



Creaming kinetics and aggregation of concentrated natural *Hevea* latex

Lazare Mesnier¹ · Nicolas Sanson¹ · Jean-Baptiste d'Espinose de Lacaillerie¹

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Abstract

Natural rubber latex (NRL), extracted from the *Hevea brasiliensis* tree, plays a pivotal role in many industrial sectors due to its unique physical properties. This study investigates the colloidal properties and creaming behavior of concentrated NRL, up to a volumetric fraction of $\Phi=0.54$. First, using a set of experimental techniques such as dynamic light scattering, electrophoretic mobility experiments and environmental scanning electron microscopy, we characterize both Small Rubber Particles (SRPs) and Large Rubber Particles (LRPs) within NRL. Then, using light scattering, we monitor across a wide range of volume fractions the creaming fronts of concentrated NRL. The creaming behavior of both SRPs and LRPs is modeled using the Richardson-Zaki (R-Z) equation for both low (unscreened surface charges) and high (screened surface charges) ionic strengths, identifying creaming speeds under laminar flow conditions with an R-Z parameter close to $n = 4.65$. In contrast to diluted suspensions, high particle volume fraction in concentrated NRL restricts diffusion and allows the development of slow moving creaming fronts with speeds in the range of nm.s^{-1} . Findings also reveal that higher ionic strengths, notably when calcium ions are involved, enhance particle aggregation, transitioning the suspension from bimodal to monomodal size distribution. Results point to the subtlety of studying latex aggregation in concentrated media to observe the onset of particle aggregation. This research provides insights into the physicochemical interactions in concentrated latex suspensions, offering implications for improved processing techniques in the rubber industry.

Keywords Colloidal stability · Richardson-Zaki · Concentrated suspensions

Abbreviations

DLS	Dynamic Light Scattering
ESEM	Environmental Scanning Electron Microscopy
R-Z	Richardson-Zaki
NR	Natural Rubber
NRL	Natural Rubber Latex
SRP	Small Rubber Particle
LRP	Large Rubber Particle
SRP _{latex}	Suspension of only SRPs
LRP _{latex}	Suspension of mostly LRPs

b	Richardson-Zaki slope intercept at $1 - \Phi = 1$ m^2
d	Particle diameter m
D	Diffusion coefficient $\text{m}^2.\text{s}^{-1}$
$d_{\text{p-p}}$	Interparticular distance
e	Elementary charge C
g	Gravitational constant m.s^{-2}
I	Ionic strength mol.m^{-3}
k	Boltzmann constant J.K^{-1}
K_{M}	Debye-Hückel parameter m^{-1}
n	Richardson-Zaki parameter
N	Soft shell charge carrier density mol.m^{-3}
Pe	Peclet number
pH	Potential of hydrogen
pKa	Potential of acid dissociation
Re	Reynolds number
t	Time s
t_{s}	Advective time s
T	Absolute temperature K
v	Particle settling velocity m.s^{-1}

✉ Nicolas Sanson
nicolas.sanson@espci.fr

✉ Jean-Baptiste d'Espinose de Lacaillerie
jean-baptiste.despinose@espci.fr

¹ Soft Matter Sciences and Engineering Laboratory, ESPCI
 Paris PSL, Sorbonne Université, CNRS UMR 7615, 10 Rue
 Vauquelin, Paris F-75005, France

Z	Soft shell charged carrier valence
δt	Time increment
$\Delta B(x, t)$	Evolution of variation in backscattered light intensity %
ε_0	Vacuum permittivity F.m^{-1}
ε_r	Liquid relative permittivity
η	Fluid dynamic viscosity Pa.s
θ	Scattering angle of measurement
κ^{-1}	Debye length m
λ^{-1}	Ion permeability thickness m
μ	Electrophoretic mobility $\text{m}^2.\text{V}^{-1}.\text{s}^{-1}$
ρ_l	Solid particle density kg.m^{-3}
ρ_s	Solid particle density kg.m^{-3}
τ_D	Diffusive time s
ϕ	Particle volume fraction
ψ_0	Surface potential V
ψ_D	Donnan potential V
$\sqrt{\langle x^2 \rangle}$	Root of the mean square displacement m

Introduction

Natural rubber (NR), primarily composed of cis-1,4-polyisoprene, is a biosourced viscoelastic solid of high industrial importance. Its production reached 15.3 million metric tons in 2023 [1]. NR is renowned for having a plethora of interesting properties such a high elasticity, tensile strength (in the order of 20 MPa), strain induced crystallization, abrasion resistance and efficient heat dissipation [2]. These elements make NR irreplaceable, particularly for its most notorious applications in the tire or glove industries. NR uses also include, among others, tubing, vibration dampening materials, rubber bands, and materials for biomedical applications [3–5].

NR is obtained from the coagulation of natural rubber latex (NRL), which is extracted from the *Hevea brasiliensis* tree [6]. NRL is a colloidal suspension of particles made of a core of polyisoprene polymer chains with an average molar mass of approximately 10^6 g.mol^{-1} , surrounded by a charged and complex corona of fatty acids, phospholipids and proteins [7]. The structure of NRL particles is thus one of core-shell particles with a hard polyisoprene core surrounded by a soft charged permeable polyelectrolyte layer [8]. The unique physico-chemical properties of this system, both as a suspension and a bulk material, arise from the combination of high molar mass polyisoprene with natural molecules chemically or physically bound to its chains [9].

To produce commercial NRL, freshly tapped latex, also known as field latex, is further stabilized by raising its pH slightly above 6 with ammonia. It is then concentrated to volume fractions $\phi \approx 0.67$ via either centrifugation or creaming [2]. The former concentration method is the fastest and

most common, while, the latter, is a more cost-effective and energy-efficient alternative. After concentration, the suspension is further stabilized by increasing its pH above 10 with ammonia. Higher dried rubber content (DRC) can then be obtained using the creaming process. However, creaming of NRL is a slow process and the use of creaming agents is necessary to increase creaming speeds (e.g. casein, alginates, cellulose, PVA) [10, 11]. Thus, studying the creaming of natural latex is of significant industrial relevance.

Current studies of NRL are difficult to compare due to the naturally present disparities between samples since research on NRL has been conducted on many different *Hevea* latex types. These include field latex [10–16], which has a lower polyisoprene concentration (around $\phi \approx 0.30$) and contains non isoprene particles such as lutoids or Frey-Wyssling particles [17, 18], as well as low or high ammonia commercial NRL (around 0.2 and 0.7 wt% of ammonia respectively) [12, 19–27], prevulcanized [28, 29], dialyzed [30], deproteinized and/or transesterified latex [15, 31–35]. All of which drastically differ in compositions and properties.

Despite the wide application of NRL, detailed studies on its physico-chemical colloidal properties remain mainly focused on diluted suspensions which are not representative of operating conditions. Concentrated latex is typically analyzed according to ASTM D1076 [36]. This norm focuses on standardized industrial parameters such as (DRC), total solid content (TSC), pH, volatile fatty acid content (VFA), KOH number, mechanical stability time (MST), or chemical stability time (CST) [10, 19, 37]. However, these properties do not address the underlying creaming mechanisms of NRL nor the fundamentals of its stability. Rheological studies have been conducted on concentrated NRL, but they require the use of a low torque rheometer [23], or pH induced coagulation [28, 29], complicating the analysis. Latex stability has also been investigated by varying pH [28, 29], salt concentration [12, 38], or by addition of reinforcing agents [12, 24, 25], with results often presented as a pseudo phase diagrams (henceforth referred to as stability diagrams for simplicity). These studies aim to better understand the aggregation and coagulation behavior of *Hevea* latex particles, a topic of significant industrial interest since the quality of NRL-based products is heavily dependent on controlled coagulation.

Different industries rely on specific coagulation methods for processing natural latex. For instance, in the tire industry, bulk rubber is produced via acid coagulation of field latex. Meanwhile, salt coagulation is the most common processing method to produce thin films for condoms or glove-making for example [39]. The most widely used coagulating agents in industry are calcium salts, notably calcium chloride, CaCl_2 , or calcium nitrate, $\text{Ca}(\text{NO}_3)_2$. While this process is widely used today, studying calcium

aggregation is particularly tedious and differing hypotheses regarding the destabilization role of calcium salts coexist. Current hypothetical mechanisms include (i) neutralization of negative surface charges by Ca^{2+} and even charge reversal [38, 40], (ii) destabilization through precipitation of dissolved species in the latex serum (followed by hetero-aggregation) [41], and (iii) calcium chelating to adsorbed reactive functional groups, binding particles together [5, 39, 42]. The actual mechanism could even be a mixture of these proposed hypotheses. NRL colloidal properties and stability have been studied using a variety of analytical techniques including, but not limited to, dynamic light scattering (DLS) [27, 28], static light scattering (SLS) [28], electrophoretic mobility (zeta potential determination) [21, 22, 38], diffusing wave spectroscopy (DWS) [28], stochastic optical reconstruction microscopy (STORM) [15, 24, 25, 32], confocal laser scanning microscopy [13], and atomic force microscopy (AFM) [12, 13, 22, 25, 43]. However, these methods require high sample dilution before analysis, which may alter the system's dispersion state.

Experimentally, a convenient way to study colloidal stability without dilution is to establish stability diagrams where macroscopic and microscopic observations are used to evaluate particle stability under the parameters of interests [44–46]. Such diagrams have been used to study the aggregation of NRL but this process is highly subjective and operator dependent since distinguishing between a fully destabilized, partially destabilized, or metastable suspension can be challenging, especially at high particle volume fraction [28, 40, 42, 47]. Furthermore, these observations are made at a specific time point after sample preparation and do not account for changes in colloidal stability over time. Despite these limitations, stability diagrams remain a simple and effective tool for studying NRL. Indeed, experimentally investigating the sedimentation and aggregation of concentrated suspensions or emulsions has proven to be quite tricky due to the system's highly opaque nature, making stability diagrams a practical alternative.

This brief literature overview reveals the need for a deeper understanding of aggregation and coagulation behavior in concentrated *Hevea* latex suspensions. This is a topic of significant industrial interest since the quality of NRL-based products is heavily dependent on controlled coagulation. Currently, understanding on the creaming behavior and salt-induced aggregation of concentrated NRL is lacking. In this article, we aim to explore the creaming behavior of concentrated *Hevea* latex suspensions using light backscattering. We present a detailed physico-chemical characterization of commercial high ammonia *Hevea* latex. Furthermore, we will address the onset of particle aggregation at low calcium concentration and high particle volume fraction. This

approach offers a novel yet simple method to investigate the creaming and stability of NRL.

Materials and methods

Materials

KNO_3 , $\text{Ca}(\text{NO}_3)_2$ tetrahydrate, and KOH, all of which having a purity higher than 90%, were purchased from Sigma-Aldrich (USA). HNO_3 65% was purchased from VWR (USA). NH_3 25% solution was purchased from S-D-S Solvents (France). Concentrated high ammonia commercial natural *Hevea* latex was provided by Resinex (UK). The suspension was filtered through a 35 μm metallic mesh and kept at $\text{pH} \geq 9.5$ by addition of ammonia. All data presented in this article were measured on a single batch of *Hevea* latex, ensuring the relevance of the study.

Methods

Particle separation Centrifugation is a commonly used method to separate natural latex particles [13, 48]. In this study, NRL was diluted to $\phi \approx 0.06$ in an ammonia solution of $\text{pH} > 10$ and centrifuged at 20 °C. Depending on sample volume, either a Hettich Mikro 220R (Germany) or Eppendorf 5804R (Germany) centrifuge was used. To isolate large particles, NRL was centrifuged at 1500 g for 30 min. Then, the creamed fraction was collected with a spatula and dispersed into a minimum amount of ammonia – to achieve the highest possible latex concentration – before being centrifuged again at 4140 g for 1.5 h. This process was repeated and the collected creamed fraction was subsequently used for measurements. To isolate small particles, NRL was centrifuged at 1500 g for 30 min. Then, the bottom fraction was collected using a syringe before being centrifuged again at 4140 g for 1.5 h. The bottom fraction was collected and filtered using a 0.45 μm PVDF filter before being subsequently used for measurements.

Environmental scanning electron microscopy (ESEM) ESEM was used to image latex particles in a water-saturated environment. No sample preparation is necessary before observation, preserving their native state which is particularly interesting for the imaging of soft particles [49–51]. ESEM images were obtained on a Quattro ESEM (TermoFisher U.S.) equipped with a gaseous secondary electron detector (GSED) and using a field emission gun at a voltage of 15 kV. Latex samples were introduced on a conical Peltier plate with particles still as a stable colloidal suspension. Samples were cooled at 2.5 °C. A pump down sequence pulling vacuum and adding gaseous water 8 times between 800 and

1200 Pa [52] was performed in order to obtain a fully water saturated chamber with pressures as low as possible while staying above the vapor pressure of water at 2.5 °C. Water droplets were added around the sample to ensure a quick increase in humidity and minimizing sample drying during the pump down sequence. The working pressure was fixed to 750 Pa while condensation and evaporation at the sample surface were controlled by adjusting the target temperature of a Peltier element. Samples were placed approximately 5 mm from the incident beam to make sure electrons travel through as little gas as possible since the presence of a saturated water atmosphere lowers the resolution obtained compared to experiments in vacuum. Images were then analyzed using ImageJ. Images were first processed through a Gaussian blur filter and a black and white threshold was used to discern particles from the background. In some cases, a Fourier transform was used to reduce brightness in homogeneities. Particles were separated using a Watershed function before being counted and analyzed. Objects under 50 nm in diameter were considered as noise or artifacts and were not counted.

Dynamic light scattering (DLS) The hydrodynamic diameter of particles as well as particle size-distribution was determined using DLS. NRL samples were diluted to $\phi \approx 10^{-6}$ in an ammonia solution of pH 10.5 previously filtered through a 0.22 μm PVDF filter in order to get rid of any contaminants such as dust. Experiments were performed using an ALV goniometer (ALV/CGS-3) equipped with a He/Ne laser operating at a wavelength of $\lambda_L = 633$ nm, in combination with an ALV/LSE-5003 correlator at 25 °C. Each sample was measured five times for a duration of 30 s at a scattering angle of 90°. The obtained correlation functions $g_2(t)$ were fitted using the ALV-7004 Correlator Software. To determine the particles' diffusion coefficient, samples were measured three times at scattering angles between 30 and 135 degrees.

Electrophoretic mobility Measurements were repeated three times for each sample on a Zetasizer Nano ZS93 (Malvern, UK) at 25 °C and using a folded capillary cell (model DTS1070, Malvern, UK). The electrophoretic mobility, μ , of NRL was measured by diluting suspensions to $\phi \approx 10^{-5}$ in a KNO_3 solution. For electric mobility measurements as a function of ionic strength, KNO_3 concentrations were fixed to ionic strengths between 1 and 200 mM. For electric mobility measurements as a function of pH, KNO_3 concentration was fixed to 10 mM and initial pH was measured at 9. pH was subsequently

increased or decreased with KOH or HNO_3 solutions respectively.

Creaming speed measurements The creaming speed of highly turbid latex suspensions was measured by static multiple light scattering using a Turbiscan Trilab (Microtrac, Germany). The method uses an 880 nm laser to scan the sample length from bottom to top, recording backscattered light intensity at a 135° angle from the incident beam every 20 μm . This measurement is repeated over time, enabling the tracking of backscattered light intensity as a function of both height and time. This process captures the backscattered light intensity profile's time evolution [53, 54]. Measurements were performed at 25 °C in volumes between 2 and 20 mL and after dilution to concentrations between $\phi = 0.05 - 0.54$ in MilliQ Type I water (conductivity < $0.056 \mu\text{S}\cdot\text{cm}^{-1}$). To examine the effect of calcium nitrate on NRL creaming speed, NRL was added with a micropipette to aqueous solutions of calcium nitrate. After preparation, samples were gently rotated for 5 min to ensure suspension homogeneity using a rotary mixer. Lastly, samples were left to sit for 10 min before measurement to allow for the meniscus to settle. Measurement times lasted approximately 2 to 21 days depending on sample concentration in order to allow for a sufficient increase in creaming front displacement for data analysis.

Modeling gravity-driven velocity of suspended particles in a fluid

Particles suspended in a fluid experience displacements driven by both thermal energy and external force fields. The former causes random motions, defined as Brownian motion which is described by a diffusion coefficient, D [55]. The free diffusion coefficient of a spherical particle can be determined using the Stokes-Einstein equation:

$$D = \frac{kT}{3\pi\eta d} \quad (1)$$

Where k is the Boltzmann constant, T the absolute temperature, η the suspending fluid viscosity and d the particle diameter. The random walk of a particle with Brownian motion is quantified by its root mean square displacement, $\sqrt{\langle x^2 \rangle}$, which is related to the diffusion coefficient through:

$$\sqrt{\langle x^2 \rangle} = \sqrt{2AD\delta t} \quad (2)$$

Where A equals 1, 2, or 3 depending on the dimension of the random process, and δt is a time increment. The root of the

mean square displacement can be used to define a particle's instantaneous velocity.

On top of Brownian motion, particles are also subjected to a gravitational force field which influences their motion. Throughout the years, the scientific community has been proposing a variety of models to explain the motion of particles subjected to gravity in a suspending fluid [56, 57]. These models are first based on Stokes' law [58] which describes how the Earth's gravitational field, g , influences the settling velocity, v , of a single spherical particle in a fluid as:

$$v_{Stokes} = \frac{g|\rho_s - \rho_l|}{18\eta}d^2 \quad (3)$$

Where ρ_s and ρ_l are the mass densities of the particle and suspending fluid respectively. Stokes' law is applicable for infinitely diluted suspensions where no interaction between particles is considered and only gravitational acceleration, buoyancy, and viscous drag are taken into account.

As particle concentration increases, hydrodynamics and direct interparticle interactions cannot be neglected, introducing greater complexity to the model. Richardson & Zaki (R-Z) [59, 60] introduced one of the most used correlations to link a suspension's settling velocity to its concentration. Essentially, when the vessel diameter greatly exceeds particle size, Stokes' expression is simply multiplied by a power law of the liquid fraction with an empirical exponent n :

$$v = v_{Stokes}(1 - \phi)^n \quad (4)$$

Where n is the R-Z parameter which can range between 2.4 and 4.65, these limits corresponding to turbulent ($Re > 500$) and laminar flows ($Re < 10^{-1}$) respectively. Here, the Reynolds, Re , is calculated through:

$$Re = \frac{d\rho_l v_{Stokes}}{\eta} \quad (5)$$

Different methods to calculate the R-Z parameter, n , have been proposed, most of which based on empirical or semi-theoretical equations [56]. Although these models were devised for ideal monodisperse suspensions of hard spheres with no direct interparticular forces, they have proven to be remarkably successful in predicting the sedimentation speeds of a wide range of systems. Since then, many other models have been introduced, often based on the Stokes, or R-Z equations, applied to specific ranges of Re numbers, polydisperse suspensions, and taking into account particle-particle interactions [61, 62].

The R-Z parameter has been shown to depend on particle size, shape [60, 63–66], polydispersity [67, 68], and surface interactions [65, 69], as revealed through both numerical

simulations [67, 68, 70–73] and sedimentation experiments. Such experiments often involve macroscopic observations in fluidized beds [60, 63, 66, 69, 74]. In cases of highly turbid suspensions where the sedimentation front is not easily discernable, light scattering techniques have been employed to study the R-Z model in suspensions of hard particles [64, 71, 75] and emulsions [76–80]. However, while light scattering has been used to study the settling of soft particles [81, 82], applications of sedimentation models remain underexplored for soft particles.

Results

Data analysis for the creaming speed measurement of concentrated NRL suspensions

The evolution of backscattered light intensity across sample height at a given time t , compared to the initial scan at $t = 0$, referred to as $\Delta B(x, t)$, was analyzed (by construction, $\Delta B(x, t = 0)$ is zero at all x). Variations in backscattered intensity indicate local changes in suspension structure and/or concentration. A reduction in particle concentration results in an intensity decrease while an aggregation process could result in a backscattered light intensity increase or decrease depending on the aggregates' structure, size, and its light diffusion properties [83]. Consequently, not considering complex structural changes, creaming of latex particles, that is upwards settling of individual latex particles, induces a drop in concentration at sample's bottom, resulting in negative values of $\Delta B(x, t)$. Representative $\Delta B(x, t)$ profiles are shown in Fig. 1A. Note that the abscissa corresponds to sample height, with the sample bottom displayed on the left-hand side. Each curve represents a creaming state at a given time.

In his theory of batch settling for concentrated suspensions, Kynch made explicit the importance of the concentration profile's inflexion point in studying sedimentation fronts [84, 85]. By convention, the creaming front position at time t can thus be defined as the inflexion point of each singular $\Delta B(x, t)$ curve. To identify each curve's inflexion point, $\Delta B(x, t)$ raw data was subjected to a first-order derivative with respect to x , smoothed by a Stavitzky-Golay filter of polynomial order 1 with a window size of 10 points [86, 87]. The result of this analysis is presented in Fig. 1B where, for clarity, only a few curves are presented. Each local maximum on the derivative indicates an inflexion point, and thus, the position of a creaming front. Plotting the evolution of inflexion points over time allows determination of latex particle creaming speeds from the resulting plot's slope.

Examination of the temporal evolution of $\Delta B(x, t)$ in Fig. 1A reveals the emergence of two distinct inflection

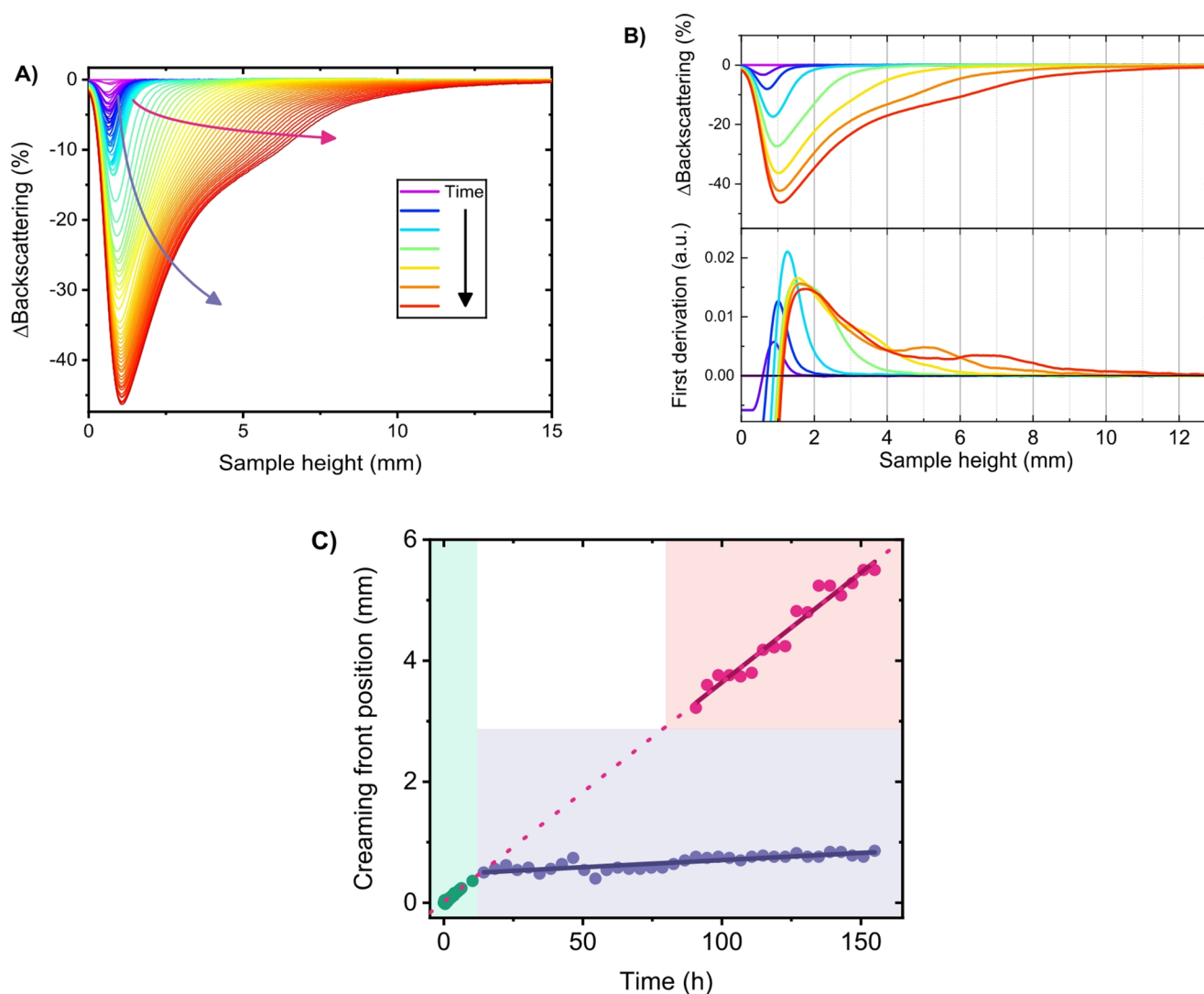


Fig. 1 Creaming speed measurement and analysis of NRL. Measurements performed at 25 °C, $\phi = 0.22$, and pH 9. **(A)** Variation of backscattering (ΔB) as a function of sample height over 155 h. Arrows represent creaming front evolutions of the slow (purple) and fast (pink) regime. **(B)** Top: Selection of the profiles from A) at the following

measurement times: t (h)=0; 0.3; 3; 11; 35; 67; 111 and 155. Bottom: First derivation of these profiles. Maxima correspond to inflexion points, thus, to the creaming front's position. **(C)** Creaming front position of the slow (purple), fast (pink), and mixed (green) regimes as a function of time. Corresponding slopes provide creaming speeds

points, as indicated by the arrows. This observation is further supported by the presence of two separate peaks in the corresponding first-derivative profile shown in Fig. 1B. Together, these features indicate the progression of two independent creaming fronts. At early times, however, the fronts are not clearly resolved and remain indistinguishable. Accordingly, the initial data points are interpreted as representing the combined evolution of both fronts, as their individual contributions cannot be reliably distinguished. The corresponding results are presented in Fig. 1C. Notably, one of the creaming fronts does not extrapolate back to the origin of the time axis. Although the origin of this behavior remains unclear, similar observations have been reported in systems

exhibiting simultaneous settling regimes, where a short-time lag phase precedes the establishment of a terminal velocity [75].

To ensure that NRL creaming properties remained unchanged throughout experiments, some samples were shaken and re-homogenized afterward, and their creaming speeds measured again. Additionally, the creaming speeds of a few NRL samples at identical particle concentrations were measured in separate experiments to verify repeatability. In all cases, no changes in creaming speed were observed, confirming the measurement's reliability (see Figure S1 in Supporting information).

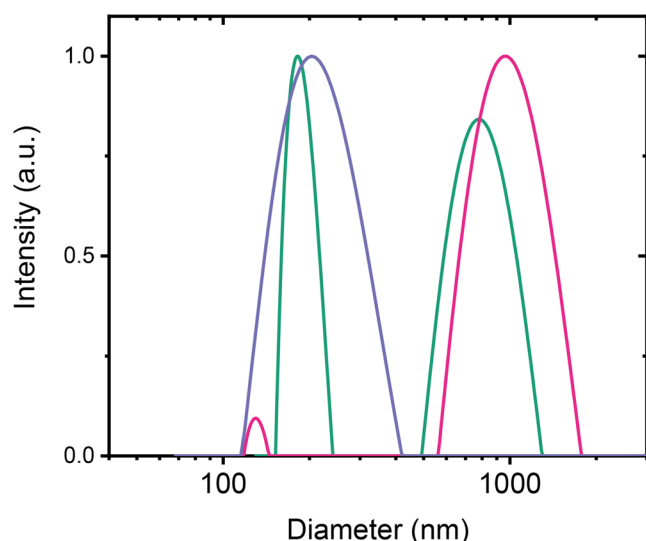


Fig. 2 Particle size determined by DLS of NRL (green), $\text{SRP}_{\text{latex}}$ (purple), and $\text{LRP}_{\text{latex}}$ (pink). Measurements performed at 25 °C, $\phi \approx 10^{-6}$, and pH 10.5

Table 1 Particle diameters for three latex systems obtained from DLS. Values represent peak maxima. Uncertainties represent the corresponding curve's width at half maximum

Latex	Intensity maxima	
	d_{SRP} (nm)	d_{LRP} (nm)
NRL	180 ± 30	780 ± 260
$\text{SRP}_{\text{latex}}$	200 ± 90	-
$\text{LRP}_{\text{latex}}$	130 ± 10	970 ± 390

Particle size

To understand what both creaming regimes represent in Fig. 1, commercial *Hevea* latex (NRL) and two additional latex systems prepared from NRL were investigated. Firstly, NRL particle size distribution was determined by Dynamic light scattering (DLS) and results are displayed in Fig. 2. All particle sizes were found to span a range of 100 to 1500 nm in diameter and two separate particle fractions were clearly evidenced. A fraction of small rubber particles (SRPs) centered around 100 to 400 nm, and the other of large rubber particles (LRPs) around 400 to 1500 nm, in agreement with literature on NRL [10, 14, 15, 22, 23, 32, 48, 88–90].

Afterward, we attempted to separate SRPs and LRPs by centrifugation, yielding two additional latex systems. One of them only composed of small particles, labelled $\text{SRP}_{\text{latex}}$ while the other, mainly of large particles, referred to as $\text{LRP}_{\text{latex}}$. Particle separation is verified by DLS as reported in Table 1 where key size parameters for each latex system are gathered. After centrifugation, the two sized fractions were efficiently separated since the $\text{SRP}_{\text{latex}}$ sample shows a monomodal particle size-distribution centered in the range of SRPs, while $\text{LRP}_{\text{latex}}$ consisted of mostly LRPs.

To further investigate the size, morphology, and number distribution of *Hevea* latex particles, environmental scanning electron microscopy (ESEM) was performed on each latex system. Numerous electron microscopy techniques have been used to observe NRL, such as SEM [26, 27, 30, 31, 89–91], Cryo-SEM [31], FESEM [24, 25], TEM [26], Cryo-TEM [15, 22]. ESEM, by contrast, allows for the observation of particles in a natural hydrated state without the need for extensive preparation, reducing the risk of permanent deformation. ESEM images and corresponding particle-count histograms of the latex systems studied are shown in Fig. 3. In these images, two differing contrasts can be observed: a bright looking background and circular dark spots. Secondary electrons, detected by the GSED, lose more energy by passing through unsaturations present in oils or polymers such as polyisoprene, than through water [92]. As a result, water appears brighter than NRL particles. Particle boundaries in these images are not sharply defined. This is firstly due to a water saturated atmosphere, lowering image resolution. Effectively, detected electrons scatter by colliding with gaseous water molecules. Secondly, particles are still dispersed in water, experiencing Brownian motion during image capture. One can observe particles present at the water-air interface, as well as particles covered by a thin water layer since the electron beam can penetrate as deep as 280 nm into the liquid [51].

Images of natural *Hevea* latex presented in Fig. 3A1 and A2 clearly reveal the polydispersity of latex particles. More specifically, the histogram presented in Fig. 3A2 illustrates that NRL is composed of 90% SRPs by number, which is consistent with literature reports [13, 22, 27]. Additionally, particles demonstrate certain heterogeneities in shape, which is not surprising considering the mechanical softness of rubber particles. Some particles appeared to form aggregates, with a portion seen attaching and detaching within seconds, while others remain aggregated for several minutes. The system $\text{LRP}_{\text{latex}}$ is represented in Fig. 3B. Its higher large to small particle ratio measured by DLS is supported in the presented ESEM data (Fig. 3B). LRPs appear mostly spherical and not in the form of clustered SRPs, indicating that the larger fraction measured through DLS does not consist of aggregates. The system $\text{SRP}_{\text{latex}}$ is represented in Fig. 3C and confirms the presence of only SRPs as measured through DLS. Artefacts appear around the image that could be due to water condensation revealing a thicker layer of water surrounding the observed area. The superposition of all histograms obtained by ESEM is presented in Figure S2 (Supporting information).

Generally, particle diameters measured by ESEM are smaller than those measured by DLS with small particles in the range of $d_{\text{SRP}} \approx 120$ nm and large particles in the range of $d_{\text{LRP}} \approx 650$ nm. This probably results from DLS measuring

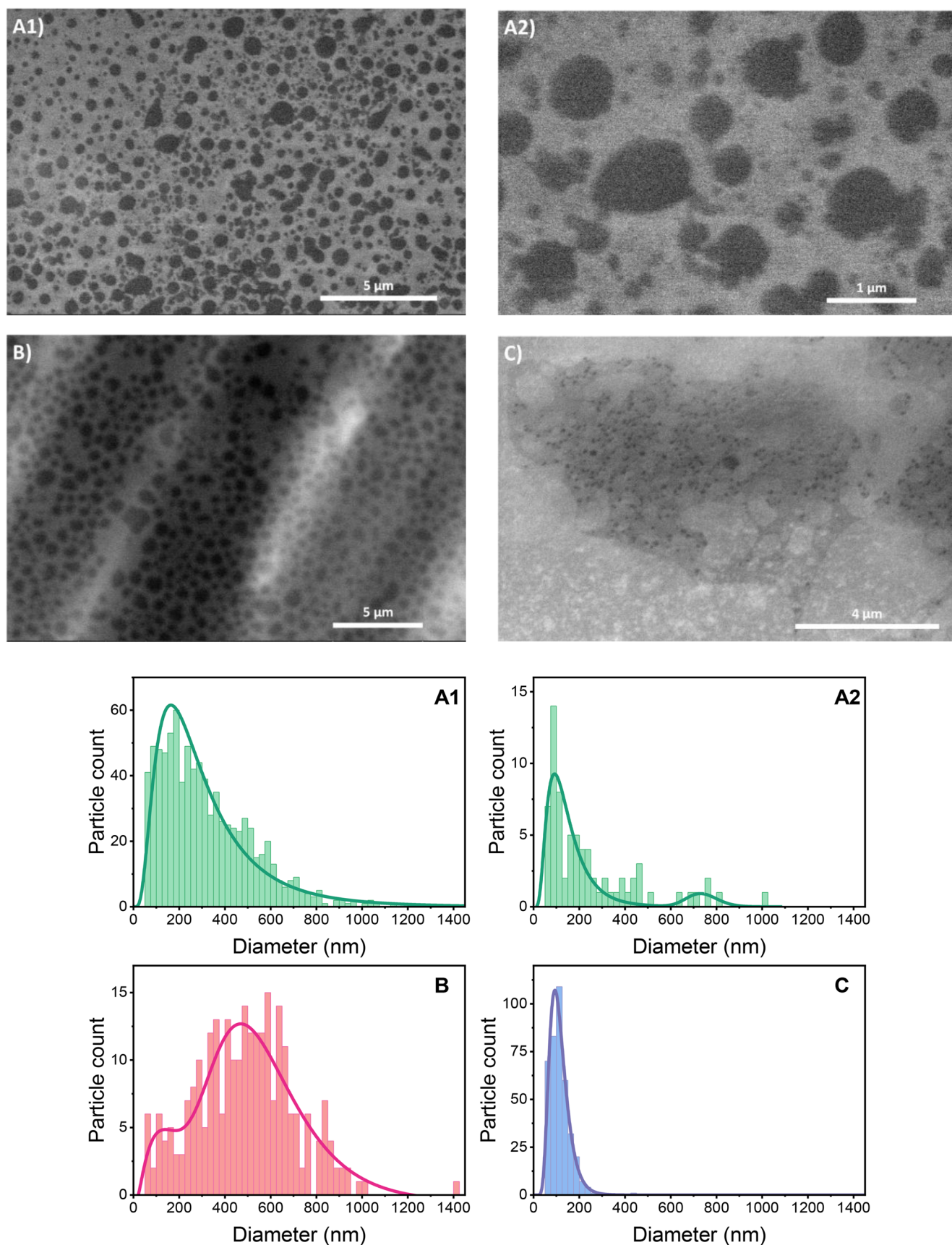


Fig. 3 ESEM images and corresponding histograms of particle sizes. Particles appear as darker spots. Curves in histograms represent lognormal distributions fitted to experimental data. **A1)** and **A2)**: NRL **B)**: LRP_{latex} **C)**: SRP_{latex}

a particle's hydrodynamic diameter, including both the particle and its surrounding solvent layer, in interaction with its soft charged surface [93].

Electrophoretic mobility

Polyisoprene, the main component of *Hevea* latex, is an intrinsically uncharged polymer and does not react with acids and bases. However, the surface of NRL particles is known to be composed of proteins, fatty acids as well as phospholipids. Their molecular charges are known to be dependent on pH and ionic strength. Hence, the electrophoretic mobility behavior of NRL can be linked to its surface composition. The electrophoretic mobility, μ , of NRL, SRP_{latex} and LRP_{latex} was measured as a function of pH and represented in Fig. 4A. Commercially, NRL is typically stored in ammonia at pH > 10. At this pH, all latex systems exhibit highly negative electrophoretic mobility, demonstrating the presence of negative charges at the particle surface. As pH decreases, $|\mu|$ decreases until reaching a null electrophoretic mobility at pH 4. This is known as the isoelectric point which is determined by the average pKa of surface molecules as a whole. On average, the isoelectric point of NRL proteins has been reported to be between pH 3.9 and 4.6 [94]. Fatty acids present in NRL particle shells are mainly saturated C12 to C16 chains and C18 chains with 0 to 2 unsaturations [37] with their pKa ranging from 4 to 5 [95, 96]. Therefore, our measured isoelectric point is consistent with those of proteins and fatty acids at the particle surface and is in agreement with isoelectric point values reported in the literature [22, 28, 30, 97]. Below pH 4, particle surface charge becomes positive due to proteins

exhibiting positive charges below their isoelectric point. Even though the surface composition differs between SRPs and LRPs [89, 98], this behavior is consistent for all three latex samples. This suggests that, regardless of particle shell composition, both small and large rubber particles exhibit similar pH-dependent electrophoretic behavior and have a similar average surface pKa.

The electrophoretic mobility of different latex samples was measured as a function of the ionic strength varying from 1 to 200 mM (KNO₃) and results are presented in Fig. 4B. Once again, all samples maintained negative electrophoretic values as expected. As the ionic strength increases, $|\mu|$ decreases due to the screening of surface charges. The behavior of NRL and SRP_{latex} is quite similar, which is to be expected taking into account that NRL is composed of 90% SRPs by number. However, LRP_{latex} exhibits a more negative electrophoretic mobility across all ionic strengths. One can deduct from this information that large particles do not possess the same electrophoretic properties as small particles and appear to be more charged. This is particularly interesting since it would suggest that the surface compositions of large and small particles differ, supporting findings from previous studies [13–15, 27, 48].

As shown in Fig. 4B, for all samples, a negative plateau value of electrophoretic mobility at high ionic strength is reached. This behavior is characteristic to particles containing a hard core and a soft, charged, ion-permeable membrane [99]. In such a case, Smoluchowski's equation does not adequately describe their electrokinetic behavior [8, 100]. Instead, Ohshima's model proves to be efficient in determining the charge density, ZN , and ion permeability thickness, λ^{-1} , of the particles' soft charged membrane. All

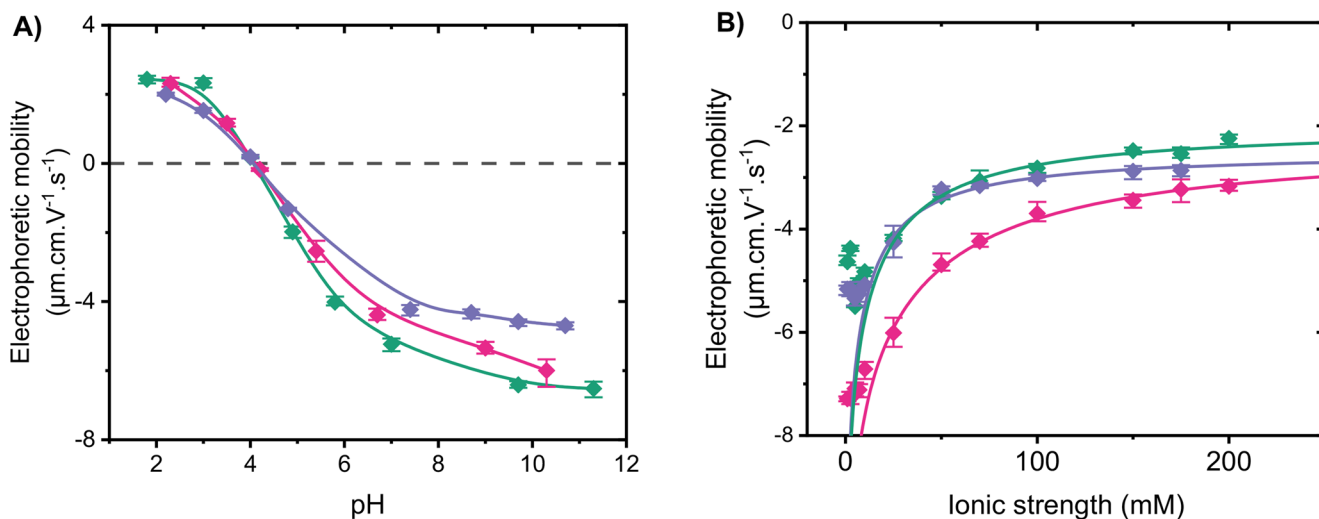


Fig. 4 Electrophoretic mobility of particles from NRL (green), SRP_{latex} (purple), and LRP_{latex} (pink). Measurements were performed at 25 °C and $\phi \approx 10^{-5}$. Error bars correspond to standard deviations. **(A)** Electrophoretic mobility as a function of pH at $I=10$ mM (KNO₃).

Lines are a guide for the eyes. **(B)** Electrophoretic mobility as a function of ionic strength at pH ≈ 9. Corresponding lines are fits of experimental data representing Ohshima's model using Eq. 7

Table 2 Values of charge density ZN (mM) and ion permeability thickness (λ^{-1}) in three latex samples, obtained by using Eq. 6 at ionic strengths of >10 mM

Latex	ZN (mM)	λ^{-1} (nm)
NRL	−100	1.4
SRP _{latex}	−60	1.0
LRP _{latex}	−220	1.9

of which are linked to the particle's electrophoretic mobility and described using the following equation:

$$\mu = \frac{\epsilon_r \epsilon_{r0}}{\eta} \frac{\psi_0 / K_M + \psi_D / \lambda}{1 / K_M + 1 / \lambda} + \frac{eZN}{\eta \lambda^2} \quad (6)$$

Where ϵ_r and ϵ_{r0} are the vacuum and suspending fluid permittivity respectively, e the elementary charge, ψ_0 and ψ_D are the surface and Donnan potentials respectively, K_M the Debye-Hückel parameter, Z the soft shell charged group valence, N the soft shell charge group density, and λ the shell's softness parameter. The model was applied to ionic strengths 10 mM in ionic strength with results gathered in Table 2.

Results show a large difference in ZN and λ^{-1} between LRP_{latex} and the two other studied latices (NRL and SRP_{latex}). This is in expectation with previous observations that SRPs and LRPs do not possess the same electrokinetic behavior in regards to ionic strength, further indicating a difference in surface charge density between SRPs and LRPs. Values of ZN and λ^{-1} found in the existing literature are in agreement with our presented data (roughly $\lambda^{-1} = 0.7$ to 2 nm and $ZN = -120$ to -400 mM) [21, 22, 28]. Our experiments are consistent with NR particles possessing a thin protein-lipid

shell endowed with remarkable surface properties that are tightly controlled by ionic strength and ion valency [38]. More extensive studies show that the shell of *Hevea* latex are composed of a dense positively charged layer covered by a negatively charged layer [21, 22].

Proteins and lipids present at the particle surface in *Hevea* latex have been extensively researched [89, 90, 101]. The most prevalent proteins include Hev b 1, 2, and 3 while prevalent lipids include chains of 16–18 carbons with 0–2 unsaturations. The average size of such molecules range from 0.5 to 2 nm depending on their conformation [102, 103], which is comparable to the soft permeable layers' length found using Ohshima's model. Furthermore, previous studies have demonstrated surface composition differences between small and large rubber particles [27, 89, 104]. Especially, LRPs possess more lipids and proteins than SRPs per surface unit, suggesting a thicker particle shell [27, 48], which aligns with our results.

Impact of the volume fraction on *Hevea* latex creaming speed

The creaming speeds of *Hevea* latex suspensions were measured as a function of particle volume fraction. Data points have been divided between each discernable creaming fronts defined as the fast and slow regimes as shown in Fig. 1. It is safe to assume that the slow and fast regimes correspond to the creaming of the small and large particles populations identified by DLS (Fig. 2). Creaming speeds of SRPs and LRPs are reported in Fig. 5. As expected, both

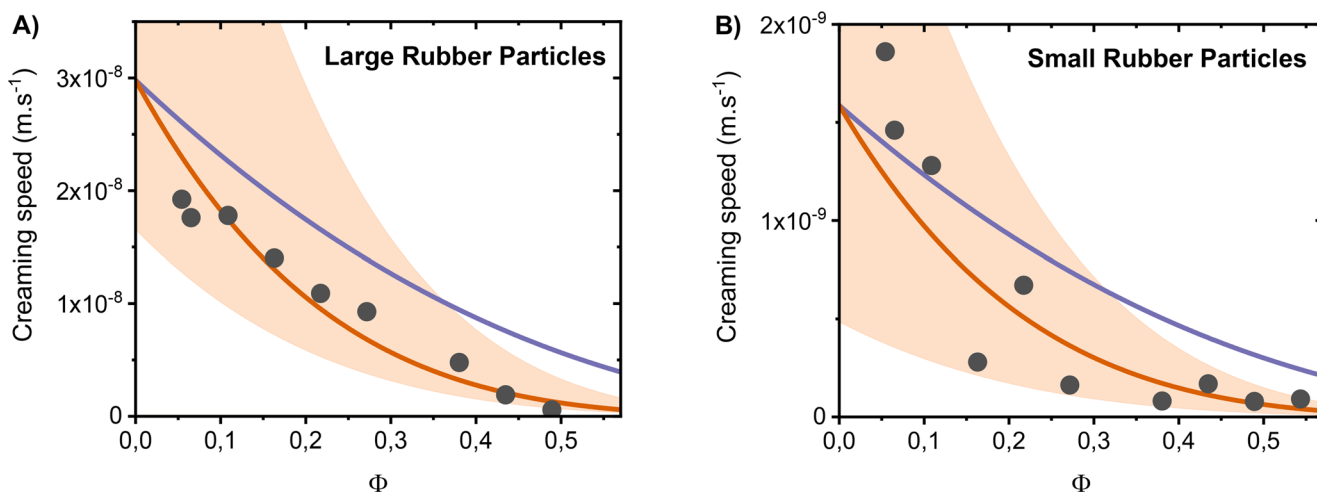


Fig. 5 Creaming speed of NRL particles as a function of total particle volume fraction. Black dots represent experimental data. Curves represent theoretical creaming speeds calculated using the Richardson-Zaki Eq. 4 for an imposed parameter $n=2.4$ (purple) and 4.65 (orange) with fixed particle sizes fixed according to average sizes shown in Table 1. Orange areas represent the R-Z equation at $n=4.65$ and covers all par-

ticle diameter shown as uncertainties in Table 1. (A) Creaming speed of LRPs. Models have been traced with a fixed particle diameter of 780 nm with an uncertainty of 260 nm for the orange area. (B) Creaming speed of SRPs. Models have been traced with a fixed particle diameter of 180 nm with an uncertainty of 30 nm for the orange area

particle populations show a decrease in creaming speed with the particle volume fraction.

Theoretical creaming speeds have been calculated using the Richardson-Zaki equation (Eq. 4) with the hydrodynamic particle diameter measured by DLS and reported in Table 1 (180 and 780 nm for SRPs and LRPs respectively). Results are presented in Fig. 5 for parameters $n=4.65$ (laminar flow) and 2.4 (turbulent flow). For $n=4.65$, particle size uncertainties from Table 1, shown as the orange area, reflect the system's polydispersity. For both large and small particles, the R-Z model with a parameter $n=4.65$ correlates best to experimental data across all volume fractions. Calculating the Reynolds number using Eq. 5 results in values in the range of 10^{-8} to 10^{-10} for LRPs and SRPs respectively. Since laminar flow is defined at Re numbers below 10^{-1} , it is reasonable to observe a satisfying correlation of an R-Z parameter of 4.65. Overall, the R-Z model with a laminar flow parameter $n=4.65$ proves to be efficient in predicting creaming speeds of NRL over a broad range of particle volume fraction.

Impact of salts on the creaming behavior of *Hevea* latex at low ionic strengths

It is widely known that calcium salts and other bidentate cations are particularly effective at destabilizing natural rubber latex [5, 39]. Industrially, $\text{Ca}(\text{NO}_3)_2$ is the most commonly used salt to coagulate concentrated *Hevea* latex. However, studying its influence without excessive dilution, or relying solely on macroscopic observations, is experimentally tedious. A stability diagram of NRL at $\phi = 0.01$ and 0.08 as a function of $\text{Ca}(\text{NO}_3)_2$ concentrations using macroscopic and microscopy images is presented in the supporting information (Figure S3, Figure S4, and Figure S5). Results show, as calcium concentrations increase, a transition between a perfectly dispersed state to the formation of aggregates, up to total NRL coagulation. However, such observations were made approximately 16 h after sample preparations and do not account for the fact that NRL aggregation can be dynamic [47]. Furthermore, microscopy observations require sample dilution, at the risk of altering the aggregation state, or reducing the likelihood of observing weak aggregation. This results in operator-dependent observations at a fixed time following sample preparation. As particle volume fraction increases, it becomes difficult to observe the subtle transition between a stable to aggregated state.

Using static multiple light scattering on NRL at high concentration, we investigate how monovalent or divalent salts influence the creaming speed of NRL. It is important to note that at such volume fractions, NRL's contribution to the sample's ionic strength, I_0 , cannot be neglected. As

such, the conductivity of NRL at $\phi = 0.22$ was measured to be $2.9 \text{ mS}\cdot\text{cm}^{-1}$. The system's complexity makes it impossible to precisely determine I_0 from conductivity measurements, nevertheless, if we suppose all contributing species as KNO_3 , we can have a general idea of the ionic strength which we calculate to be $I_0 \approx 20 \text{ mM}$. From now on, any reported ionic strengths refer to added ionic strengths on top of the already present I_0 . The creaming speed of NRL at $\phi = 0.22$ was measured as a function of the ionic strength imposed by $\text{Ca}(\text{NO}_3)_2$ or KNO_3 . Results are presented in Fig. 6A. As calcium is known for causing latex particle aggregation [39], it is no longer possible to unambiguously attribute the slow and fast regimes to SRPs and LRPs respectively. Nevertheless, we can still discern two distinct slow and fast regimes in latex creaming as calcium is being added.

Firstly, at ionic strengths ranging from 0 to 12.6 mM through $\text{Ca}(\text{NO}_3)_2$ addition, the evolution of two distinct inflexion points remains discernable, measured according to the protocol described in the materials and methods section. If we take a look at the fast regime of particles from 0 to 4.5 mM, creaming speeds are not affected by $\text{Ca}(\text{NO}_3)_2$ addition. Subsequently, in a range of 5.4 to 12.6 mM, the fast regime's creaming speed increases by up to twofold. Oppositely, the creaming speed of the slow regime decreases continuously with $\text{Ca}(\text{NO}_3)_2$ addition. Secondly, at ionic strengths ranging from 12 to 24.6 mM by addition of Ca^{2+} , a new behavior is observed where two distinct inflection points are no longer discernable. For example, the variation in backscattered light intensity across the sample $\Delta B(x, t)$ in an ionic strength of 24.6 mM is represented in Fig. 6B. Here, a single, much larger creaming front is observable as opposed to Fig. 1B, and creaming speed increases tenfold compared to NRL diluted in water. Only one regime is distinctly observed suggesting a monomodal colloidal suspension. Note that, experimentally, higher $\text{Ca}(\text{NO}_3)_2$ concentrations than those presented result in an irreversible coagulation, easily visible macroscopically. Furthermore, creaming speed variations of NRL upon potassium salt (KNO_3) addition was compared to the effect of $\text{Ca}(\text{NO}_3)_2$, and results are shown in Fig. 6A. In the case of KNO_3 , both creaming regimes remain clearly distinguishable, and no differences in creaming speed are observed at ionic strengths of 12 and 25 mM.

Discussion

Discussion on the conditions to observe extremely slow creaming speeds

As observed in Fig. 6A, creaming speeds from hundreds to tenths of nanometers per second are measured, which are extremely slow. Intuitively, one would expect such small

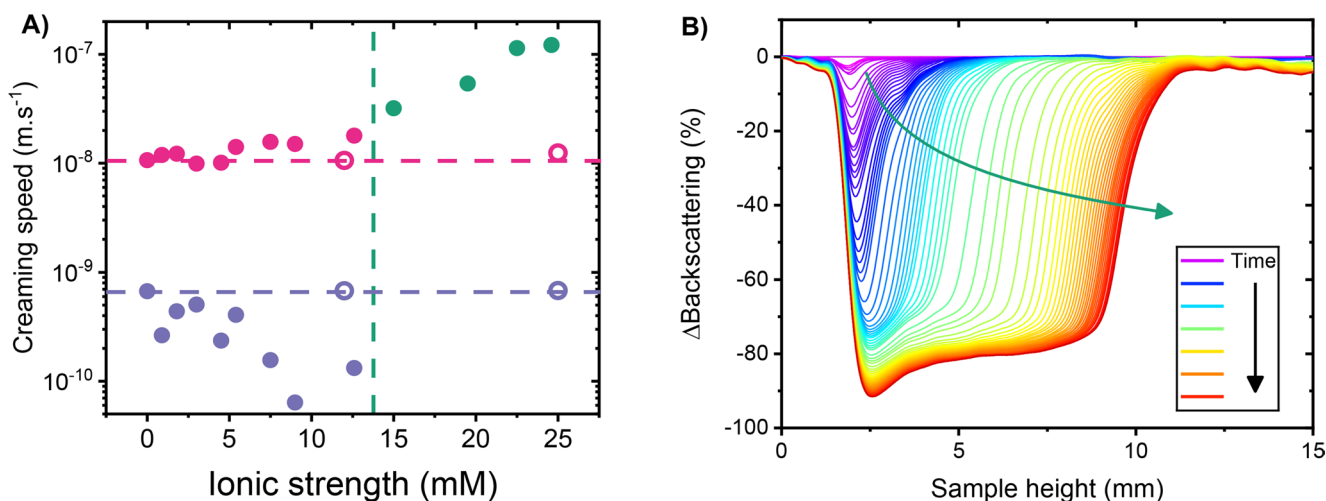


Fig. 6 (A) Creaming speed as a function of ionic strength for NRL at for sample diluted with Ca(NO₃)₂ (●) or KNO₃ (○). (B) Variation of backscattering (ΔB) as a function of sample height over for NRL suspended in 8.2 mM of Ca(NO₃)₂ representing an ionic strength of 24.6 mM. Measurements performed at $\phi = 0.22$ and pH 9 at 25 °C over 91 to 211 h. (A) Creaming speeds are divided when slow (pur-

ple) and fast (pink) regimes can be discerned, or when one regime is observed (green). Horizontal lines represent the creaming speed of NRL diluted only with water. The vertical line represents the change in regime when adding Ca(NO₃)₂, from bimodal (left) to monomodal (right). (B) The arrow represents the creaming front evolution of the single discernable regime

displacements to be overcome by Brownian motion but this is clearly not the case here since a creaming behavior was observed. To determine if such thermal motions are indeed negligible compared to gravitational forces (more generally referred to as advective drifts), the dimensionless Peclet number, Pe , is commonly used. It is defined as the ratio of a particle's diffusive, τ_D , to advective time, t_S , necessary to travel a distance in the range of its own size d . Here, since advection is due to the earth gravitational field, the advective time is determined by the particle settling speed. Additionally, the diffusive time, characterized by Brownian motion, is approached from Eq. 2 identifying the root mean square diffusive displacement with the particle size. As such, the Peclet number is generally defined as [105]:

$$Pe = \frac{\tau_D}{t_S} = \frac{d^2/D}{d/v} = v \frac{d}{D} \quad (7)$$

To observe the settling due to advection, the observation time scale must be long enough so that advection, evolving as t , overcomes diffusion, evolving as $t^{1/2}$, leading to the condition [55]:

$$t > \frac{\tau_D}{Pe^2} = \frac{D}{v^2} \quad (8)$$

The diffusion coefficient D can be assessed experimentally by DLS measurements at differing scattering angles. According to our measurements, for our NRL, $D = (1.2 \pm 0.1) \cdot 10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$ (Figure S6 of the supporting information). Creaming speed measurements have been conducted

in a timescale on the order 10^6 s and velocities in the order of 10^{-8} to $10^{-10} \text{ m} \cdot \text{s}^{-1}$ were measured. By injecting those speeds into Eq. 8, advective drift should overcome Brownian motion at observation times $t > 10^4$ to 10^8 s respectively (the latter representing over a thousand days). As such, we cannot satisfyingly explain our experimental results. Such slow creaming speeds have already been described in the literature where polymer particles creaming speeds decrease when surrounded by a protein corona, suggesting the influence of a soft shell on creaming behavior [106]. There are several complementary factors that may explain why the Pe number estimated through the diffusion coefficient, is not the right metric to describe the settling regime of concentrated suspensions.

High volume fraction: Firstly, measurements to obtain the diffusion coefficient were performed at $\Phi = 10^{-6}$. Yet, increases in volume fraction restrict particle movement leading to a decrease in apparent D , which has been experimentally shown for a variety of hard colloidal systems [107], including polydisperse [108] or charged colloids [109, 110]. This can be explained by a decrease in interparticle distance as volume fraction increases. An estimation of interparticle distance based on DLS data (Fig. 2) is shown in Figure S7 alongside the calculated $\sqrt{\langle x^2 \rangle}$ using Eq. 2. At $\Phi = 10^{-6}$ this interparticle distance, d_{p-p} , is in the order of $50 \mu\text{m}$ and shrinks to $\sim 1 \mu\text{m} - 400 \text{ nm}$ at particle volume fractions used in our creaming experiments. This reduction falls well below $\sqrt{\langle x^2 \rangle}$, hindering Brownian motion.

Long observation time: Secondly, D is further decreased when observed in long time regimes at times $t \gg \left(\frac{d}{2}\right)^2/D \approx 0.1 \text{ s}$ for LRPs representing long enough

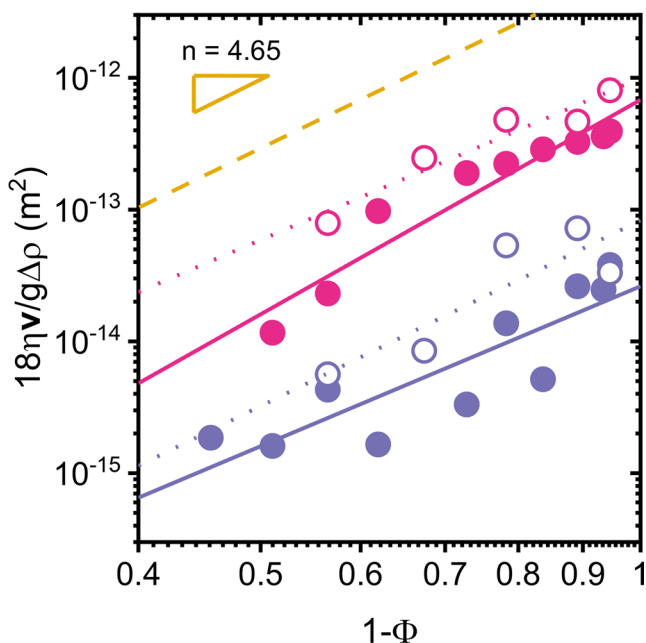


Fig. 7 Normalized creaming speed of SRPs (purple) and LRPs (pink) as a function of $1 - \phi$. Measurement performed at 25 °C for samples diluted in water (●) or screened at $I = 150$ mM using KNO_3 (○). Curves represent fits using Eq. 9 for samples diluted in water (solid line) or screened at $I = 150$ mM (dashed line), and a theoretical slope at 4.65 (gold)

times where particles can interact with each other [111, 112]. We are clearly in the long diffusion regime during our creaming experiments. However, one must note that this decrease in long-time diffusion coefficient is much less drastic for core shell, or soft, particles as their electro-osmotic interactions are considerably reduced compared to hard particles [113].

Along the same line, simulations have shown that advective drift rule the decrease in sedimentation speed as particle volume fraction increases, regardless of the Pe number [114]. Such observations reported in the literature provide a basis for reflection to help explain these extremely slow creaming speeds measured on natural *Hevea* latex.

Impact of volume fraction on creaming speed

As the Richardson-Zaki equation has been shown to satisfactorily correlate to the creaming speed of *Hevea* latex according to Fig. 5, we will use it to further study the creaming of NRL. To this end, Eq. 5 is reorganized as:

$$\frac{18\eta}{g|\rho_s - \rho_l|}v = d^2(1 - \Phi)^n \quad (9)$$

The data of Fig. 5 are then plotted in log-log in Fig. 7, together with measurements at higher ionic strength, where the R-Z factor, n , represents the slope, and the particle diameter is given by $d = 10^{\frac{n-b}{2}}$, where b is the intercept at $1 - \phi = 1$. As opposed to Fig. 5, no variables of the R-Z equation have been imposed. Linear regressions of the presented data in Fig. 7 for both SRPs and LRPs, and fit results of n and d are shown in Table 3. In both cases, we obtain values of n close to the theoretical 4.65 expected for experiments under laminar flow. Interestingly, particle diameters are sensibly identical to the ones measured by DLS shown in Table 1 for both SRPs and LRPs. This confirms the validity of R-Z equation's efficiency in determining particle size in concentrated colloidal systems thanks to gravitational particle settling experiments at high concentrations.

Impact of electrostatic screening on creaming speed

Given the electrokinetic behavior of *Hevea* latex particles, non-negligible particle-particle interactions are responsible for its stability. This raises the question of whether surface charge screening influences NRL creaming. To investigate this, NRL samples were diluted in KNO_3 to achieve a final concentration of 150 mM, much higher compared to what was explored in Fig. 6. According to electrophoretic mobility measurements shown in Fig. 4B, at this ionic strength, the surface charge plateau value is reached. At such a high monovalent salt concentration, no coagulation is observed and we are able to measure NRL creaming. Normalized creaming speed as a function of $(1 - \phi)$ for screened particles is represented Fig. 7 for comparison with unscreened ones (dispersed in water). One can observe that the creaming speeds for screened particles are generally higher than suspensions diluted in water at equivalent concentrations. Data points were fitted using the R-Z equation.

Values of the R-Z parameters and particle diameters from the corresponding linear regressions are listed in Table 3. Once again, n values hover around the theoretical 4.65 corresponding to advective drifts purely under laminar flow. Previous studies have shown that a change in particle-particle interaction could alter the R-Z parameter n [69], but this does not seem to be the case for NRL. In the light of obtained results, the correlation of creaming speed with

Table 3 Values of R-Z parameters n and particle diameters obtained from the Richardson-Zaki Eq. 4 with experimental data represented by the curves in Fig. 7. Errors represent fit uncertainties

	SRP	LRP	SRP $I = 150$ mM	LRP $I = 150$ mM
Richardson-Zaki parameter n	4.2 ± 0.8	5.1 ± 0.6	4.7 ± 1.6	4.1 ± 0.7
Particle diameter d (nm)	170 ± 30	820 ± 90	290 ± 90	1000 ± 120

particle concentration is not influenced by surface charge. On the other hand, values of d listed in Table 3 seem to have increased compared to the ones measured by DLS, even considering fit uncertainties. As individual rubber particles cannot grow in size, this increase in d likely results from weak particle aggregation. In other words, the reduced interparticle interactions caused by screening may contribute to such aggregation, resulting in increased creaming speed.

The Debye length's value in a 150 mM 1:1 electrolyte solution such as KNO_3 is approximately 0.8 nm [115]. The Debye length's shrinkage induces attractive interactions leading to possible flocculation as reported in the literature [116] which would explain both the increase in creaming speed and in apparent particle size calculated with the R-Z equation. However, as previously discussed, NRL particles are soft in nature. In such a case, particles exhibit persisting electrostatic interactions at high ionic strengths¹ [117]. This is made evident by the fact that the Debye length is in the same order of magnitude as soft particle shell thicknesses, λ^{-1} , reported in Table 2. Consequently, the Debye length's shrinkage is less effective than in hard colloids, meaning particle aggregation is expected to remain limited. This is supported by the fit of creaming speeds presented in Fig. 7, which shows only a moderate increase of the apparent particle sizes. Knowing that individual rubber particles cannot grow in size, the values of d in Table 3 suggest that, in this screened state, the suspension forms aggregates averaging only ~ 1.5 particles per aggregate, which is indeed limited thanks to the soft shell's remaining electrostatic repulsion. As a reference, the average hydrodynamic diameter associated to an aggregated doublet is ~ 1.38 times that of a single particle, highlighting the extent of this limited aggregation [118]. Having observed and rationalized how monovalent ions do not substantially destabilize concentrated NRL suspensions, we now investigate the important case of divalent ions.

Impact of calcium interaction on the creaming behavior of NRL

Both Figs. 6 and 7 show that introducing differing salts or drastically increasing the ionic strength in NRL alters its creaming speed. It is well established that divalent

cations such as Ca^{2+} and Mg^{2+} prove to be more effective at coagulating NRL than monovalent cations at the same ionic strength [5]. As observed in Fig. 6A, K^+ is ineffective at coagulating NRL as opposed to Ca^{2+} at the measured added ionic strengths. This effect is even more pronounced when considering the minimal impact of excessively high K^+ concentrations on creaming speed, as seen in Fig. 7, compared to Ca^{2+} in Fig. 6A. Furthermore, experiments in Fig. 6A were conducted at ionic strengths that, according to Fig. 4B, should not be sufficient to screen NRL. Yet, we still observe considerable aggregation, notably evidenced by the transition from a bimodal to a monomodal particle size distribution. This indicates that even slight changes in creaming speeds caused by dilution in Ca^{2+} are noteworthy and prove the presence of a specific interaction of calcium ions with NRL. To our knowledge, no previous studies have discussed or measured this shift regime from a bimodal to a monomodal particle size-distribution in NRL upon the addition of divalent cations, particularly in such a concentrated system.

As discussed previously, increases in creaming speeds reflect intensified particle aggregation. However, the peculiar decrease in creaming speeds observed for the slow regime (depicted in purple in Fig. 6A) cannot be attributed to aggregation. In this case, we can safely assume that these creaming speeds are representative of individual particle settling. Consequently, the Richardson-Zaki equation using a parameter $n = 4.65$ can be used to estimate a representative particle sizes across varying $\text{Ca}(\text{NO}_3)_2$ concentrations. Results indicate a reduction in average particle diameter from approximately 200 to below 100 nm as added ionic strength ranges from 0 to 12.6 mM by calcium addition. This suggests that, within the SRP population, larger particles preferentially aggregate and transition into the fast regime (depicted in pink in Fig. 6A). In other words, calcium addition may narrow the polydispersity of SRPs by promoting aggregation of the larger particles, while the smallest particles remain largely independent. This trend would persist until the system transitions into a monomodal particle size distribution (depicted in green in Fig. 6A), where particles across the entire SRP population become incorporated into aggregates. This interpretation appears consistent with our observations, but remains speculative. To the best of our knowledge, this preferential calcium aggregation behavior has not been reported in the literature. While differences in surface composition between SRPs and LRPs have been extensively investigated in the literature [27, 89, 104], potential variations in surface composition as a function of particle size within the SRP population have not been explored.

Overall, detecting such minimal aggregation in a diluted suspension presents significant experimental challenges.

¹ The persisting electrostatic potential at high ionic strengths is induced by the Donnan potential, ψ_D . Its existence is conditioned by $\kappa d > 1$ and $\kappa \lambda^{-1} \gg 1$, where κ^{-1} is the Debye length [117]. At $I = 150$ mM, the former condition is evident. However, we obtain $\kappa \lambda^{-1} \approx 2$. In other words, we are in a case where the soft particle shell thickness is not significantly larger than the screening distance. We are thus at the limit of when a Donnan potential is present within the soft shell of NRL particles. We cannot safely assume that the Donnan potential dictates electrostatic repulsion but we cannot either neglect the influence of permanent charges in the particle shell.

However, our approach enables us to quantify and analyze aggregation in highly concentrated suspensions. While our findings do not represent a fundamental breakthrough in the understanding of NRL colloidal stability, we are the first to rationalize systematically the creaming behavior of highly concentrated NRL. Moreover, we can accurately detect subtle aggregation onset and particle modality changes without the need for dilution.

Conclusion and outlooks

This study presents a comprehensive analysis of the creaming dynamics and stability of highly concentrated natural rubber latex (NRL) suspensions, underscoring the impact of ionic environment on particle behavior. Our findings demonstrate that both small and large rubber particles, exhibit creaming rates that align closely with the Richardson-Zaki (R-Z) model predictions, particularly at laminar flow conditions with an R-Z parameter of $n = 4.65$. The substantial influence of salts, particularly calcium ions, in promoting aggregation through specific interactions illustrates the role of divalent ions in destabilizing NRL suspensions. We emphasize that our observations are both repeatable and quantifiable, while detecting such small-scale aggregation in a more diluted suspension would be highly challenging. This work underscores the importance of studying the NRL colloidal stability directly in concentrated conditions close to industrial settings. Finally, studying the surface modification of NRL with the use of surfactant, fillers, or creaming agents through concentrated light scattering measurements could help in unlocking the comprehension of the underlying mechanisms governing NRL stability, leading to improved applications in the rubber industry.

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Author Contributions L. Mesnier: Conceptualization, Methodology, Investigation, Writing original draft. N. Sanson: Conceptualization, Methodology, Writing – review & editing, Supervision. J.-B. d’Espinose de Lacaillerie: Conceptualization, Methodology, Writing – review & editing, Supervision.

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Data Availability No datasets were generated or analysed during the current study.

Declarations

Competing interests The authors declare no competing interests.

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