

Numerical and Experimental Study of Suspensions Containing Carbon Blacks Used as Conductive Additives in Composite Electrodes for Lithium Batteries

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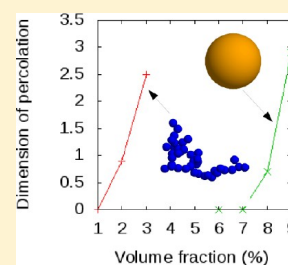
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ABSTRACT: Suspensions of carbon blacks and spherical carbon particles are studied experimentally and numerically to understand the role of the particle shape on the tendency to percolation. Two commercial carbon blacks and one lab-synthesized spherical carbon are used. The percolation thresholds in suspensions are experimentally determined by two complementary methods: impedance spectroscopy and rheology. Brownian dynamics simulations are performed to explain the experimental results taking into account the fractal shape of the aggregates in the carbon blacks. The results of Brownian dynamics simulations are in good agreement with the experimental results and allow one to explain the experimental behavior of suspensions.



1. INTRODUCTION

Carbon materials are widely used in electrochemical devices as conductive additives. They generally ensure electron transfer within the electrodes. Such materials are introduced, for example, in formulation of lithium battery electrodes^{1–3} or supercapacitor electrodes.^{4–6}

One of the most common carbon additives used in preparation of lithium battery electrodes is carbon black. These electrodes, which are often composite materials, are shaped by a colloidal route process. Several studies have recently shown that the battery performance is linked to repartition of carbon black inside the electrodes, which depends on the behavior of the suspensions used during their shaping processing.⁷ To improve the performance of the battery, it is therefore mandatory to understand the behavior of carbon black in suspension. This need was recently reinforced with the development of new flow devices such as the “lithium-based redox flow batteries”^{8,9} or “flow capacitors”,¹⁰ where the suspensions are directly used as electrodes.

Since many parameters can influence the behavior of suspensions (temperature, pH, ...), numerical simulations appear as a useful and powerful tool to understand the role of each parameter in the suspension behavior. Recently, Zhu et al. developed Brownian dynamics simulations for suspensions of composite electrodes of a lithium battery where carbon black particles are modeled as spheres.¹¹ This model gives interesting results but does not take into account the real shape of carbon black. Its fabrication process results indeed in a more complex structure than a sphere. Carbon black is composed of

elementary graphitic particles of around 10–50 nm which are fused together to form aggregates with a size around 100–300 nm.¹² These elementary particles are thus chemically bonded, and the aggregates do not break up during processing. Because of van der Waals interactions, these aggregates form agglomerates with a size of several micrometers. When a carbon black suspension is prepared, agglomerates are separated into the original aggregates by counterbalancing these interactions.¹³ However, because of the strong bonds between elementary particles, aggregates are not destroyed and appear as the smallest entities in the suspensions. These aggregates are not spherical but rather exhibit a fractal-like structure. Therefore, they may behave differently from spheres, especially for what concerns the percolation phenomenon. Experimentally, several studies have in fact reported that low percolation thresholds are obtained in carbon black suspensions which could be attributed to the aggregate shape.^{14–16}

In this study, Brownian dynamics simulations are developed to take into account the particular shape of carbon black aggregates. They are modeled as small particles linked together to form fractal aggregates. These aggregates are then moved as a whole by introducing constraints. To choose realistic parameters, this study is based on experimental suspensions prepared in propylene carbonate which was recently used as solvent in the formulation of suspensions for flowable

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electrodes of redox flow batteries.¹⁷ Two kinds of commercial carbon blacks are studied as well as one kind of lab-synthesized carbon spherical particles to observe the difference in behavior depending on the shape of the entities in suspension. Particular attention is paid to the tendency of particles to percolate in suspension. To our knowledge, this is the first time that Brownian dynamics simulations taking into account the shape of carbon blacks are achieved.

2. EXPERIMENTAL SECTION

Two different commercial carbon blacks were used in this study, namely, the Super P (BET surface = $62 \text{ m}^2 \text{ g}^{-1}$, ash content = 0.01 wt %, and total Fe content = 5 ppm) and the C-Energy Super C45 (BET surface = $45 \text{ m}^2 \text{ g}^{-1}$, ash content = 0.01 wt %, and total Fe content = 2 ppm) supplied by TIMCAL Ltd.¹ These two carbon blacks were selected because they are commonly used as conductive additives in the formulation of electrodes for lithium batteries. As a control, spherical particles were synthesized by a hydrothermal route as proposed in ref 18. Typically, 1.197 g of sugar was dissolved in 35 mL of Milli-Q water and introduced in a 50 mL Teflon-lined stainless steel autoclave. After 2 h of hydrothermal treatment at 180°C , the obtained solid was rinsed 4 times with osmosed water. The resulting powder was carbonized in a tube furnace at 800°C under Ar/H_2 (5%) atmosphere to eliminate oxygen groups from the surface and render it an electronic conductor. For simplicity, in this study, we considered a density of $\rho_c = 2 \text{ g cm}^{-3}$ for all carbon types. Calculations with densities comprised between 1.8 and 2.1 g cm^{-3} have indeed not shown a significant difference in the results. In the following the carbon Super P, carbon C-Energy Super C45, and synthesized carbon are denoted as Carbon SP, Carbon C45, and hydrothermal carbon respectively.

In the following, these carbon powders are dispersed in propylene carbonate as model systems due to their interest for flowable electrodes. However, before studying these suspensions, different characterizations were performed to better understand the properties of the different raw carbon powders. Therefore, they were observed by transmission electron microscopy (TEM) using a Hitachi H9000 NAR electron microscope operating at 300 kV. To this end, samples were dispersed in ethanol by ultrasonication for 5 min in an ultrasonic bath to obtain very dilute suspensions (lower than 0.05 vol % of carbon). Then, a drop of the suspension was deposited on a copper grid and dried at room temperature before its introduction in the TEM. Ethanol was used for this characterization because it permits a relatively good dispersion of carbon particles and evaporates faster than propylene carbonate.

Then, to determine the size of the smallest entities of carbon in a well-dispersed suspension, dynamic light scattering measurements (DLS) were carried out in a Zetasizer Nanoseries from Malvern Instruments. Dilute suspensions of carbon blacks in ethanol were prepared; however, because of the difficulties to keep a dispersed suspension during the whole time of measurements, a water-based suspension with a dispersant was preferred. Therefore, suspensions of carbon black were prepared in Milli-Q water with sodium carboxymethylcellulose (Aldrich, DS = 0.7, $M_w = 90 \text{ kg mol}^{-1}$) by ultrasonication for 5 min in an ultrasonic bath. Before analysis, suspensions were kept at rest to allow settling of agglomerates which were always flocculated. Then the supernatant was analyzed by DLS. This measurement gives only an approximate value of the size of carbon black aggregates first because carbon blacks are not spherical particles and second because the presence of CMC is neglected. The size of the hydrothermal carbon particles was also investigated by DLS. For this case, dilute suspensions were prepared in ethanol.

The second part of the experimental work focuses on determination of the percolation thresholds in suspensions prepared in propylene carbonate (PC anhydrous 99.7%, Sigma Aldrich), systems of interest in this study. The viscosity of PC at 25°C is taken at $\eta = 2.5 \times 10^{-3} \text{ Pa s}$.¹⁹ Dispersions were obtained by ball milling for 2 h at 500 rpm at room temperature. The volume concentrations of carbon in suspensions varied from 0.25 to 3 vol % for the commercial carbon

blacks and from 1 to 10 vol % for the hydrothermal carbon. The low concentrations and soft conditions of ball milling preserve the carbon black aggregates from being destroyed during the dispersion. This point is discussed in the following. The percolation thresholds were determined by two complementary methods: electrochemical impedance spectroscopy (EIS) and rheology. The protocols used in this study were already described elsewhere.¹⁷ The impedance and rheology measurements were carried out on a stress-controlled rheometer Physica MCR 101 from Anton Paar using plate–plate geometries (plate diameter 50 mm for the carbon SP and C45 and plate diameter 25 mm for the hydrothermal carbon). The gap is fixed at 1 mm and the temperature at 25°C by a Peltier system. Experiments performed with both plates for the carbon C45 indeed did not show a strong influence of the plate on the results. Therefore, a smaller plate was used for the hydrothermal carbon in order to save the raw materials because of the small yield of the synthesis. Oscillatory frequency sweep measurements were conducted with a strain amplitude of $\gamma = 0.1\%$ for carbon SP and the hydrothermal carbon and of $\gamma = 0.4\%$ for the carbon C45. The strain amplitude was chosen for each carbon suspension such as the response remains in the linear regime while having better sensibility of the measurement. For impedance spectroscopy, the rheometer was connected with a standard potentiostat/galvanostat SP2000 from Biologic. EIS measurements were performed in a frequency range of 10^{-2} – 10^5 Hz with an alternating voltage amplitude of 100 mV. Lower values of the amplitude revealed no significant changes due to the current value. Before each measurement, the suspension was presheared at $\dot{\gamma} = 1000 \text{ s}^{-1}$ for 10 min and left at rest for 30 min to erase the shear history.¹⁷ All measurements were thus carried out on the suspension at rest.

3. RESULTS OF EXPERIMENTAL CHARACTERIZATION

Figures 1a and 1b show TEM images obtained with the two different commercial carbon blacks. These carbon blacks are composed of “spherical” elementary particles with inhomogeneous size comprised in majority between 10 and 50 nm. Image analyses show an average size of the elementary particles of 27 nm (standard deviation of 10 nm) for carbon SP30 and 34 nm (standard deviation of 8 nm) for carbon C45. The observed elementary particles of carbon C45 are a bit larger than the SP ones, which can be correlated with the lower specific area of carbon C45, i.e., 45 vs $62 \text{ m}^2 \text{ g}^{-1}$, respectively. The average distributions obtained in three DLS measurements with these carbon blacks are shown in Figure 1d. As mentioned in the Introduction, carbon black is composed of aggregates of elementary particles chemically linked together. These entities are the smallest ones which can be dispersed in a suspension. DLS measurements allow thus determination of the size of these aggregates and not of the size of the elementary particles. According to the curves, the size dispersion of aggregates is small since only one narrow peak is observed. This peak is centered on 190 nm for the carbon SP and 220 nm for the carbon C45. Therefore, for both carbon blacks, the aggregate size is around 200 nm, which is in agreement with the aggregate size mentioned in the literature.¹² Our results show also that carbon C45 appears to have a smaller distribution than carbon SP.

TEM images of hydrothermal carbon show spherical particles with size comprised in majority between 200 and 500 nm (see Figure 1c). Analyses performed on images obtained by SEM also confirm that the average size of the carbon particles is 380 nm with a standard deviation of 69 nm. For the hydrothermal carbon, the size distribution obtained by DLS measurements is reported in Figure 1d. This distribution is narrow, but a small peak appears around $10 \mu\text{m}$, which can be explained by the

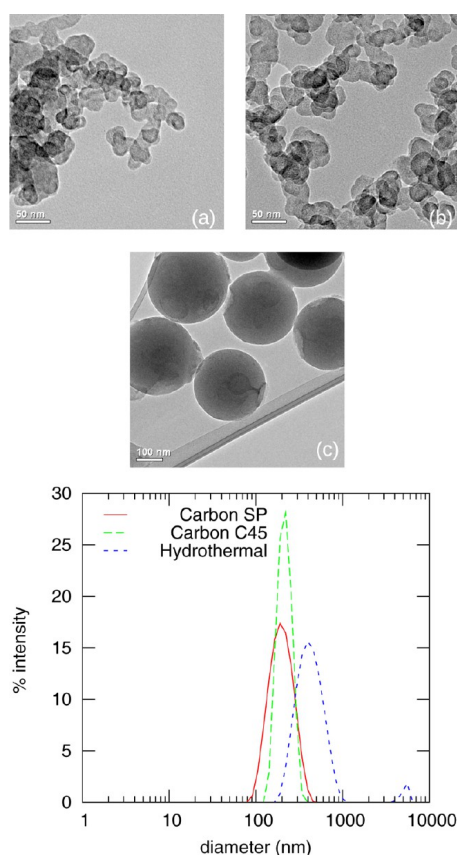


Figure 1. TEM pictures of the different carbon powders: (a) carbon SP, (b) carbon C45, and (c) hydrothermal carbon. Different magnifications were used between the commercial carbon blacks and the hydrothermal carbon to better distinguish the elementary particles. (d) Size distribution obtained by DLS measurements: carbon blacks are dispersed in Milli-Q water with CMC, and hydrothermal carbon is dispersed in ethanol.

presence of few agglomerates. The main peak is centered on 440 nm. Since the TEM observations show that particle sizes are around 200–500 nm, it can be concluded that the particles are in majority not fused, contrary to SP and C45.

The following experiments consisted of determination of the electrical and mechanical thresholds of suspensions prepared in PC with these different kinds of carbon particles. Suspensions were prepared by varying the volume percent of carbon ϕ in suspension, and then they were analyzed by EIS measurements and rheology. The results obtained for the EIS measurements are shown in Figure 2a. As mentioned in refs 17 and 20 the current flow in the carbon network should be observed at low frequencies. This is the reason why, for our purpose, we focus on the right-hand side part of the Nyquist diagram. At the lowest frequencies, two different behaviors can be observed depending on the volume percentage of carbon. For the lowest concentrations in carbon, a linear behavior is observed, whereas for the highest concentrations, a portion of a loop is measured. In the latter case, the carbon particles can form a network through which the current can flow, giving rise to a resistive loop in the Nyquist diagram. For the lowest concentrations, there are not enough particles to create a continuous network

and the linear behavior may correspond to a capacitive behavior due to accumulation of ions at the electrodes. From the EIS, we estimate that the electrical percolation threshold is reached when the loop appears. For carbon SP, the loop appears for a carbon concentration of 0.5 vol %; therefore, it is deduced that the percolation threshold is in the range of carbon concentrations of 0.25–0.5 vol %. With the same approach it is found that the percolation threshold is comprised in the ranges of carbon concentration of 1–1.5 vol % and 2–5 vol % for carbon C45 and hydrothermal carbon, respectively. Both commercial carbon blacks percolation thresholds are in agreement with the values reported in the literature,¹⁴ which let us believe that the anisotropy of the initial fractal aggregates is preserved during dispersion and that the aggregates are not broken.

The results obtained in the rheological measurements are reported in Figure 2b. This measurement indicates that the suspension behaves like a liquid or gel (suspension for which a percolated network of particles is formed). Suspensions are considered as a gel if the values of the elastic modulus (G') are higher than the values of the viscous modulus (G''). In Figure 2b1, for suspensions with a carbon loading of 0.25 vol %, G' is not higher than G'' ; therefore, at this concentration the suspension is not a gel. However, it is observed that for carbon SP, G' is higher than G'' for suspensions with a carbon concentration of 0.5 vol % or higher. For these suspensions, mechanical percolation is obtained. According to this result, the mechanical percolation threshold is found to be in the range of carbon concentrations of 0.25–0.5% for carbon SP. With the same argument, the mechanical percolation threshold lies in the concentration ranges 1–1.5% and 2–5% for carbon C45 and hydrothermal carbon, respectively.

Both mechanical and electrical percolation thresholds are situated in the same ranges of concentrations, which suggests that the current can flow when the suspension becomes a gel. Therefore, percolation appears first for carbon SP, then for carbon C45, and finally for hydrothermal carbon. This result shows that the carbon shape influences the value of the percolation threshold. The fractal shape of carbon blacks favors lower percolation thresholds. In the following, this result is interpreted by means of numerical simulations.

4. SIMULATION METHODOLOGY

In the following, Brownian dynamics simulations were carried out to explain the behavior of the different experimental systems presented in section 2. To take into account the particular shape of the carbon black aggregates a specific model is developed. For simplicity, the polydispersity in size of elementary particles is not taken into account in this model. However, for the carbon black aggregates, since we are interested in understanding the role of structure, a polydispersity in the size of aggregates is included. This section is divided as follows: first, the methodology to model the commercial carbon blacks aggregates is described; then the simulations as well as parameters used for the three kinds of carbon are presented.

4.1. Modeling of Carbon Black Aggregates. In the Experimental Section it was observed that for carbon black and hydrothermal carbon percolation does not occur at the same volume percent, requiring a higher concentration for hydrothermal carbon. To understand the role of the particle shapes, we propose here to model the carbon blacks as nondeformable fractal-like aggregates composed of small spheres (elementary

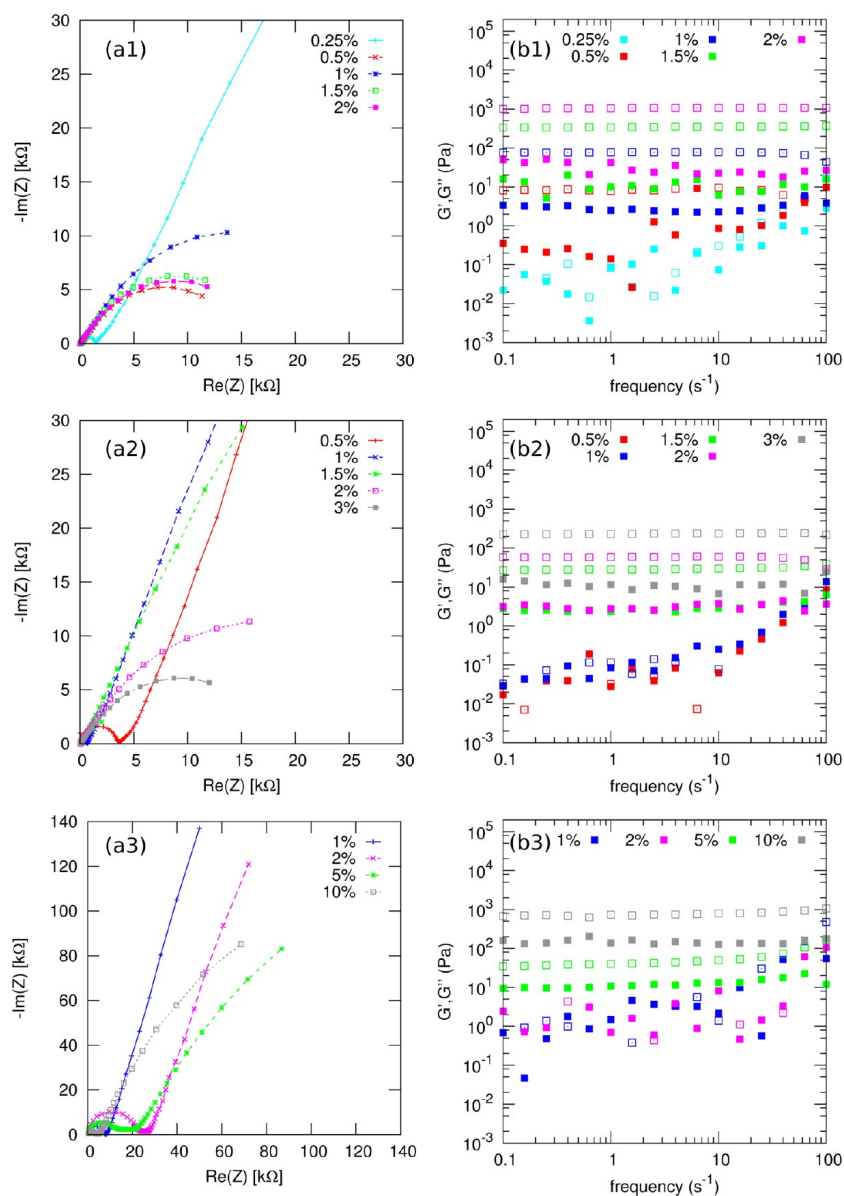


Figure 2. Nyquist diagrams obtained by impedance measurements (a), and results of oscillatory frequency sweep measurements (b) carried out on carbon/PC suspensions prepared with different volume percents of powder ϕ . G' is represented by the open symbols and G'' by the filled ones. (1) Carbon SP, (2) carbon C45, and (3) hydrothermal carbon. For clarity, different scales were used in the Nyquist diagrams for the two commercial carbon blacks and the hydrothermal carbon.

particles) linked together. Analysis of MET images in section 3 has shown that the elementary particle sizes of carbon SP and carbon C45 are 27 nm with a standard deviation of 10 nm and 34 nm with a standard deviation of 8 nm, respectively. For the sake of simplicity elementary particles of 30 and 40 nm are used to model carbon SP and carbon C45, respectively, to check what is the effect of the size of elementary particles in the simulations. In the literature, it is reported that carbon black aggregates have a fractal structure with a fractal dimension between 1.7 and 2.2.²¹ To obtain initial conditions for the Brownian dynamics simulations, where carbon black aggregates have to be generated with fractal dimensions of this order,

simulations of cluster cluster aggregation (CCA) were performed. The method used is similar to the one described in ref 22, only the end condition was changed. Therefore, here, we summarize the main points of the simulation method. At the beginning, the spherical particles are randomly distributed in a cubic box whose size is determined by the volume fraction of carbon, while the number of elementary particles is kept fixed at 2880. Periodic boundary conditions are applied. During the simulation, a particle (or an aggregate) is randomly chosen and allowed to diffuse to a constant distance according to Monte Carlo Metropolis rules. The probability of diffusion is given by $P_{\text{diff}} = D_i/D_{\text{max}}$ where $D_i = D_0 \times a/R_{\text{gyr}}$ with D_0 being the

diffusion coefficient of the elementary particle of radius a and R_{gyr} the radius of gyration.²³ After diffusion, if two aggregates are in contact, they stick together with a probability of 1 in order to have the smallest fractal dimension at the end. If particles are overlapping, the approaching cluster is moved back until no particles are overlapping and then the procedure is repeated. Simulations are stopped when the desired number N_C of aggregates is obtained (rather than when only one aggregate is present as in ref 22). At the end, the numbers of elementary particles in the aggregates are not the same, which allows us to have a size distribution for aggregates as in experiments (see Figure 1d). A snapshot of the simulation is shown in Figure 3, in which the different aggregates are represented with different colors. The obtained aggregates are well distributed and ramified as expected.

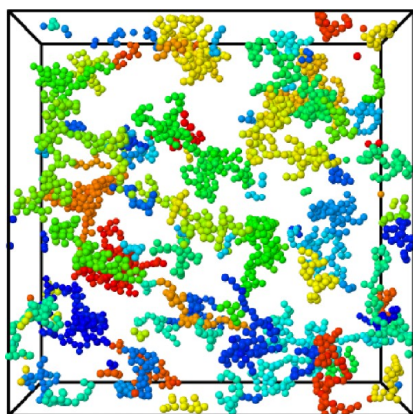


Figure 3. Snapshot of a result of CCA simulation performed at $\phi = 1\%$ with elementary particles of $a_1 = 20$ nm and $N_C = 87$. Different carbon black aggregates are represented with different colors.

To obtain a distribution of aggregate sizes similar to the experimental distribution, CCA simulations were performed changing the number N_C of final aggregates. For each number N_C , 10 independent simulations were performed with a volume percent of elementary particles fixed at $\phi = 1\%$. At the end of the simulation, the fractal dimension of aggregates as well as their radius of gyration, which is an estimation of the size of aggregate, were calculated. The average results obtained in the 10 simulations with elementary particles of radii $a_1 = 15$ nm and $a_2 = 20$ nm are reported in Table 1.

As the number N_C decreases, the average radius of gyration naturally increases. By comparing the results obtained with the elementary particles of $a_1 = 15$ nm and $a_2 = 20$ nm, it is found that N_C has to be higher for $a_2 = 20$ nm than for $a_1 = 15$ nm to

Table 1. Average Radius of Gyration R_{gyr} and Mean Fractal Dimension D_f Obtained in 10 Simulations with a Final Number of Aggregates N_C for $a_1 = 15$ nm and $a_2 = 20$ nm

$a_1 = 15$ nm			$a_2 = 20$ nm		
N_C	R_{gyr} (nm)	D_f	N_C	R_{gyr} (nm)	D_f
96	89	1.66	192	88	1.63
72	102	1.67	144	100	1.65
58	114	1.70	96	120	1.67
48	125	1.71	87	125	1.68
41	132	1.72	72	138	1.70

obtain aggregates of the same size. Moreover, in all cases, the aggregates have a fractal dimension comprised between 1.63 and 1.72, which is in conformity with the experimental structure of carbon black aggregates. According to the experimental results, aggregates of carbon black have a size around 200 nm. At $\phi = 1\%$, the distributions obtained with $N_C = 72$ for $a_1 = 15$ nm and $N_C = 144$ for $a_2 = 20$ nm could be used. However, CCA simulations performed increasing the volume percent of elementary particles have also shown that the radius of gyration decreases a little bit when the volume percent is increased. In the following, in order to have aggregates around 200 nm whatever the concentration, we choose to generate aggregates with $N_C = 48$ and 87 when $a_1 = 15$ nm and $a_2 = 20$ nm, respectively. Distributions of aggregate sizes obtained in 10 simulations for different volume percents of elementary particles are reported in Figure 4. The obtained

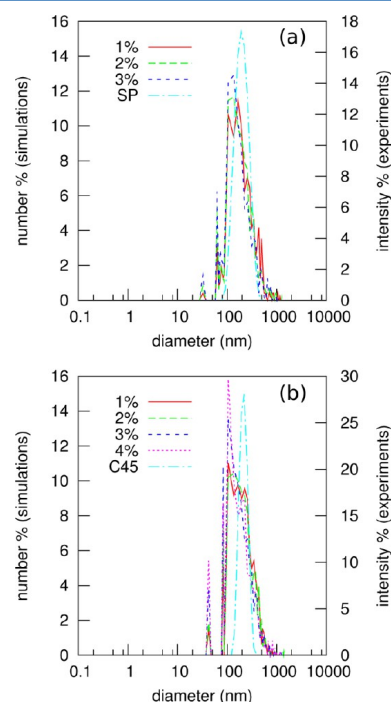


Figure 4. Size distribution of aggregates obtained in 10 simulations for different volume concentrations of carbon: (a) $a_1 = 15$ nm and $N_C = 48$; (b) $a_2 = 20$ nm and $N_C = 87$. Experimental curves of DLS measurements obtained for the carbon SP and carbon C45 were reported in a and b, respectively.

distribution of aggregate sizes in simulations is centered around 200 nm whatever the concentration or size of elementary particles. Some particles are isolated as revealed by the presence of a small peak for a size 30 or 40 nm in agreement with the size of elementary particles. These distributions match quite well the experimental ones reported in Figure 1d. In the following the results of the CCA simulations will thus be used as initial conditions for the Brownian dynamics simulations.

4.2. Brownian Dynamics Simulations. Brownian dynamics simulations were performed with the Ermark algorithm in a cubic box with periodic conditions.²⁴ The size of the box was determined by the volume percent of carbon.

To model the hydrothermal carbon, spherical particles with a radius of $a = 220$ nm were used. Initially, particles were randomly placed at nonoverlapping distances. Simulations were performed with 2871 particles and a time step fixed at $\delta t = 10^{-7}$ s. The results were analyzed at $t = 2.5$ s.

For the simulations concerning the carbon blacks, the results of CCA simulations were used as initial conditions. During the simulations, the elementary particles have to remain linked together and the aggregates have to keep their shape. To this end, a SHAKE algorithm was introduced to constrain all distances between the elementary particles of each aggregate.²⁴ Particles belonging to the same aggregate were not supposed to interact with each other. The time step of simulation was fixed at $\delta t = 10^{-9}$ s, and results were analyzed at $t = 0.025$ s (same number of iterations as for the spheres).

All simulations were performed at a temperature of $T = 298$ K with a solvent viscosity of $\eta = 2.5 \times 10^{-3}$ Pa s (PC). In the following, the results are averaged over 10 simulations.

The interactions between carbon particles in an organic medium are not very well established and generally assumed to be van der Waals interactions. However, in section 3, rheological measurements have shown that for the three kinds of carbon gels are formed for low solid concentrations. Gelification is due to attractive interactions between particles in suspensions. Therefore, as a first approximation, a short-range attractive 18–36 Lennard–Jones potential was chosen to model the interaction between two hydrothermal carbon particles or two elementary particles belonging to different carbon black aggregates

$$U^{LJ}(r_{ij}) = 4\epsilon_a k_B T \left[\left(\frac{2a}{r_{ij}} \right)^{36} - \left(\frac{2a}{r_{ij}} \right)^{18} \right] \quad (1)$$

where k_B is Boltzmann constant and ϵ_a is the well depth. In the following, this depth is fixed at $\epsilon_a = 14$. The influence of changes in this value is evaluated in the last paragraph.

In the following, we use the terminology of elementary clusters to describe the entities that cannot be broken in the simulation, which means that in the case of spherical carbon the elementary clusters are single-spherical particles and in the case of the carbon blacks the elementary clusters are aggregates formed by spherical particles permanently linked together.

5. SIMULATION RESULTS

5.1. Influence of the Carbon Type. Figure 5 shows the kinetics of aggregation observed in the different simulations. This kinetics is followed by the evolution of the number of clusters, composed of at least two particles, as a function of time. For the spherical carbon particles since elementary clusters are simply individual particles, the aggregation process is comprised of two steps, as already explained in a previous work.²⁵ In the first step, the number of clusters increases, which corresponds to dimer formation being predominant. Then, the number of clusters decreases which indicates that coalescence is predominant. This evolution is clearly observed for a concentration of $\phi = 2\%$. For higher concentrations, the first step is very fast and out of the range of the figure. For both carbon blacks, since elementary clusters are composed of more than one particle at the beginning of the simulation, the first step does not exist and only coalescence is observed. Whatever the carbon used in simulations, aggregation is faster in more concentrated suspensions. At the end of the simulations it can

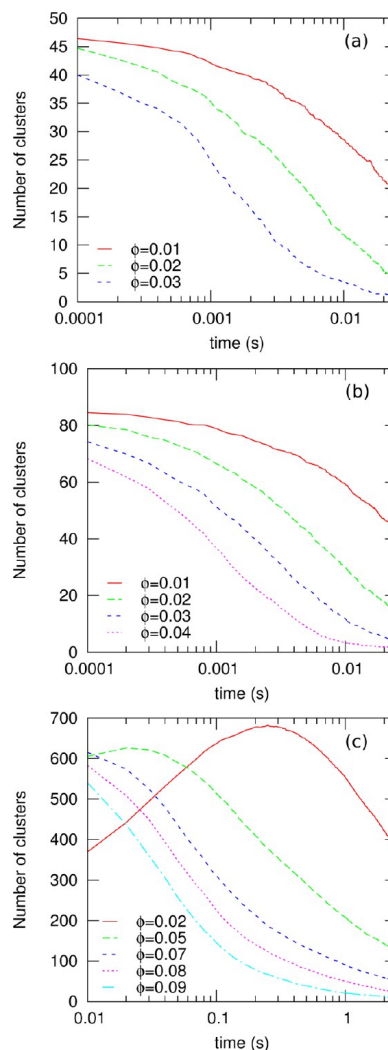


Figure 5. Number of clusters of at least 2 particles as a function of time for different volume percent of carbon: (a) carbon black with $a_1 = 15$ nm, (b) carbon black with $a_2 = 20$ nm, and (c) spherical carbon particles with $a = 220$ nm. Note that the time scale is not the same in c vs a and b.

also be noted that aggregation is finished only for the highest concentration in each case.

Figure 5 shows also the differences in aggregation kinetics between both carbon blacks and hydrothermal carbon. The particles of the latter, being larger, diffuse slower. Therefore, to compare the results obtained for the spherical carbon with the results obtained for carbon blacks at the same aggregation stage, different simulated times must be used. In the following, results of simulations with carbon blacks are analyzed at 0.025 s and with the hydrothermal carbon at 2.5 s.

Snapshots of simulations obtained for the different carbon types at $\phi = 2\%$ are reported in Figure 6. This figure shows that the structures obtained with the carbon blacks in Figure 6a and 6b are different from that obtained with spherical carbon particles in Figure 6c. Clusters obtained in the simulations with the spherical carbon are more compact than the clusters

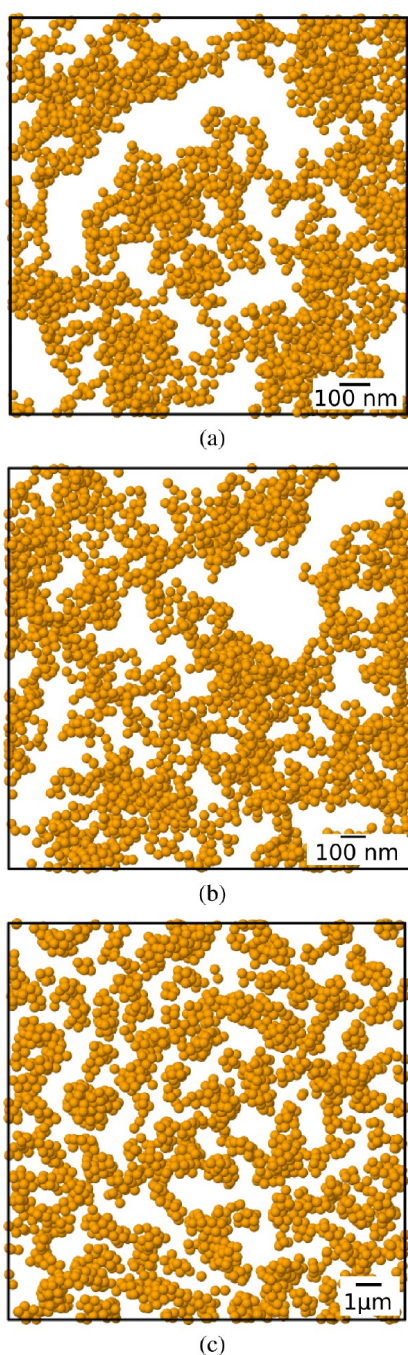


Figure 6. Snapshots of simulations at $\phi = 2\%$: (a) carbon black with $a_1 = 15$ nm at 0.025 s (volume of box $\approx 2 \mu\text{m}^3$), (b) carbon black with $a_2 = 20$ nm at 0.025 s (volume of box $\approx 4.8 \mu\text{m}^3$), and (c) spherical carbon particles with $a = 220$ nm at $t = 2.5$ s (volume of box $\approx 6400 \mu\text{m}^3$).

obtained with the carbon blacks. To characterize percolation in the simulations, the technique described in ref 26 was applied. In this method, the dimension of percolation is related to the way one cluster spans from one side to the other of the simulation box. Therefore, the system has a percolation

dimension of 1, 2, or 3 if this cluster crosses the box in only 1 direction, 2 directions, or 3 directions, respectively. Figure 7

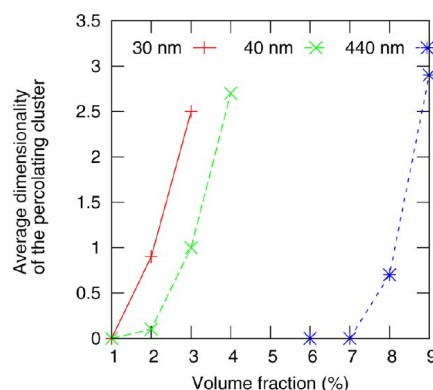


Figure 7. Dimension of the percolating cluster as a function of the volume percent of carbon: at $t = 0.025$ s for the carbon blacks with elementary particles of 30 and 40 nm and at $t = 2.5$ s for the spherical particles of 440 nm.

shows the mean dimensionality obtained at $t = 0.025$ s for the carbon blacks and at $t = 2.5$ s for the spherical carbon. For each type of carbon, the percolation dimension increases with concentration, which is in agreement with the occurrence of a percolation threshold. Figure 7 shows also that a 1D percolation is obtained at about 2% of carbon black with $a_1 = 15$ nm, 3% of carbon black with $a_2 = 20$ nm, and 8% for the spherical particles, which means that in our simulations these concentrations might be high enough to create a conductive path in the suspension. The three-dimensional percolating network is then obtained for around 3% of carbon black with $a_1 = 15$ nm, 4% of carbon black with $a_2 = 20$ nm, and 9% for the spherical particles. This result is in good agreement with our experiments, in which the percolation is first observed for carbon SP, then carbon C45, and finally hydrothermal carbon (see section 3).

However, this result is obtained at a short simulation time at which aggregation is not totally finished for the smallest concentrations of carbon. Therefore, one may wonder whether this result is still valid when aggregation is finished. To answer to this question, some simulations were extended until a 3D network appears or only one cluster remains in the simulation. We focus on the case of $\phi = 2\%$. For both carbon blacks complete aggregation is indeed rapidly obtained at this concentration. At the end of simulation, for both carbon blacks, generally a 2D percolating network is formed (mean dimensionality of percolation is 1.6 for elementary particles of $a_1 = 15$ nm and 1.9 for elementary particles of $a_2 = 20$ nm). At $t = 0.025$ s, the time at which aggregation is not finished, nevertheless it was observed that the percolation dimension is higher for the carbon black with $a_1 = 15$ nm than for the carbon black with $a_2 = 20$ nm, which seems to indicate that formation of the network occurs faster for this carbon. For a direct comparison also with the spherical carbon, 10 simulations were performed again at $\phi = 2\%$ with only 500 spherical particles to reduce the computation time. These simulations were stopped at $t = 80$ s. At that time, only one simulation shows a total aggregation. For this one, no percolation is observed. For the others, few clusters are present (between 2 and 4) and no percolation is observed. The clusters are compact and cannot

percolate by their assembly. This result is in qualitative good agreement with the experimental results, which have shown that the percolation threshold is lower for the carbon blacks than for the hydrothermal carbon (see section 3). According to these results, our model seems accurate enough to single out the difference between the carbon blacks and the spherical particles, but it is too simple to differentiate between the two carbon blacks. Some of the approximations in the model can have indeed some effect. First, the elementary particles are supposed to have the same diameter. The interaction potentials are very simple, and it is likely that in reality they are not exactly the same for the two carbon blacks (cf. carbon C45 has more oxygen on surface¹). Then, hydrodynamic interactions are not included. These can influence the aggregation kinetics and then the final structures, especially in the case of aggregates with different size and composition. As shown in other works, diffusion of clusters and their reorganization depend on their composition and are influenced by the hydrodynamic interactions which could lead to different percolation thresholds.^{27,28}

Our numerical results can nevertheless be used to explain the difference between the hydrothermal carbon and the carbon blacks. According to the simulations, the difference in the percolation thresholds is essentially explained by the structure of the system, which is directly linked to the shape of the carbon. When particles are spherical, they can indeed reorganize themselves more easily in a compact shape to minimize the potential energy, which increases the percolation threshold. However, for carbon black, because of the constraints between the elementary particles, there are steric effects which prevent them from reorganization in a compact shape, leading to more open structures and therefore to a lower percolation threshold. This observation confirms the importance of taking into account the shape of particles to explain the physical properties of the suspensions. The more an elementary cluster is fractal, the more it will build easily a percolating network in suspension, which notably impacts the mechanical or electrical properties. Thus, experimentally, in order to obtain a percolating network of carbon in suspension with a low amount of carbon, it is more suitable to use carbon blacks than spherical carbon particles. This is typically the case in the electrodes of chemical devices, where carbon is added as a conductive additive in a small quantity to build an electrical path. On the contrary, to have a concentrated suspension of carbon without percolation, for example, for preparing printing inks, spherical carbon particles should be selected.

5.2. Influence of the Interaction Potential. In the previous simulations, the well depth of the interaction potential was kept fixed at $\epsilon_a = 14$. In order to verify if this value has an influence on the results concerning the carbon blacks, further simulations were performed by changing ϵ_a . Two values, $\epsilon_a = 10$ and 18, were chosen. Since interactions between the carbon blacks are strongly attractive, lower values of ϵ_a are not considered here. Simulations were performed with the initial configurations used for the carbon black elementary clusters with elementary particles of $a_2 = 20$ nm and $N_c = 87$. Different concentrations were considered. Whatever the concentration used, results of simulations obtained with the new values of ϵ_a are very similar to the results obtained with $\epsilon_a = 14$. Figure 8 shows, for example, the kinetics of aggregation obtained at $\phi = 4\%$ for the different values of ϵ_a . Analyses of snapshots of simulations and of the percolation dimension confirmed that the value of ϵ_a has little influence on the results.

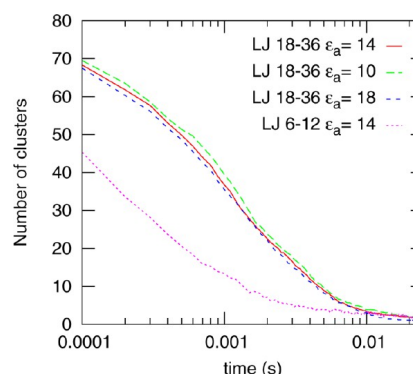


Figure 8. Number of clusters of at least 2 elementary particles as a function of time for carbon black with $a_2 = 20$ nm at $\phi = 4\%$ for different potentials of interaction: 18–36 Lennard–Jones potential with $\epsilon_a = 10, 14$, or 18 and a 6–12 Lennard–Jones potential with $\epsilon_a = 14$.

Nowadays, formulations of suspensions of carbon black are preferentially made with water for environmental purposes. It could be thus interesting to check the influence of the range of the interaction potential in our simulations. When carbon black is immersed in water, particles interact with hydrophobic interactions which are known to establish at longer range.²⁹ For that, simulations were performed with a 6–12 Lennard–Jones potential

$$U^{\text{LJ}}(r_{ij}) = 4\epsilon_a k_B T \left[\left(\frac{2a}{r_{ij}} \right)^{12} - \left(\frac{2a}{r_{ij}} \right)^6 \right] \quad (2)$$

with $\epsilon_a = 14$. This type of potential has already been used for modeling hydrophobic interactions.³⁰ Results of aggregation kinetics obtained at $\phi = 4\%$ for elementary clusters with particles of $a_2 = 20$ nm are reported in Figure 8. The number of clusters decreases faster with a 6–12 Lennard–Jones potential (LJ 6–12) than with a 18–36 Lennard–Jones potential (LJ 18–36), which means that aggregation is accelerated. This tendency is also observed for lower values of concentration ϕ . At $t = 0.025$ s, Figure 8 shows that only one cluster is present in the different simulations so that aggregation is finished. Both with LJ 18–36 and with LJ 6–12 percolation is observed. Snapshots of simulations at $t = 0.025$ s also show that clusters obtained with LJ 6–12 seem more compact than with LJ 18–36 (see Figure 9). To quantify this phenomenon, the average number of contacts between particles belonging to different elementary clusters at $t = 0.025$ s are calculated. For the LJ 6–12 potential, an average of 904.2 particles belonging to different elementary clusters is in contact instead of 627.8 for the LJ 18–36 potential.

This result could be explained by the fact that the LJ 6–12 potential, having a longer range, forces a higher state of reorganization of the clusters. The clusters reorganize to increase the number of contacts between particles, thus decreasing their potential energy. Moreover, the energy landscape of the potential with longer range is smoother than that of the short-range potential, and this accelerates the reorganization kinetics. Considering that the viscosity of water and PC are close ($\eta = 10^{-3}$ and 2.5×10^{-3} Pa s for water and PC, respectively), the results of our simulations could be correlated to experimental results obtained in suspensions with

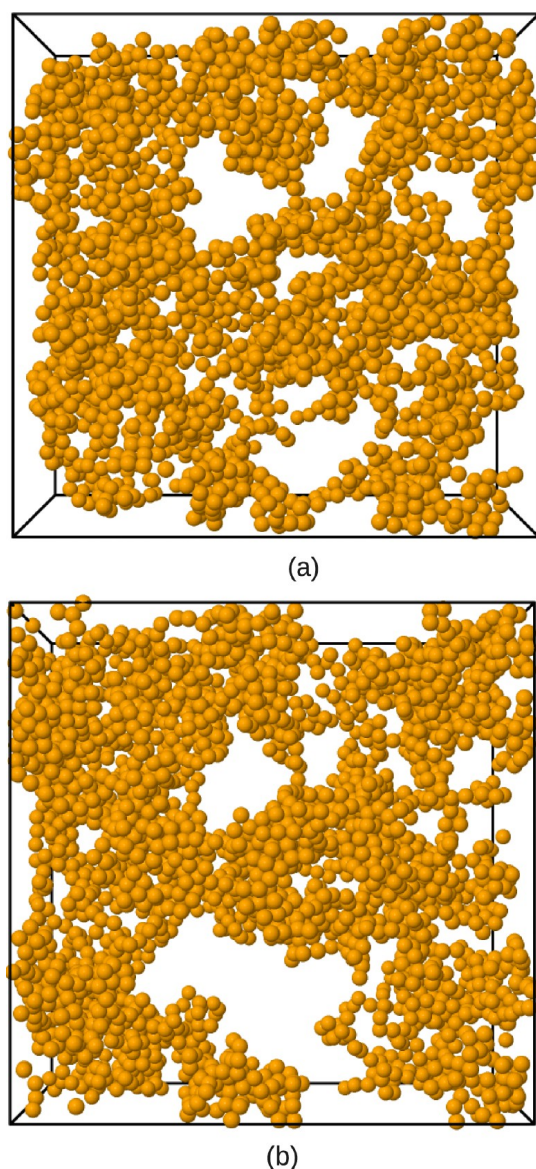


Figure 9. Snapshots of simulations at $t = 0.025$ s obtained at $\phi = 4\%$ with particles of $a_2 = 20$ nm: (a) LJ 18–36 and (b) LJ 6–12 (volume of box $\approx 2.4 \mu\text{m}^3$).

C45 carbon black in water. Rheological frequency sweep measurements performed on C45 carbon black suspensions indeed always show that G' and so the plateau modulus G_0 is higher for aqueous suspensions than for suspensions prepared in PC. At $\phi = 4\%$, it is found in water $G_0 = 13.9$ kPa and in PC $G_0 = 3.3$ kPa. Since G' and G_0 can be correlated to the number of bonds in suspensions,^{17,31} this experimental result could suggest that for the same concentration of carbon black more bonds are present in aqueous suspensions.

6. CONCLUSION

Suspensions of carbon black and spherical carbon in propylene carbonate were studied experimentally and numerically. Particular attention was paid to the percolation properties.

Specific Brownian dynamics simulations were developed by introducing constraints between elementary particles in order to take into account the specific shapes of carbon black in suspensions. Our experimental and numerical results are qualitatively in good agreement, suggesting that the simple model used here is sufficient to reproduce the main features of real suspensions and shed light on the elementary aggregation mechanisms.

Both experimentally and numerically, percolation was demonstrated to appear at lower concentrations for carbon black than for spherical particles. This could be explained by the different ease of the clusters to reorganize in the different cases. When particles are spherical they can rearrange rather easily to form more compact clusters. This gives a higher percolation threshold. Because of the shape of carbon black, reorganization is much more difficult, which leads to an open structure, with the consequence that percolation is obtained with a lower percentage of carbon. All results confirm the importance of taking into account the shape of carbon elementary clusters to explain the mechanical and electrical properties of suspensions, both in experiments and in simulation. According to our results, spherical hydrothermal carbon is more suitable than carbon black to prepare concentrated carbon suspensions without percolation of particles. However, to prepare suspensions in which percolation is achieved with a low amount of carbon, carbon blacks should be preferred. In simulations, the influence of changes in the interaction depth and shape was also verified. It was found that the potential range has an important influence on the reorganization of clusters.

Because the structuration and percolation properties are crucial in determining the properties of electrodes in electrochemical devices such as lithium batteries, our modeling of carbon black opens new perspectives for the understanding of these complex systems. As a further development of this work, it would be interesting to introduce other components in the simulations such as the active materials particles and polymers, in order to have a more realistic composition of electrode inks. Moreover, since in practical applications the electrochemical devices are operating under varying potentials, introducing an external potential in the simulations would be relevant to take into account the movement of particles induced by this field. This will be the subject of further simulation studies.

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Notes

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