Creaming agent concentration and surfactant type, and interaction between them are significative factors.

Table S3. ANOVA for HEC selection as creaming agent. Values marked with red are statistically significative for TSC variable.

Factor	**F-Ratio**	**P-value (< 0.05)**
Creaming agent concentration	95.00	0.0000
Surfactant Type	21.17	0.0000
Time	0.96	0.4157
Creaming agent concentration: Surfactant type	7.05	0.0000
Creaming agent concentration: time	1.76	0.0863
Surfactant type: time	1.41	0.1956

Analysis of Variance for TSC - Type III Sums of Squares

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
MAIN EFFECTS					
A:BLOCK	2,25781	1	2,25781	0,28	0,5976
B:Concentracion Agente cremante	2317,23	3	772,41	96,00	0,0000
C:Tipo Surfactante	511,011	3	170,337	21,17	0,0000
D:Tiempo	23,1506	3	7,71688	0,96	0,4157
INTERACTIONS					
BC	510,255	9	56,695	7,05	0,0000
BD	127,718	9	14,1909	1,76	0,0863
CD	102,122	9	11,3469	1,41	0,1956
RESIDUAL	724,131	90	8,0459		
TOTAL (CORRECTED)	4317,88	127			

All F-ratios are based on the residual mean square error.

The StatAdvisor

The ANOVA table decomposes the variability of TSC into contributions due to various factors. Since Type III sums of squares (the default) have been chosen, the contribution of each factor is measured having removed the effects of all other factors. The P-values test the statistical significance of each of the factors. Since 3 P-values are less than 0,05, these factors have a statistically significant effect on TSC at the 95,0% confidence level.

S4. Factorial 3^2 ANOVA for DRC and Z-potential

This ANOVA were made using RStudio software

DRY RUBBER CONTENT (DRC)

Table S4. Significance table for time and SDS concentration on DRC from ANOVA (** correspond to 0.05 significance)

Factor	P-value (< 0.05)		
	HEC 2%	**HEC 5%**	**HEC 8%**
Time	0.21528	4.735e-07**	6.719e-06**
SDS concentration	0.86677	0.001114**	0.09015
Time: SDS	0.06889	0.493541	0.64085

Time is significative statistically for systems HEC 5% v/v, HEC 8% v/v. Significance level was 0.05 according to p-value. Interaction between time and SDS concentration is not significant for DRC.

Table S5. Significance table for factors HEC and SDS concentration on DRC for each creaming day from ANOVA. (** corresponds to 0.05 significance)

Factor	P-value (< 0.05)		
	2 Days	**15 Days**	**30 Days**
HEC concentration	1.107e-06 **	0.007703**	0.5867
SDS concentration	0.5301	0.007691**	0.3913
HEC: SDS	0.6663	0.022711**	0.2528

Effect of HEC concentration and SDS concentration into DRC. HEC concentration is statistically significative at days 2 and 15, and SDS concentration is significative at day 15. Interaction between both factors is significative for creaming day 15. Significance level was 0.05 according to p-value

Z-POTENTIAL

Table S6. Effect of time and SDS concentration on Z-potential from ANOVA. (** corresponds to 0.05 significance)

Factor	P-value (< 0.05)		
	HEC 2%	**HEC 5%**	**HEC 8%**
Time	0.00512 **	0145137	0.936679
SDS concentration	5.185e-05**	0.001067**	0.0008673
Time: SDS	0.63731	0.865046	0.1829053

Time and SDS concentration are statistically significative for HEC 2%v/v, SDS concentration are significative for HEC 5%v/v but not for HEC 8% v/v. Interaction between both factors are not significative for Z-potential. Significance level was 0.05 according to p-value

Table S7. Effect of HEC and SDS concentration on Z-potential from ANOVA for each creaming day. (** corresponds to 0.05 significance)

Factor	P-value (< 0.05)		
	Day 2	**Day 15**	**Day 30**
HEC concentration	0.0903	0.4574	0.00362**
SDS concentration	4.379e-05**	1.163e-05**	0.01119**
HEC: SDS	0.9511	0.4735	0.21817

HEC and SDS concentration are statistically significative for HEC and SDS concentration only ay day 30. For 15 and 2 creaming days only SDS concentration is significative. Interaction between factors is not significative for Z-potential.

S5. Surface response ANOVA for DRC and Z-potential.

The surfaces were also made for day 2, 15 and 30. In main document are presented surfaces for 30 days.

DAY 30

DRC

Table S8. DRC surface response ANOVA and parameters for each factor in model. ** corresponds to 0.05 significance level

Parameter	Estimate	P-value (< 0.05)
Intercept	42.02331	2.812e-09**
HEC concentration	5.21269	0.0006328**
SDS concentration	13.64539	0.0427981**
HEC^2	-0.60065	0.0001388**
SDS^2	-23.32778	0.0042529**
HEC: SDS	1.35170	0.0365056**

Multiple R-squared: 0.8133, Adjusted R-squared:0.7355. F-statistic: 10.46 on 5 and 12 DF, p-value: 0.0004782. ** corresponds to 0.05 significance

Model for DRC surface response is significative, and therefore all the factors, included quadratic. Model has a good adjustment as mentioned on manuscript.

Z-potential

Table S9. DRC surface response ANOVA and parameters for each factor in model. ** corresponds to 0.05 significance level

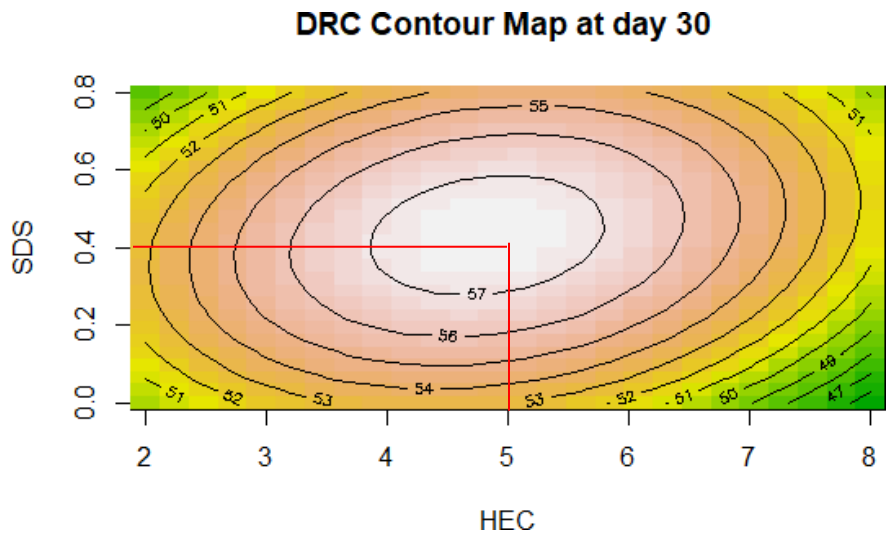
Parameter	Estimate	P-value (< 0.05)
Intercept	-80.02352	1.069e-10**

HEC concentration	6.05063	0.03027**
SDS concentration	-9.98628	0.270794
HEC^2	-0.54074	0.00488**
SDS^2	-6.21667	0.526379
HEC: SDS	1.40026	0.115375

Multiple R-squared: 0.8096, Adjusted R-squared: 0.7302, F-statistic: 10.2 on 5 and 12 DF, p-value: 0.000536

Model for Z-potential surface response is significative, and therefore all the factors, included quadratic. Model has a good adjustment as mentioned on manuscript.

S6. Contour plots



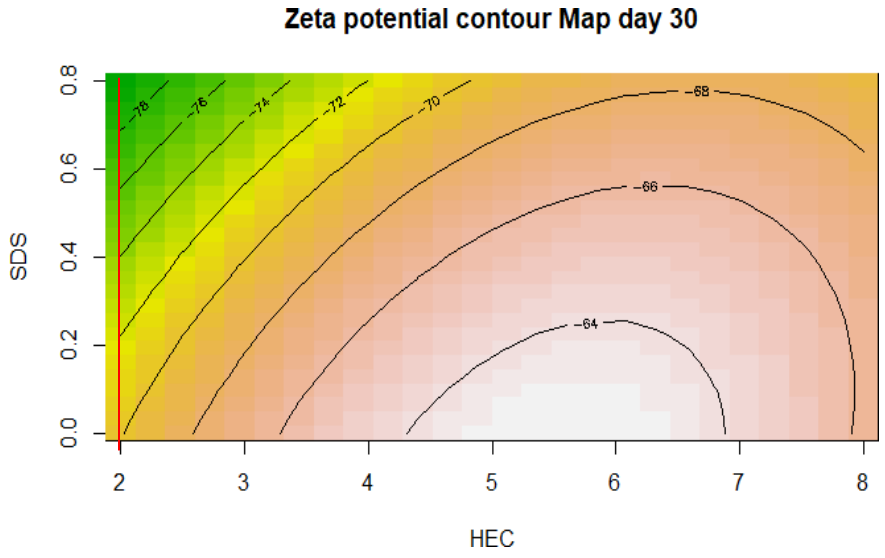
Contour plot for DRC response. Optimal point by empirical method. 5%v/v HEC and 0.4%v/v SDS are adequate for the NRL concentration.

***nlminb* function**

Allows to minimize functions to obtain optimal points. Negative of function allows to obtain maximum.

```
> conc= function (x) {-((5.2127 * x[1]) + (13.6454* x[2])-(0.6006* (x[1]^2))
 -(23.3278 * (x[2]^2))+ (1.3517* (x[1])*(x[2])) + (42.0233))}
> nlminb(c(2,0.0),conc,lower=0,upper = 60)
$par
[1] 4.8260331 0.4322904

$objective
[1] -57.55101

$convergence
[1] 0

$iterations
[1] 5

$evaluations
function gradient
       8       10

$message
[1] "relative convergence (4)"
```

Calculation of optimal point by *nlminb* function for DRC response.4.826%v/v HEC and 0.432%v/v SDS are adequate for NRL concentration.



Contour plot for DRC response. All ranges of HEC and SDS are into colloidal stability range. Optimal point was identified into 2.0% v/v HEC concentration, and SDS concentration 0.8%v/v for being the highest z-potential value.

S7. Surface response for days 2 and 15

At these days, the SR is forming to give rise to a clearer trend, like the one shown on day 30 in the main manuscript. DRC is increasing with time for each run of the experiment and z-potential is turning into a more stable system.

DRC

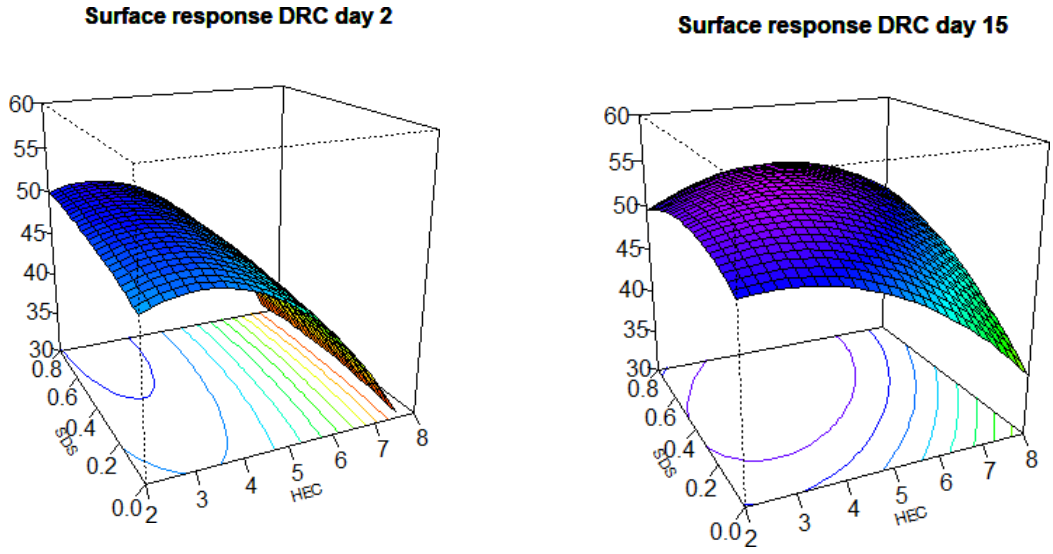


Figure S1. Surface response for DRC at day 2 and 15.

Z-potential

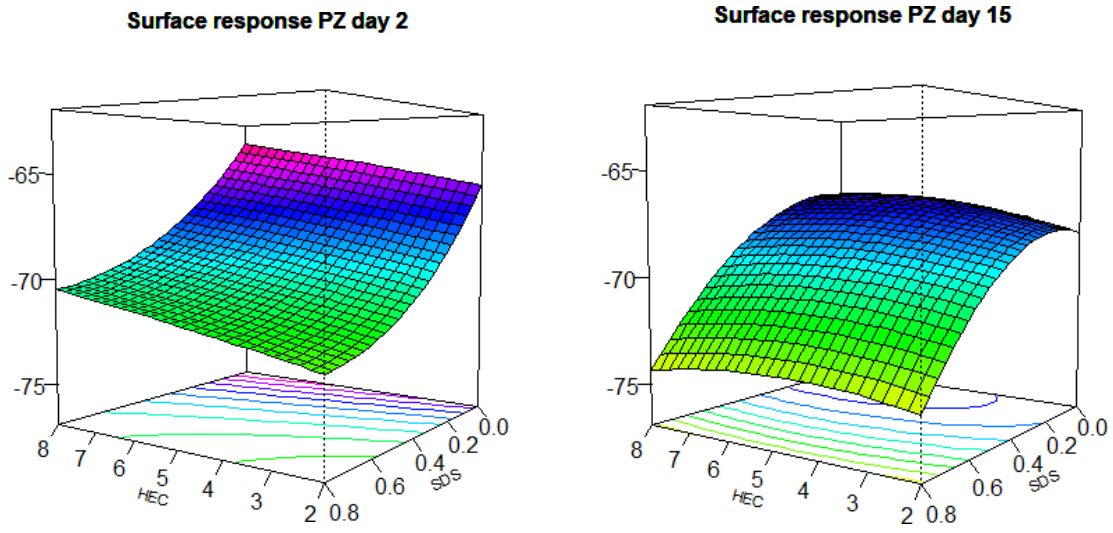


Figure S2. Surface response for z-potential day 2 and 15

S8. Rheology plots

Figure S1, S2, S3 ,S4 and S5 shows rheology plots made for each HEC and SDS system at day 30 to show that SDS concentration modifies viscosity but not as HEC does.

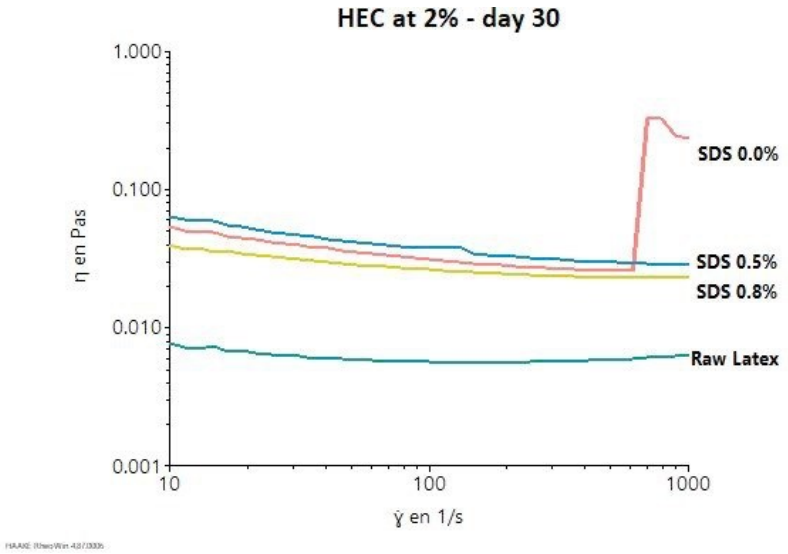


Figure S1. Curve Flow of NRL concentrated with HEC at 2% v/v at different SDS concentrations

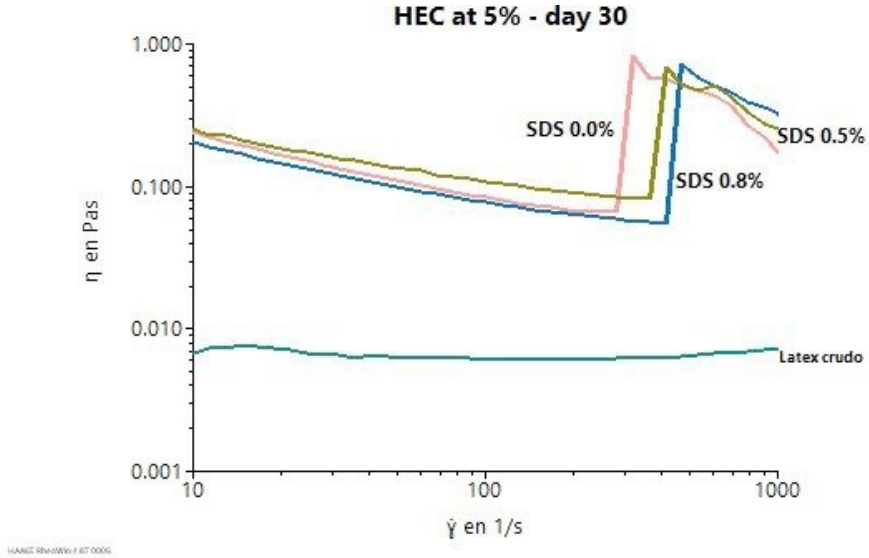


Figure S2. Curve Flow of NRL concentrated with HEC at 2% v/v at different SDS concentrations

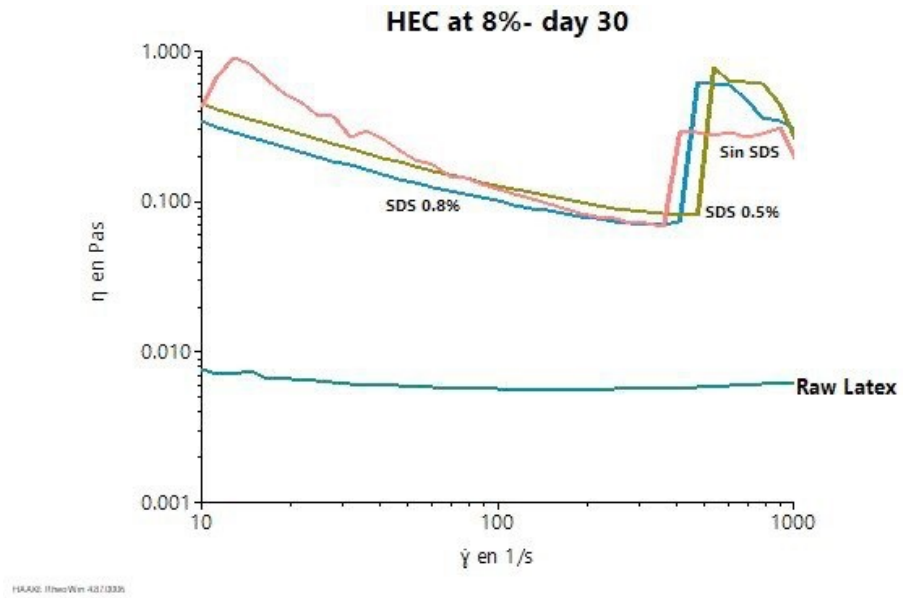


Figure S3. Curve Flow of NRL concentrated with HEC at 8% v/v at different SDS concentrations

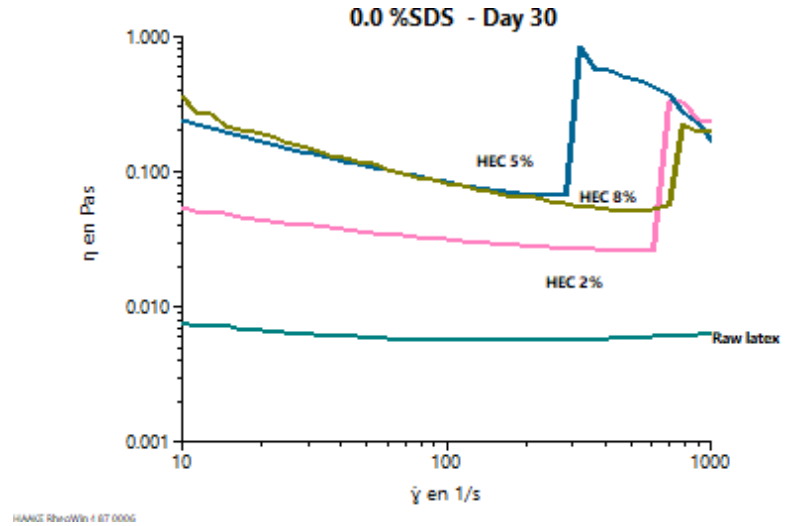


Figure S3. Curve Flow of NRL concentrated without SDS at different HEC %v/v concentrations

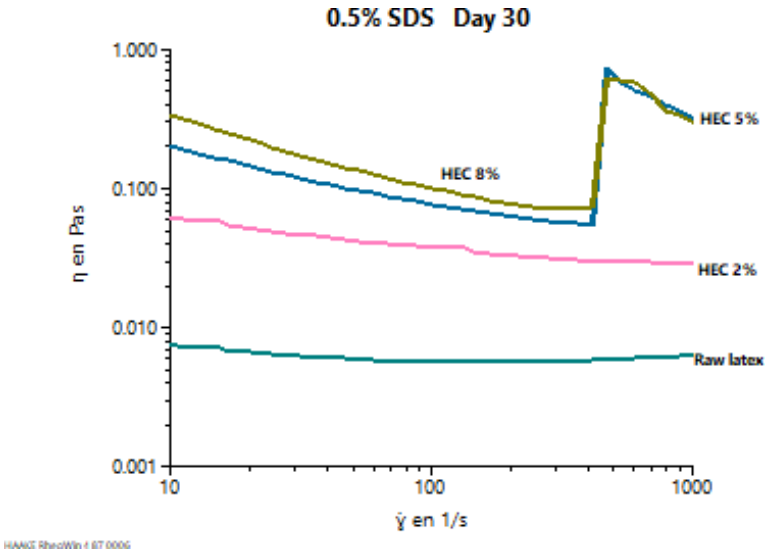


Figure S4. Curve Flow of NRL concentrated with 0.5%v/v SDS at different HEC %v/v concentrations

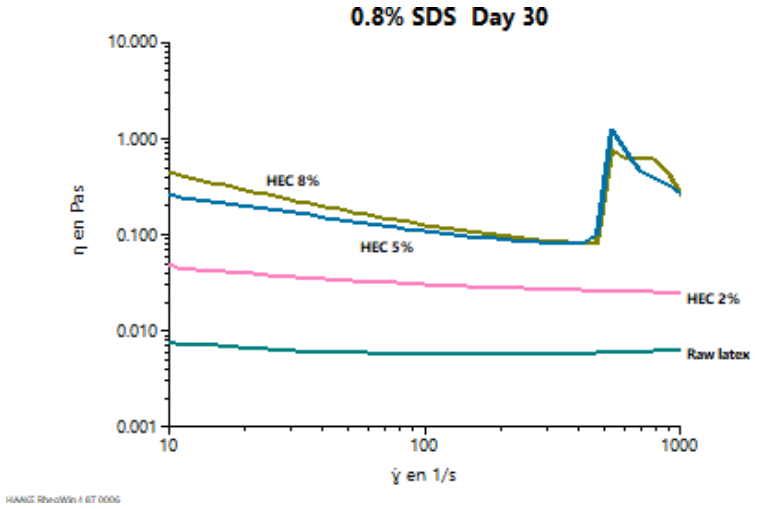


Figure S5. Curve Flow of NRL concentrated with 0.8%v/v SDS at different HEC %v/v concentrations