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# Natural rubber-carbon black coagulation: Following the nanostructure evolution from a colloidal suspension to a composite

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## Abstract

Making elastomeric composite materials via heteroaggregation of a binary colloidal suspension of Natural Rubber (NR) latex and Carbon Black (CB) filler is an interesting production method to obtain an efficient dispersion in the polymer matrix. This study successfully employs an original approach of field emission scanning electron microscopy (FESEM) to investigate for the first time the nanostructure evolution of a coagulum originated from the aggregation of NR globules with CB filler in suspension. More specifically, we exploited a chemical fixation method allowing simultaneous acquisition of backscattered electron (BSE) and secondary electron (SE) imaging modes. Additionally, the role of external physical stresses, like mechanical shear and sonication was also investigated in terms of structural effect induced on the formed coagulum at the nanoscopic scale. Our results highlight destabilization of NR globules, either induced by direct interaction with small CB aggregates or governed by solvent evaporation. Reduction in the size of CB agglomerates, obtained using sonication, highly improved filler distribution and confirmed that the size of CB aggregates is an important parameter responsible for the destabilization of NR globules.

## KEYWORDS

colloids, composites, microscopy, nanostructured polymers, rubber

## 1 | INTRODUCTION

Field natural rubber (NR) latex extracted from *Hevea brasiliensis* is a colloidal dispersion of first importance for many applications,<sup>1</sup> especially in the tire industry. In

its raw state, it is composed of ~35% rubber, 5% nonrubber components (proteins, lipids, sugars) and ~60% water.<sup>2</sup> The rubber fraction is contained in the form of colloidal NR particles, corresponding to a bimodal distribution of small rubber particles (SRPs) and

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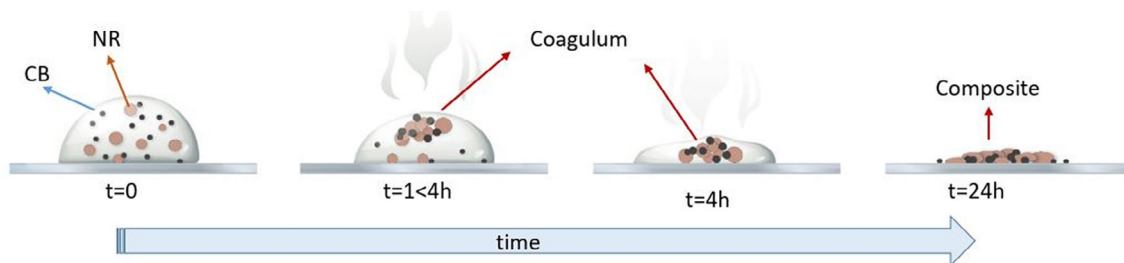
large rubber particles (LRPs), with diameters ranging from 100–500 nm and 500–1,000 nm, respectively. Both types are characterized by a polyisoprene core surrounded by a thin biomembrane primarily made of lipids and proteins<sup>3,4</sup> (thickness  $\sim 3.5$  nm). Despite its unique properties, NR is seldom used in its raw state because of lack of strength, hardness and wear resistance needed for a desired application. For this reason, particulate fillers such as carbon black (CB) have been widely used to improve the mechanical properties (modulus, durability, etc.) of NR.<sup>5–7</sup> However, mixing NR and fillers is a critical step that determines the performance characteristics of rubber compounds. It has long been thought that if a CB dispersion could take place in a liquid phase process, many of the shortcomings in the dry mixing method could be eliminated.<sup>8</sup> For example, it might be possible to break all filler agglomerates in a pre-processing CB treatment obtaining a homogeneous filler dispersion, resulting in improved vulcanizate properties (lower dissipation at low frequency cyclic strain and better wear resistance). Over the past decades, efforts have been made to produce master batches by mixing NR latex with a slurry of CB under mechanical stress,<sup>9–11</sup> giving rise to a coagulated material that is further subjected to dehydration and drying. This type of mixing is called the “liquid route” or “colloidal dispersion pathway.” Industrially, the technological process parameters are controlled at the engineering level, but studies are required to understand the fundamental mechanism regulating the heteroaggregation between the NR particles and CB fillers as well as the structural evolution of the formed coagulum. Such investigations are essential to improve the preparation of elastomeric composite materials and cannot be undertaken without the availability of highly resolved imaging methods. In this context, we employed an original field emission scanning electron microscopy (FESEM) approach to study the nanoscale structural evolution of an NR-CB coagulum along with solvent evaporation. In FESEM, osmium tetroxide is routinely used as fixative agent in solution.<sup>12,13</sup> However, the originality of our approach relies on the specific chemical fixation of the sample using vapor of osmium, preventing the immersion in a liquid solution containing the fixative agent, while preserving the colloidal structure of the NR particles. Additionally, this allowed us to exploit both secondary electron (SE) and backscattered electron (BSE) FESEM imaging modes. We successfully visualized the structural evolution dynamics of the coagulum from the early stage of particle contact to the formation of a composite material. In particular, the role of mechanical shear stress and sonication was investigated at the nanoscopic level in terms of the structural effects induced on the formed coagulum.

## 2 | EXPERIMENTAL

A slurry of CB (N234; density =  $1.8 \text{ g cm}^{-3}$ ; surface area =  $120 \text{ m}^2 \text{ g}^{-1}$ , Cabot Corporation, Boston, US) at 5 wt% was obtained by mixing the black powder with distilled water while using an Ultra-Turrax for 5 min to prevent the formation of large CB agglomerates. Highly ammoniated NR latex (Michelin, Clermont Ferrand, France) was used for most of the experiments, which was obtained by centrifugation of field NR latex containing 0.7 wt% ammonia to eliminate free components and nonrubber particles as well as to preserve the structure of NR globules.<sup>14</sup> Some experiments were also realized with deproteinized natural rubber (DPNR) latex obtained from a proteinase enzyme treatment of the highly ammoniated latex. Regardless of the type, latex was diluted to 0.075 wt % rubber content and combined with the CB slurry with a CB/rubber mass percent ratio fixed at  $\sim 40\%$  in the binary colloidal suspension to approach to the industrial process. Immediately after mixing, 100  $\mu\text{l}$  of this suspension was deposited on a rounded glass cover slip (coverslip thickness: 170  $\mu\text{m}$ , MENZEL-GLASER), resulting in a casted drop with a spherical cap shape, as illustrated in Figure 1. Under these conditions, flocculation occurred on the deposited drop, inducing phase separation, which was macroscopically visible at  $t = 1$  h. At  $t = 4$  h, when most of the solvent was evaporated, the floating objects adhered on the glass surface. A schematic representation showing the formation of such a phase-separated material is illustrated in Figure 1. Herein, the term “coagulum” refers to the phase-separated material floating on the top of the deposited drop, while the term “composite” refers to the material obtained after the complete evaporation of the solvent 24 h after the deposition of the sample on the coverslip ( $t = 24$  h). In case of samples composed of only NR latex, and absence of CB filler, the deposition follows the same protocol.

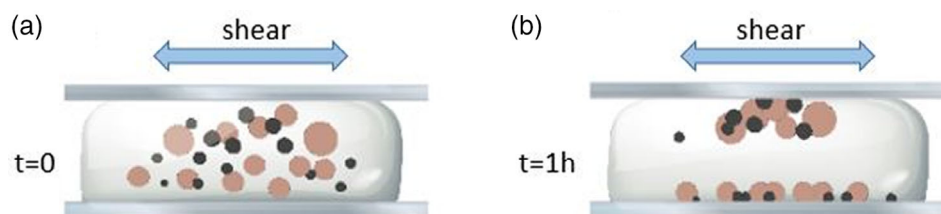
### 2.1 | Application of controlled mechanical shear in the liquid suspension

For these experiments, the preparation of the sample followed the detailed description given above; this glass coverslip constituted both the sample support and one of the shearing plates. A second microscopy coverslip was placed above the deposited drop and corresponded to the second shearing plate. The perfect planarity and parallelism of these two microscopy coverslips were suitable for the application of controlled shear. This was obtained using a commercial device called RheOptiCAD<sup>15,16</sup> (CAD instrument). It provided the ability (a) to move the top plate down at a constant and low speed to prevent



**FIGURE 1** Schematic illustration showing the coagulum and composite formation after the deposition of the NR-CB binary colloidal suspension on the glass coverslip [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

**FIGURE 2** Schematic illustration showing the application of mechanical shear on the binary NR-CB suspension (a) and the formed coagulum (b) [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]



excessive compression of the sample until a gap width of 500  $\mu\text{m}$  was reached between the plates and (b) to connect each plate to a motor controlled by software that allowed straight translation. In these experiments, only the upper plate was displaced. The applied shear consisted of 10 oscillation cycles for a total of 10 min. Each oscillation cycle corresponded to a total displacement in the upper plate of 1 mm (500  $\mu\text{m}$  on either side from the central position) at a frequency of 10 Hz for 60 s, thereby keeping a constant gap between the plates. The shear stress was applied immediately after the deposition of the NR-CB binary suspension ( $t = 0$ ) (Figure 2a) or once the floating coagulum was formed ( $t = 1$  h) (Figure 2b). Additionally, the shearing device was designed to fit on an inverted microscope, allowing shearing and simultaneous transmission imaging of the sample. Herein, it was installed onto an inverted microscope (Axiovert, ZEISS) equipped with a 60x high numerical aperture (1.1) water immersion objective (Olympus) and a charge-coupled device (CCD) camera (UCBO, Olympus).

## 2.2 | NR-CB mixing under sonication

NR-CB mixing under sonication was performed using an ultrasonic homogenizer probe (Sonopuls homogenizer HD 2070, Sound frequency: 20 kHz, BANDELIN, electronic GmbH, Berlin, Germany). The NR latex particle suspension was placed in a glass vial and sonicated for 1 min with a power of 35 W and a 13 mm sonication probe (SH 70 G). The CB slurry was then inserted from the top using a pipette, and 15 ml of the binary NR-CB suspension was kept under sonication for 2 min. After

the total sonication time (3 min), 100  $\mu\text{l}$  was extracted and deposited on a glass coverslip, as illustrated in Figure 1.

## 2.3 | FESEM

One of the novelties of our approach relies on the chemical fixation of the sample, which can be applied in the presence or absence of solvent. Fixation was performed by depositing 50  $\mu\text{l}$  drops of osmium tetroxide (EMS, USA) solution (1% in water, prepared extemporaneously) around the coverslip of the sample in a hermetic box protected from light. In this condition, vapors of osmium tetroxide are created inside the box, fixing the structure of the sample. After 30 min, the fixation was considered complete. This vapor fixation allowed us to (a) avoid immersing the deposited specimen in a solution of the fixative agent, (b) preserve the colloidal structure of NR and (c) exploit both SE and BSE imaging based on topographic and chemical contrast, respectively. Indeed, the high affinity of osmium tetroxide for NR particles (osmium tetroxide interacts directly with carbon-carbon double bonds in unsaturated rubber phases) resulted in an important differentiation between NR and CB in the BSE images: CB fillers appeared dark, while NR globules were bright (Figure 3). This chemical fixation was applied to samples at the following times  $t = 1$  h,  $t = 4$  h,  $t = 5$  h and  $t = 24$  h. The fixed sample coverslips were mounted on 25.4 mm aluminum pin stubs (Micro to Nano, the Netherlands) with double-sided sticky and conductive tabs (EMS, USA). Samples were left on stubs until completely dry. Afterwards, samples were coated with a 10-nm carbon

layer by double thread evaporation in high vacuum ( $10^{-5}$  mbar) with an ACE600 device (Leica, Germany) to enhance conductivity. FESEM was then performed using a Gemini 500 (Zeiss, Germany) driven by SmartSEM (version 6.3), operated at high vacuum ( $10^{-6}$  mbar in the observation chamber), a voltage of 3 kV, with high current mode, a 20  $\mu\text{m}$  aperture (beam current on the specimen experimentally measured as 43.2 pA under these conditions), and an approximately 2-mm working distance. The SE signal was collected with the corresponding in-lens detector. The BSE signal was collected with the energy-selective BSE in-column detector using a filtering grid ( $>400$  V) to filter out the SE signal. Images were acquired with a definition of  $1024 \times 768$  pixel, with a dwell time of 6.4  $\mu\text{s}$  per pixel and a line averaging of 25. Please note that both the SE and BSE signals were surface selective. The SE images were generated at the extreme surface (depth of a few nanometers), whereas the BSE images were capable of providing information from a depth of a few tens of nanometers.<sup>17</sup> For each sample, at least two different zones were recorded using a range of magnification power spanning from  $\times 5000$  to  $\times 80000$ .

## 2.4 | Determination of the NR particle Feret diameter

The quantification of rubber globule elongation was derived from the BSE images recorded at  $\times 5000$  at two different zones for each sample. A nonlocal means filter was first applied to subtract the noise from the image. Subsequently, the MorphoLibJ Plugin (ImageJ) was employed on the binary image with the application of watershed segmentation to detect only NR particles. Their size was reported in terms of the maximum Feret diameter,<sup>18</sup> which meant the longest direction of the globule (Figure 4c). This parameter is used in microscopy measurements for the size analysis of nonspherical particles. The obtained Feret diameter was the result calculated by the average of approximately 1000 NR particles regardless of their size. Thus, the elongation of NR particles was calculated from the difference between the average Feret diameter at  $t = 4$  h and its corresponding measurement at  $t = 1$  h.

## 3 | RESULTS AND DISCUSSION

### 3.1 | NR-CB coagulum: Its structural evolution during drying

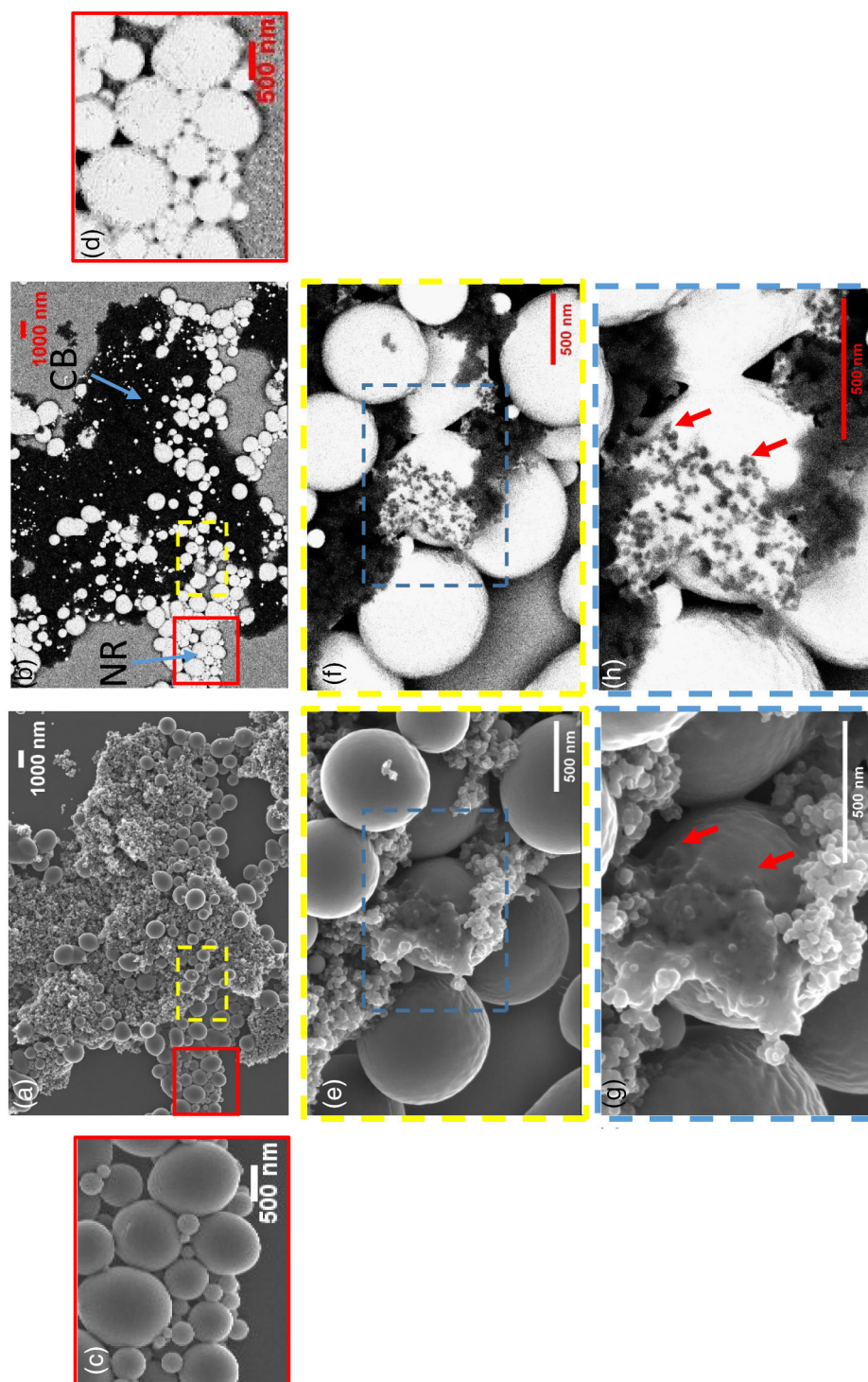
The nanoscale structure of the coagulum was imaged using FESEM with both BSE and SE detection, at

different aging times, so that its structural evolution dynamic during drying was reported.

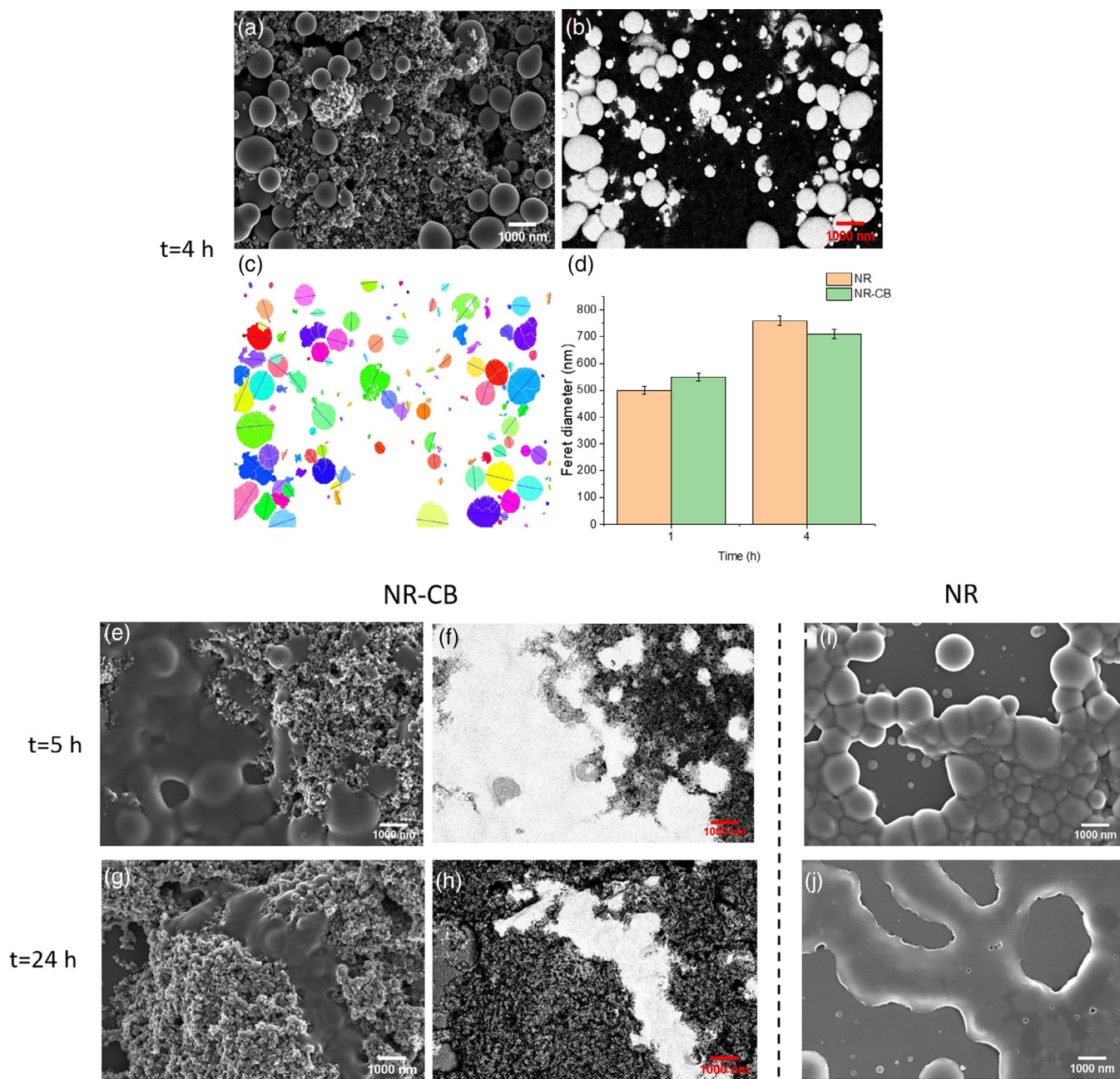
Figure 3 illustrates the typical structure of the NR-CB coagulum early after its formation ( $t = 1$  h) when the solvent is still present. One major observation is that the NR particles and CB fillers are not homogeneously distributed; this can be specifically highlighted by the BSE images (Figure 3b,f).

The comparison of the SE and BSE microstructures in Figure 3a,b reveals regions composed of homoaggregated NR particles that maintain their original colloidal structure, which is clearly visible in the magnified images of Figure 3c,d. Outside these regions, NR particles are essentially dispersed together with large agglomerates of CB filler. This general dominance of homoaggregation can be related to the mixing strategy. CB agglomerates are present in the aqueous slurry, and their size depends on various parameters, such as the shear stress during mixing. Standard mixing using a simple bench-top stirring device leads to object sizes ranging from 1 to 5  $\mu\text{m}$ , with a minor population of objects ranging from 100 to 300 nm. This is confirmed by a control sample of CB slurry prepared and imaged with the same protocol as that used when in the presence of NR globules (Figure S1), thus revealing the formation of CB agglomerates. Despite the dominance of CB agglomerates, we can point out localized regions having particular morphological characteristics. First, some persisting small CB aggregates ( $\sim 100$ – $300$  nm) are in close contact with NR globules and can be covered by the rubber material (Figure 3e,f). Additionally, some of them seem to sink into the surface of the globule, as indicated by the red arrows in Figure 3g,h. These local morphological features suggest a specific interaction between the small CB aggregates and NR globules. Similar observations are reported for a coagulum made of DPNR latex and CB filler (Figure S2), indicating that lipids may play an important role in the nanomechanism responsible for the abovementioned morphological characteristics; this phenomenon will be further discussed later. The mass percent ratio between the CB filler and NR was also drastically decreased to 5 and 1 wt% (by maintaining a constant NR concentration) to assess whether the interaction of NR globules with small CB aggregates was dependent on the CB concentration (Figure S3). The results show no difference in comparison to the one obtained for a mass percent ratio of 40%.

At  $t = 4$  h, the distribution of CB and NR particles is similar to that observed for the coagulum at  $t = 1$  h (Figure 4a,b compared with Figure 3a,b), with domains composed of only NR-NR homoaggregation and other domains consisting of large agglomerates of CB filler with scattered NR particles. The most striking difference in



**FIGURE 3** Typical FESEM micrographs of the NR-CB coagulum fixed at  $t = 1$  h. The mass ratio in liquid suspension is 40% CB/rubber. (a) SE and (b) BSE images where CB appears completely dark while NR particles are bright (magnification:  $\times 5000$ ), which highlights the two different microregions of the corresponding coagulum. The glass surface presents some background noise probably due to a thin layer of osmium deposited on the support. (c) Magnified SE and (d) BSE views of the NR-NR homogeneity corresponding to the red-squared zones in (a and b). (e) Magnified SE and (f) BSE views of the yellow-boxed regions shown in (a and b), composed of the CB filler and NR particles (magnification:  $\times 40000$ ). (g) Magnified SE and (h) BSE views corresponding to the blue-boxed region in (e and f, magnification:  $\times 80000$ ). Red arrows indicate regions in which the CB aggregates seem to sink into the NR globule [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]



**FIGURE 4** Typical FESEM micrographs of the NR-CB coagulum and NR latex over time. SE images and corresponding BSE micrographs of the NR-CB coagulum at  $t = 4$  h (a and b),  $t = 5$  h (e and f), and  $t = 24$  h (h and i). SE images recorded on a sample composed of only NR latex:  $t = 5$  h (g) and  $t = 24$  h (j). All images were taken with a magnification power corresponding to  $\times 10000$ . (c) Illustration of the Feret diameter determination of NR particles in image (a). (d) Histogram showing the elongation of NR particles in terms of the average Feret diameter between  $t = 1$  h and  $t = 4$  h [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

the structure of the coagulum between  $t = 4$  h and  $t = 1$  h is in the elongation of all the NR globules. Such elongation was quantified by the increase of 200–250 nm in the average Feret diameter (Figure 4c,d). A similar elongation of the NR particles is also found for the sample composed of only NR latex (Figure 4d). At  $t = 5$  h, as more of the solvent has evaporated, we observe a clear destabilization in the whole population of NR globules in

the NR-CB sample: NR globules lose their spherical shape (Figure 4e,f). Again, similar results are found for a sample composed of only NR latex (Figure 4g). After 24 h and the complete evaporation of solvent in both samples, NR globules completely lose their shape (Figure 4h,i and Figure 4j), resulting in a polymer film. In summary, the structural evolution of the NR-CB coagulum can generally be attributed to a typical film formation process of

NR due to solvent evaporation. This process is composed of the elongation and coalescence between rubber globules along with the diffusion of the polymer chain, thereby giving rise to a polymer film.<sup>19</sup> More interestingly, some NR globules in contact with small CB aggregates lose their original colloidal shape at earlier stages than those deformed due to solvent evaporation (Figure 3g). We hypothesize that this deformation at an early stage may be related to an interaction with the small CB filler that is capable of inducing the destabilization of the globule surface. To assess this hypothesis, we tried to boost the contact between the surface of NR globules and CB filler by the application of physical stress, thus aiming to reduce CB agglomeration.

### 3.2 | Effect of shear stress in the liquid suspension

Controlled mechanical shear stress was employed to reduce CB agglomeration. The mechanical forces were initially applied using the RheOptiCAD module right after the deposition of the NR-CB suspension on the coverslip ( $t = 0$ ) (Figure 2a). Light transmission images recorded during the applied oscillation cycles highlight the formation and combination of irregular flocs, growing in size and quickly leading to a macroscopically visible phase-separated coagulum at the end of 10 oscillation cycles ( $\sim 10$  min) (Figure S4). On the other hand, approximately 1 h is needed to macroscopically observe phase separation without the application of shear. Such behavior is typical of a shear-induced aggregation mechanism, where the applied shear forces can increase NR-CB contact and drive the particles to overcome the interaction energy barrier.<sup>20</sup> Prior to the observation of the NR-CB coagulum structure, a control sample was imaged attesting that the confinement between the parallel plates does not induce any deformation of the NR globules, as shown in Figure S5. Figure 5a illustrates the structure of the coagulum formed under shear. We can observe that the distribution of CB filler is not improved when shear is applied; the large CB agglomerates are not broken down by the applied force. Furthermore, in zones where NR-NR homoaggregation is dominant, no shear effect on the original form of the NR globules is highlighted (see the red boxed region in Figure 5b). Interestingly, regions of the sample where NR globules are in contact with small CB aggregates exhibit different structures. In these zones, the original spherical form of NR globules appears flattened upon the application of shear stress. Polymer leakage and diffusion is increased toward the surrounding CB aggregates (Figure 5c,d). Additional experiments were performed by applying shear on the floating NR-CB

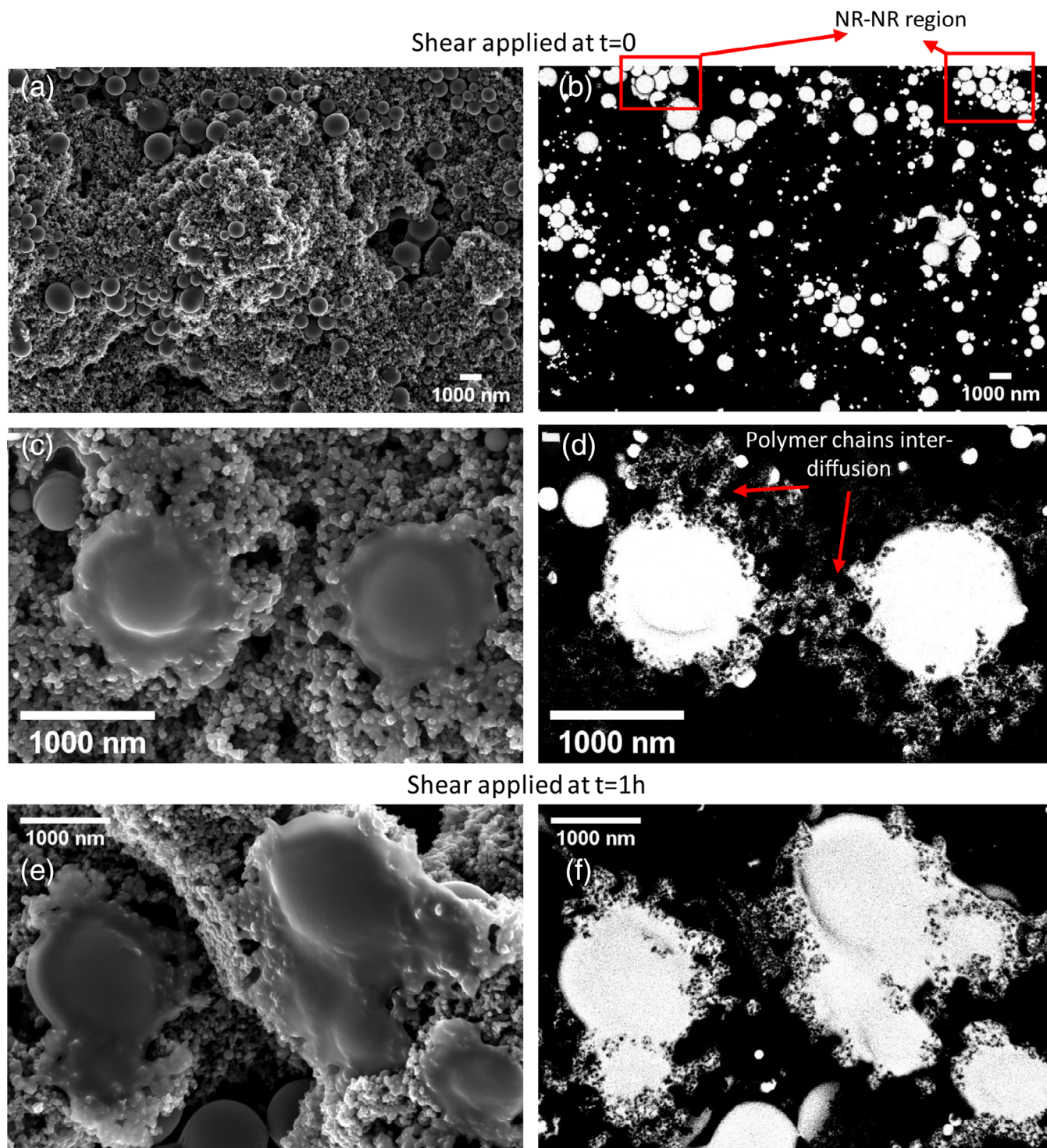
coagulum formed at  $t = 1$  h (Figure 2b). In this case, the shearing effect shows remarkable distortion of the NR globules in contact with the CB filler (Figure 5e,f). In summary, we can state that in our experimental conditions, the applied shear did not improve the dissociation of CB agglomerates. However, it accelerated the formation of a phase-separated NR-CB coagulum together with NR particle distortion in regions where they are in close proximity to CB aggregates, thus leading to polyisoprene diffusion through the sample. In an attempt to improve CB distribution and favor its interaction with NR globules, the two components were then mixed under sonication.

### 3.3 | NR-CB mixing under sonication: Effect on the structure of the formed coagulum

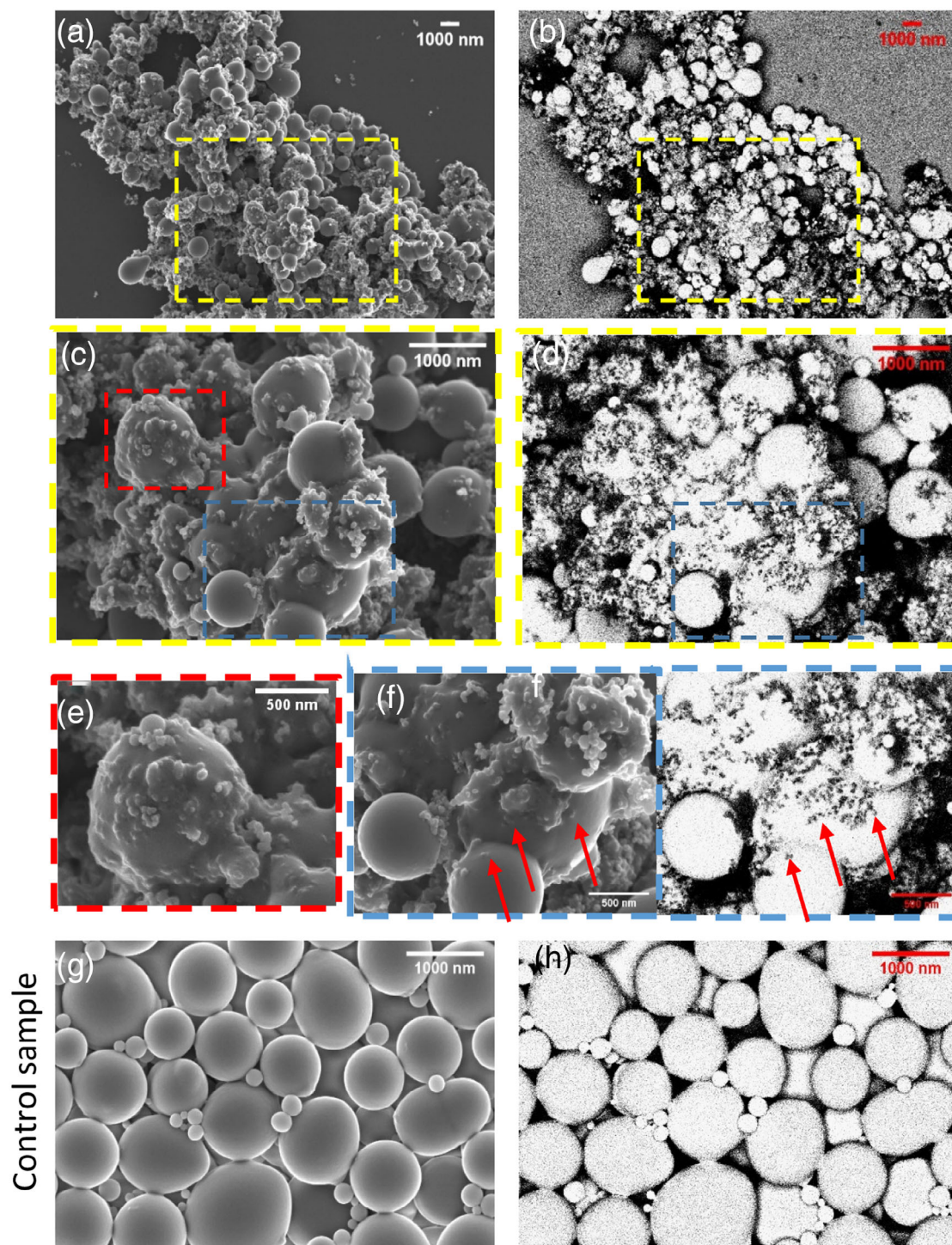
Sonication is known to break down CB agglomerates into smaller objects, down to a size that depends on the energy and on the sonication time. Our experimental conditions were defined so that sonication applied on only NR globules does not affect their structure (Figure 6g,h). When sonication is applied during mixing of NR globules with CB slurry, the formed coagulum has remarkable properties compared with those obtained from the previously used conditions: neither CB micrometer-sized agglomerates nor NR-NR homoaggregated regions are observed. Small CB aggregates (20–200 nm) and NR globules are homogeneously distributed. This leads to a coagulum mainly formed through heteroaggregation (Figure 6a,b). Additionally, SE and BSE images recorded with high magnification (Figure 6c,d) highlight the partial coalescence between the NR globules, which are this time surrounded by several small CB aggregates (20–200 nm). These aggregates establish notable contact with the globule surface (Figure 6e), and some of them are found to partially sink into the globule, as indicated by the red arrows in Figure 6f. Thus, what is locally observed without sonication (Figure 3g,h) is here extended to the whole coagulum. These morphological features confirm a specific interaction between the small CB aggregates and NR globules. This interaction induces the destabilization of the colloidal form of NR particles and results in the ability of the polyisoprene chains confined in the inner part of the globule to diffuse toward the outside, thus leading to partial coalescence.

Altogether, these results indicate (a) that the size of CB aggregates is a key parameter in the binary colloidal dispersion pathway controlling the structure of the formed NR-CB coagulum and (b) that the hydrophilic





**FIGURE 5** FESEM micrographs of the NR-CB coagulum formed under the application of mechanical shear stress at  $t = 0$  and of the coagulum formed after 1 h and then subjected to shear stress. (a) Large view SE and (b) BSE images of the NR-CB coagulum formed after the application of 10 shearing cycles at  $t = 0$  (magnification:  $\times 5000$ ), showing large areas of CB agglomerates. The red boxed area highlights domains of NR-NR aggregation. (c) Magnified SE and (d) BSE views of NR globules deformation in the NR-CB coagulum formed under shear applied at  $t = 0$ , thereby highlighting polymer diffusion into the surrounding CB filler (magnification:  $\times 20000$ ). (e) SE and (f) BSE images recorded on the NR-CB coagulum subjected to shear applied at  $t = 1$  h (magnification:  $\times 20000$ ), thus showing similar results as those in (c) and (d) [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]



**FIGURE 6** FESEM micrographs of the NR-CB heterocoagulum obtained with sonication during mixing: Mass ratio in the liquid suspension = 40% CB/rubber and the structure was fixed at  $t = 1$  h. (a) Large view SE and (b) BSE images of the same region showing the homogeneous distribution of NRs and CB filler (magnification:  $\times 5000$ ). (c) Magnified SE and (d) BSE views corresponding to the yellow-squared region in (a and b) (magnification:  $\times 10000$ ), highlighting the partial coalescence between the NR globules that are surrounded by several small CB aggregates. (e) Magnified SE of the red boxed region in (c) (magnification:  $\times 80000$ ). (f) Magnified SE and BSE views of the blue-boxed region shown in (c and b) (magnification:  $\times 40000$ ), showing that the CB filler partially sinks toward the inner part of the NR globules. (g) Magnified SE and (h) BSE views corresponding to the control sample composed only of sonicated NR globules [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

character of proteins and lipid head groups at the surface of NR globules (in contrast to the hydrophobic nature of CB) does not prevent the two particles from interacting. These important indications allow us to formulate hypotheses on the microscopic mechanisms involved in the interaction between the NR particles and CB filler. In a previous study on the interfacial structure of NR globules, it has been reported that the hydrophilic heads of lipids protrude toward the solvent phase, forming a very thin second layer ( $\sim 0.6$  nm) above the mixed protein and lipid layer that has a thickness of  $\sim 3.5$  nm.<sup>3</sup> Thus, we can reasonably presume that small CB aggregates can reach the hydrophobic alkyl chain of lipids located on the biomembrane. This can subsequently result in lipid reorganization and adsorption on the hydrophobic domains of CB. The biomembrane being partially shared with the CB aggregates will leave small and transiently uncovered patches on the globule surface, leading to the observed coalescence between them. The aforementioned hypothesis is also supported by a recent study on the efficiency of carbon nanotubes to penetrate phospholipid bilayers.<sup>21</sup> The researchers used single-chain mean field theory to report a possible migration of the phospholipid tails on the surface of hydrophobic nanotubes. Moreover, the work of Amornwachirabodee et al<sup>22</sup> on the penetration of oxidized carbon black (OCBs) (prepared from commercially available CB) into cell-sized liposomes also reported the adsorption of phospholipids on OCBs. Additionally, a study on the effect of CB incubated with giant unilamellar phospholipid vesicles (GUV) reported a decreasing number of GUV over time,<sup>23</sup> thus supporting our hypothesis.

## 4 | CONCLUSIONS

This study reports new insights into the processes occurring during the coagulation between NR latex and a CB slurry. The structural evolution dynamics at the nm scale were investigated, and the impacts of external physical stresses (shear and sonication) were tested.


We highlighted the dependence of NR-CB heteroaggregation vs. NR-NR or CB-CB homoaggregation based on the way the filler and NR particles came into first contact. Mixing the two components in colloidal suspensions under sonication maintained CB filler in the form of small aggregates (20–200 nm), resulting in the good homogenization of filler around the NR globules. When small CB aggregates were in contact with NR particles, a structural modification of the NR colloidal form was observed. We hypothesize a local membrane destabilization

induced by the adsorption of lipids on the hydrophobic domains of CB, thus leading to the coalescence between the NR globules. To our knowledge, this is the first time that the nanoscale structural characterization of a NR-CB heteroaggregate obtained through liquid coagulation has been described, highlighting that the interaction between CB filler and NR globules leads to a coalescence state. In an application perspective, understanding the origin of high affinity between CB (for different CB morphology and surface chemistry) and NR globules (either from field or treated latex) and the nanoscopic mechanisms that rule the transition toward a coalescence state will be of importance in the field of composite materials obtained by the liquid route.

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### SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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# Supporting information

## Natural Rubber - Carbon Black coagulation: following the nanostructure evolution from a colloidal suspension to an elastomeric composite

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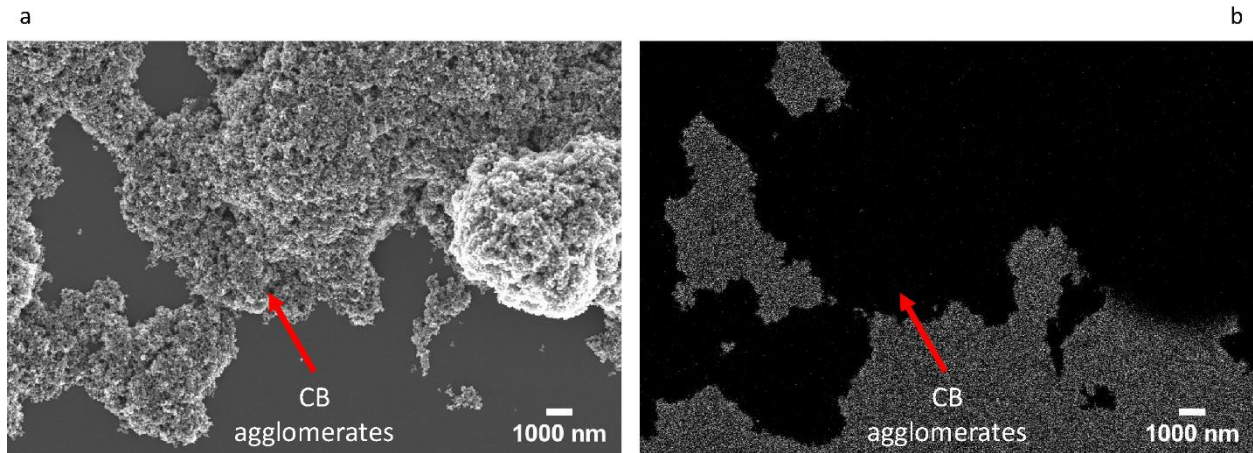
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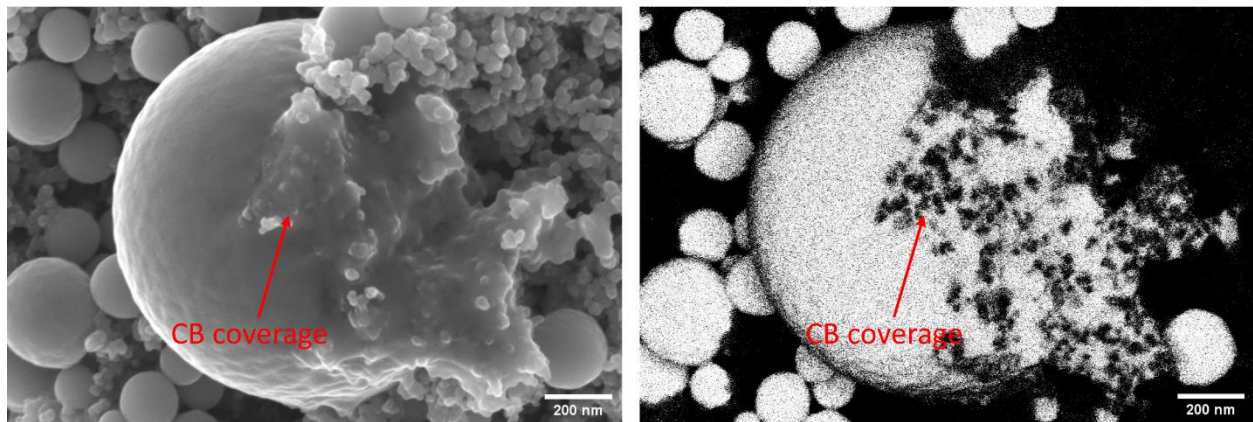
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**Supporting Information 1 (S1):** FESEM images of the CB slurry showing the agglomeration of CB in the liquid medium. (a) SE image. (b) BSE image.



**Supporting Information 2 (S2):** (a) SE and (b) BSE image showing CB aggregate in interaction with a DPNR globule. DPNR latex was produced via treatment of highly ammoniated NR latex with a bio-enzyme (proteinase), which hydrolyzes the proteins into a water soluble forms. It was subsequently mixed with CB in the same way as for NR latex.

DPNR-CB

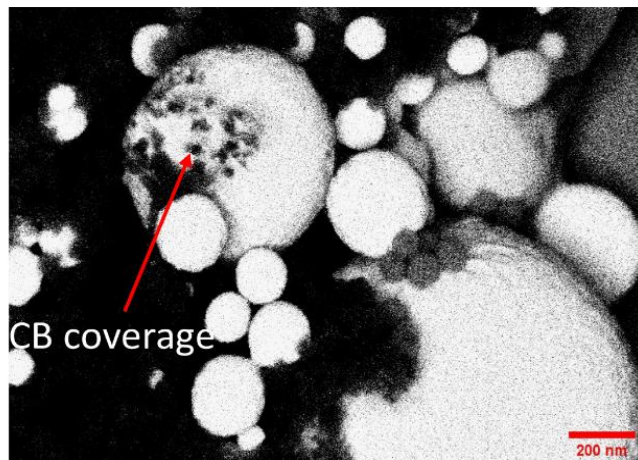
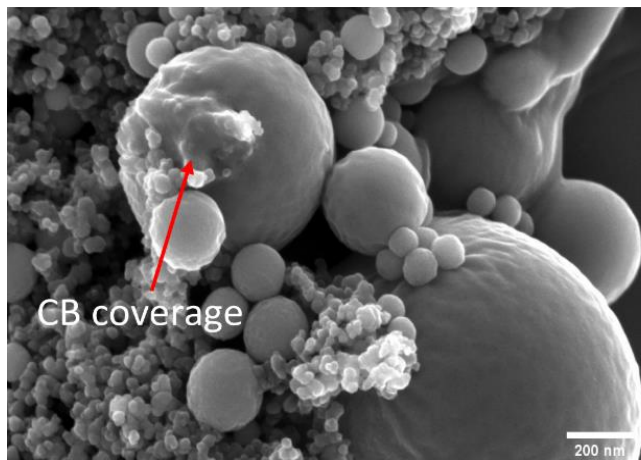


**Supporting Information 3 (S3):** (a) SE and (b) BSE images showing CB aggregate in interaction with a NR globule - mass ratio in liquid suspension = 5% CB/rubber

a

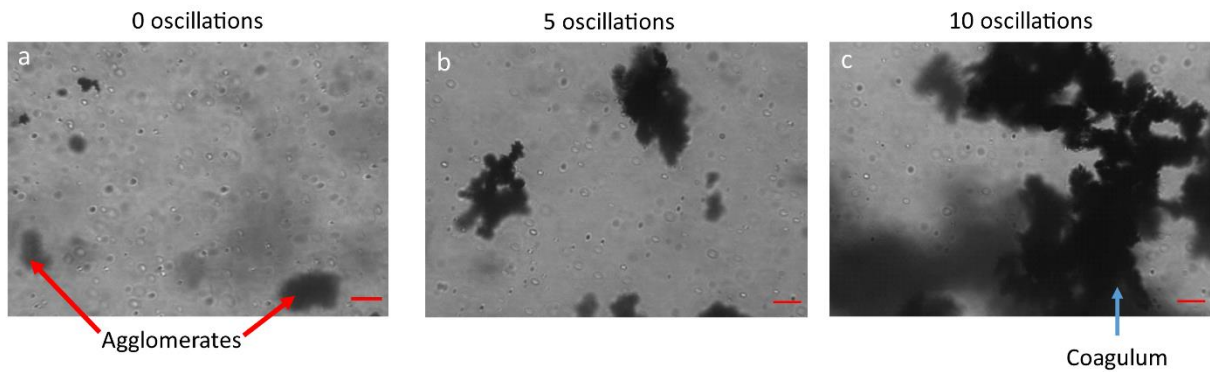
NR-CB 5% mass ratio (CB/rubber)

b



**Supporting Information 4(S4):** Transmission images recorded along with oscillation cycles for the NR-CB binary colloidal suspension. Mechanical forces were applied using the RheOptiCAD module right after the deposition of the sample on the coverslip ( $t=0$ ). The parameters of each oscillation correspond to 10 Hz frequency; total displacement of 1  $\mu\text{m}$  displacement; 500 $\mu\text{m}$  of gap; and 60s of application. Scale bar corresponding to 10 $\mu\text{m}$ .

$t=0$





**Supporting Information 5(S5):** FESEM micrograph of NR-CB coagulum formed at  $t=1$  h inside the shearing module without the application of mechanical shear. It shows the maintenance of NR globular structure, attesting that the parallel plate geometry used for the application of shear does not influence the NR-CB coagulum structure as well as the NR globular form. (a) SE and (b) BSE images.

