SC5236, ID02 – Resume of experiments conducted on carbon black suspension in march 2022

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September 2022

1 Introduction

When attractive forces are present, colloidal suspensions are unstable and aggregate into ”floc” or ”clusters” [9]. Because of the weak and reversible interactions between colloids, the structure of clusters varies depending on the shear rate and shear history. Such dynamic structure leads to a diversity of rheological behaviors including shear thinning, thixotropic recovery or the presence of a yield stress, that are responsible of the functional use of colloidal suspensions in our everyday life.

The structural changes may occur over a broad range of length scales, ranging from colloid particles to percolated networks. In the limit of strong colloid attraction and low volume fraction, fractal approaches have been widely used to relate the structure and the rheology of suspensions, either in the liquid or gel state, and numerous models can be found in the literature [15, 19]. However, a general understanding of the interplay between structure and rheology is still lacking. Recently, it was shown that the mechanical properties of carbon black (CB) gels at a fixed volume fraction could be tuned by varying the shear history, leading to different gel structures [3]. The authors proposed an original scenario were clusters interpenetrates at low shear rate, increasing the elasticity of the gel after flow cessation. On a theoretical basis, some authors have also suggested the existence of double fractal structures [1], providing new insights to interpret micro-structural data of colloidal suspensions.

In the present study, rheometric tests coupled with small angle scattering (SAXS) experiments were conducted on CB suspensions in mineral oil, as reported in [3]. This system has been extensively studied as a model for yield stress fluids [17, 10, 5, 6, 11] and is especially convenient as it does not dry and is chemically inert, allowing for long time analysis and reproducible measurements. The objective was to determine if characteristics of gels structure reported in [3] could be observed under flow and more generally, to relate the structure of CB suspensions with their rheological properties. Rheo-SAXS measurements were conducted over 3 rheological tests, namely flow curve, flow cessation and flow step down. Flow cessation data have not been analyzed yet. The following sections report on the results of the flow step down and flow curve tests.

2 Results

2.1 Flow step down

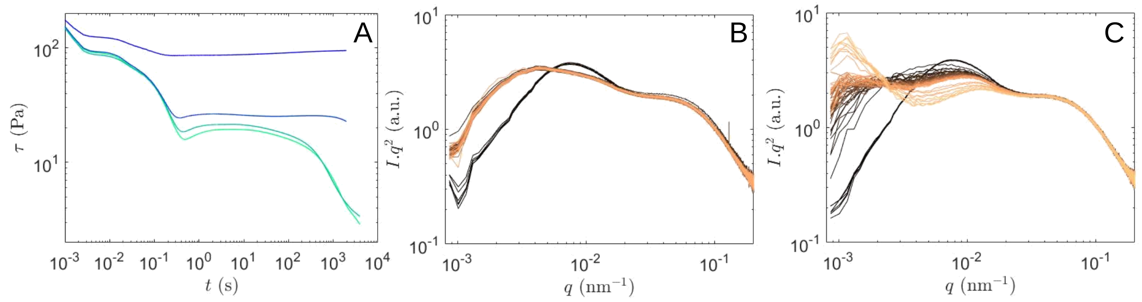

Figure 1: (A) Stress response of carbon black suspension (8 % w/w) after a step down in shear rate from $\dot{\gamma} = 500\ s^{-1}$ to 100, 10, 1 and 0.5 s^{-1} (top to bottom on the graph). (B-C) Krakty plot of the scattered intensity $I.q^2$ as function of the scattering angle q after a step down of shear rate from 500 s^{-1} to (A) 100 s^{-1} and (B) 0.5 s^{-1}. The color of curves indicates the temporal evolution and goes from dark to light orange

A flow step down is rheological experiment that consists a step down in shear rate from a high shear rate to a lower shear rate. Wang and Ewoldt have recently reported on the transient dynamics of CB suspensions during flow step down tests [18]. At low final shear rate ($\dot{\gamma} < 5\ s^{-1}$) CB suspension showed thixotropic stress recovery followed by anti-thixotropy. Using orthogonal superposition rheometry, the authors proposed that the anti-thixotropic evolution of the stress involved a shear induced restructuring of the suspension. In this study, we aimed to provide direct characterization of the structure of CB suspension during flow step down tests and to further investigate the anti-thixotropic behavior reported in [18].

Flow step down tests have been performed on 8 % (w/w) CB suspension from an initial shear rate $\dot{\gamma} = 500\ s^{-1}$ down to $\dot{\gamma}_0 = 100$, 10, 1 and 0.5 s^{-1} (Figure 1A). As reported in [18], an anti-thixotropic decrease of the stress was observed at low shear rate. The radially averaged intensity measured during flow step down is displayed in Kratky representation for $\dot{\gamma}_0 = 100$ and 0.5 s^{-1} on Figure 1B and C, respectively. The first bump at $q \sim 10^{-1}$ nm^{-1} have been attributed to the carbon black particles while bumps at higher q values resulted from the structuring of these particles [6, 3].

For $\dot{\gamma}_0 = 100\ s^{-1}$ a steady state was rapidly reached (Figure 1A). The second bump at $q \sim 10^{-2}$ nm^{-1} indicates that the suspension consisted of a single population of clusters, whose size quickly increased after flow step down (Figure 1B). For $\dot{\gamma}_0 = 0.5\ s^{-1}$, no steady state was achieved and the stress showed a non-monotonic evolution of the stress with time (Figure 1A). From SAXS data (Figure 1C), the scattered intensity displayed 2 bumps at low q values ($q \sim 10^{-2}$ and $q \sim 10^{-3}$ nm^{-1}) as observed in [3]. It was suggested that the shear-induced restructuring process responsible for the anti-thixotropic behavior was anisotropic [18], but we observed no anisotropy in all the SAXS data, i.e. over a scale range comprised between ∼30 nm and 6 μm. The excess of scattering intensity at $q \sim 10^{-3}$ nm^{-1} suggests the formation of an interface in the gap of the geometry. It may correspond to the formation of dense structures as proposed by [18]. However, it was well described using rheological measurements coupled to ultra sonic velocimetry (USV) that the flow of yield stress fluids at low shear rate is possibly heterogeneous [4, 12]. Using the setup reported [12], we found that the flow involved shear banding and slipping at the walls for $\dot{\gamma}_0 = 1$ and 0.5 s^{-1} (data not shown). The occurrence of such heterogeneities during flow strongly depends on the dimensions of the geometry. Thus, we aim to perform the rheo-USV measurements using the same Couette geometry used for rheo-SAXS measurements at the European Synchotron Radiation Facility. The geometry, that has to be made of plexglass as required for rheo-USV measurements, is currently being manufactured. An extensive characterization of the local flow is thus required before further analysis of the SAXS data during flow step down tests.

2.2 Flow curve

Flow curves measurements are standard rheological tests to assess the stress dependence of suspensions over a broad range of shear rate and to determine the dynamic yield stress. The structure of carbon black suspension along flow curves was characterized by the group of Wagner using small angle neutron scattering [6, 7]. They provided an extensive analysis of the scattering data but they did not used the structural parameters to model the shear rate dependence of the stress. Kim and Koo have modeled the flow curve of carbon black suspension using by means of fractal models and the calculation of an effective volume fraction [8]. However, their structural parameters were obtained from rheometric tests only. In the present study, we aimed to relate the rheometric and SAXS data by appropriate models and to provide a general understanding between the structure and rheology of carbon black suspensions.

Flow curves were performed on 1.5, 3 and 8 % (w/w) carbon black suspension in oil from $\dot{\gamma} = 10^3$ to 10^{-2} s^{-1} (10 points per decade), allowing 1 s of step time between each point (Figure 2A). A typical evolution of the scattered intensity $I(q)$ with the shear rate is displayed on Figure 2B and Figure 3. Data were fitted using a 2 levels Beaucage model, to account for carbon black particles and the fractal

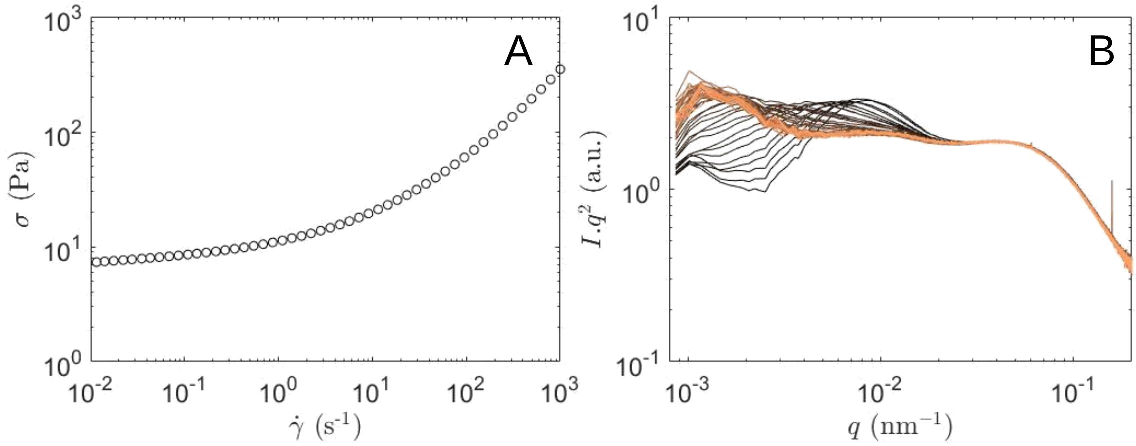

Figure 2: (A) Flow curve of a 8 % (w/w) carbon black suspension performed from 10^3 to 10^{-2} s^{-1} with $\Delta t = 1$ s between each point. (B) Kratky plot of the scattered intensity associated with each point of the flow curve. The color of curves indicates the temporal evolution and goes from dark to light orange

clusters. Fit parameters, i.e. the cluster size ξ and their fractal dimension d_f are displayed on Figure 4A&B. Figure 4A shows a power law increase of the cluster size with a decrease of the shear rate $\xi \propto \dot{\gamma}^{-m}$ with $m = 0.5$. When $\xi > 10^3$ nm, the cluster size becomes too large to be probed by the SAXS set-up as evidence by the constant value of ξ for all CB concentration. As in [3] and during flow step down tests, an intermediate level of structure was observed (Figure 2B). Interestingly, the fractal dimension of clusters was constant but decreased with a decrease of the shear rate (Figure 4B). CB suspensions with various concentrations showed the same dependence regarding the cluster size and the their fractal dimension with the shear rate. It suggests that at high shear rate, clusters do not interact with each other and their size and structure is determined by the stress of the fluid.

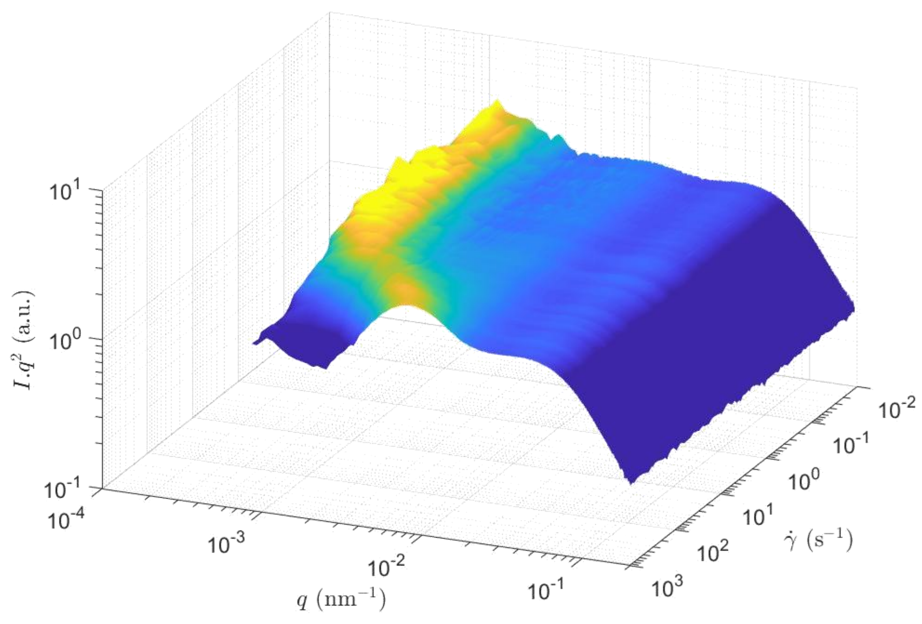

Figure 3: Evolution of the scattered intensity during the flow curve test. Data of Figure 2B are displayed as function of the shear rate

To relate micro-structural data to rheometric data, micro-structural models introduce an effective volume fraction of the fractal clusters ϕ_{eff} that is a function of the cluster size and fractal dimension $\phi_{eff} = \frac{\phi}{\left(\frac{\xi}{r_0}\right)^{d_f-3}}$ where r_0 and ϕ are the size and volume fraction of elementary carbon black particles, respectively [14, 13, 16]. The effective volume fraction have been related to the viscosity of the suspension using semi-empirical equation $\eta(\dot{\gamma}) = \eta_0 \times \left(1 - \frac{\phi_{eff}}{\phi_m}\right)^{-2}$ where η_0 is the medium viscosity and ϕ_m the maximum packing fraction. This approach allowed us to successfully model the initial part of the flow curve (i.e. at high shear rate) where the contribution of the stress is hydrodynamic (Figure 3C), i.e. down to a characteristic shear rate obtained from the three component model [2]. Indeed, this model attributed physical processes to the different parts of the flow curve. Ongoing analysis is now dedicated to model the elastic contribution to the stress as clusters start to percolate, in view of the double fractal model mentioned in the introduction [1] or the interpenetration model of [3]. Results about the flow curve analysis are expected to be submitted for publication by the end of the year.

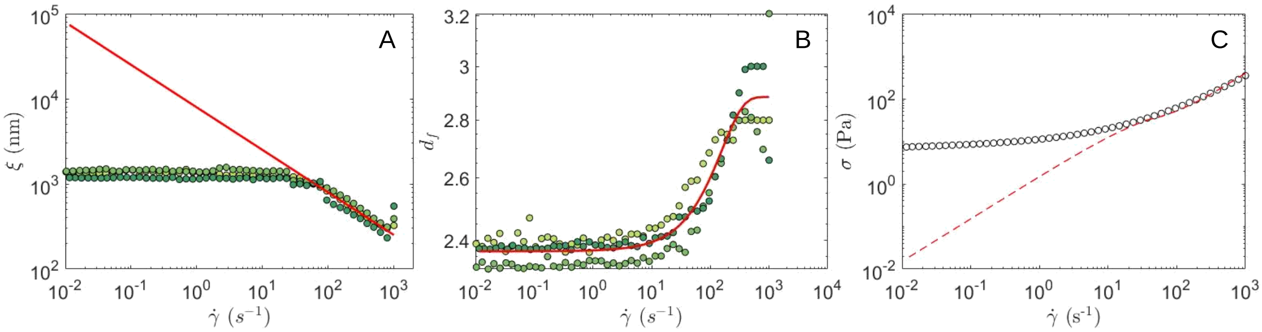

Figure 4: (A) Cluster size ξ and (B) their fractal dimension d_f displayed as function of the shear rate $\dot{\gamma}$ for 1.5, 3 and 8 % (w/w) carbon black suspension (from light to dark green, respectively). Structural parameters were obtained from fitting the SAXS data with a 2 levels Beaucage model. (C) Modeling of the hydrodynamic contribution of the stress (see text)

3 Conclusion

Dagès et al. have reported a 3 level structure for carbon black gels pre-sheared at low shear rate [3]. In this study, we found that carbon black suspensions during shear also displayed 3 structural levels at low shear rate, both during flow step down and flow curve tests. A careful assessment of the velocity gradient in the gap of the geometry is required for further analysis of the flow step down tests, but results have already shown valuable information in relation to the study of Wang and Ewoldt [18]. The modeling of the flow curve was based on concrete micro-structural data and will contribute to a better understanding of the rheology of CB suspensions.

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