Aggregates or Agglomerates?

Case study of Carbon Black Printex 90

The PowMaster particle analyzer is capable of measuring aggregate and agglomerate structures independently, when combined with a suitable sample pretreatment procedure. Here, we tested the Printex 90 carbon black (CB) produced by Orion Engineered Carbons. Printex 90 is a widely used reference material in toxicology studies, aerosol research and other fields.
Most studies do not address the difference between CB-aggregates and agglomerates, which severely limits the validity of the obtained results. Moreover, both terms are used interchangeably quite often. The structural differences are illustrated in Fig. 1.

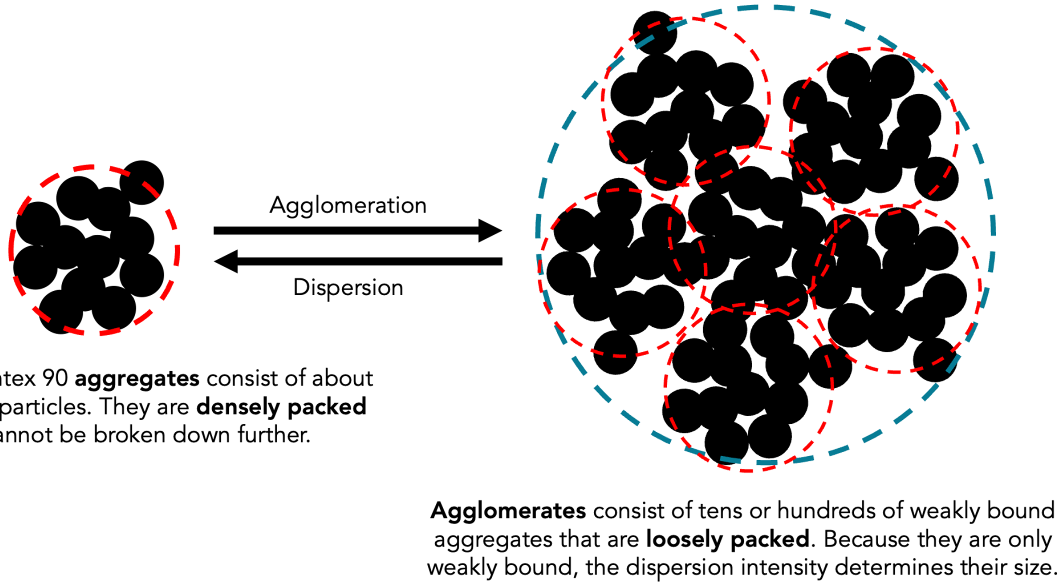

Figure 1: Differences between aggregates and agglomerates in size and structure.

Experimental procedure and results

To isolate aggregates (the smallest dispersible unit) from the Printex 90 powder, the material was suspended in iso-propanol, deagglomerated with ultrasound and spray-dispersed. To measure the agglomerated particles, a much less intense dry dispersion method with venturi nozzles was used. The then aerosolized particles were analyzed with the PowMaster system, which simultaneously measures **mass in femtograms and diameter in nanometers** at all points of the size distribution. From the measured mass and diameter, other parameters like particle packing densities, are calculated.

Table 1: Median values and characteristic parameters

Median values	Aggregates / Ultrasound dispersion 400 J/mL	Agglomerates / Dry-dispersion at different air pressures		
		5 bar	3 bar	1 bar
Mass m_{50}	0.138 fg	0.338 fg	0.705 fg	7.163 fg
Diameter d_{50}	64 nm	99 nm	132 nm	324 nm
Density $\rho_{part,50}$	1.00 g/cm³	0.66 g/cm³	0.59 g/cm³	0.40 g/cm³
Particles per gram	$4.2 \cdot 10^{15}$ g^{-1}	$6.6 \cdot 10^{13}$ g^{-1}	$1.9 \cdot 10^{13}$ g^{-1}	$3.1 \cdot 10^{12}$ g^{-1}
Mass-diameter correlation ($m = preF \cdot d^{Df}$)				
Pre-Factor preF	$9.55 \cdot 10^{-7}$ fg/nm³	$2.39 \cdot 10^{-6}$ fg/nm³		
Scaling exponent Df *(fractal dimension)*	2.86	2.58		

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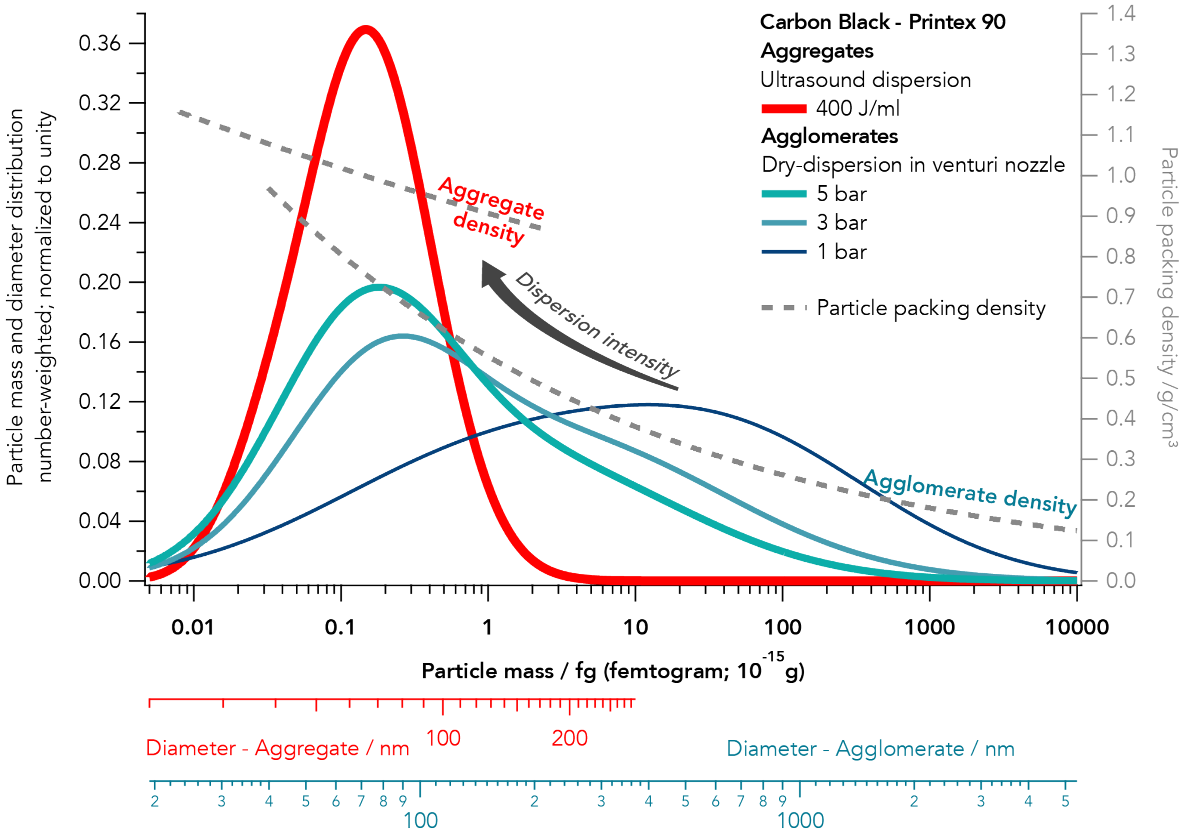

Figure 2: Number-weighted distributions of particle mass, diameter, and packing density for Printex 90 aggregates (left mode) and agglomerates (right mode).

In Fig. 2, the full mass and diameter distributions of Printex 90 aggregates and agglomerates are shown. The aggregates (red line) form very light and small particles (m_{50}: 0.138 fg; d_{50}: 64 nm) with a density that is significantly below the material density ($\rho_{part,50}$: 1.00 g/cm³; $\rho_{skeletal}$: 1.85 g/cm³). By comparing the mass of an aggregate $m_{Aggregate}$ with the calculated mass of a 14 nm primary particle m_{PP}, the degree of aggregation is obtained.

$$\text{degree of aggregation} = \frac{m_{Aggregate}}{m_{PP}}$$

At the median value m_{50}, **an aggregate consists of 52 primary particles**. Furthermore, integrating the number-weighted distribution over the particle mass gives an aggregate concentration in the powder. **One gram of Printex 90 contains $4.2 \cdot 10^{15}$ individual aggregates.**

The non-dispersed agglomerates are much heavier and larger. Their size distributions are also asymmetric, which is best explained by the coexistence of aggregates and agglomerates. Only for the lowest dispersion intensity of 1 bar (thin blue line), seemingly no isolated aggregates are present. This correlation between particle size and dispersion intensity varies across carbon black products and can be used to quantify the mechanical strength of agglomerates.

Packing density implications on particle size

Aggregates and agglomerates have in common that they are porous and open-structured. Therefore, the particle packing density (ρ_{part}) declines as the particle size increases. However, the rate at which ρ_{part} decreases is different. Here, it becomes clear why the mass is so useful for describing the particle size. The mass is independent of the particle shape, structure or composition.

Fractality of aggregates and agglomerates

A particle is defined by its mass and geometric dimensions (~diameter). For an ideal carbon black sphere, the particle mass m_{sphere} can be simply calculated from the diameter d and the material density of 1.85 g/cm³:

$$m_{sphere} = \frac{\pi}{6} \cdot 1.85 \frac{g}{cm^3} \cdot d^3$$

Printex 90 aggregates and agglomerates are neither spherical nor do they have a constant and defined density. Instead, their complex particle structure is described by the mass-diameter correlation and its fractality, which can be described as a power law between the measured masses and diameters:

$$m_{measured} = preF \cdot d_{measured}^{Df}$$

The pre-factor preF for an ideal carbon black sphere equals "$\pi/6 \cdot 1.85$ g/cm³ $\cdot 10^{-6}$ fg/nm³" and its scaling exponent Df is 3. Deviations from those values are due to more complex, open particle structures. In the context of carbon blacks, Df is also commonly referred to as the "fractal dimension". To better understand preF and Df, it is advantageous to calculate the particle packing density ρ_{part} from it:

$$\rho_{part} = \frac{m}{\frac{\pi}{6} \cdot d^3} = \frac{preF \cdot 6}{\pi} \cdot d^{Df-3}$$

In Fig. 3, the theoretical density curves are shown. For ideal spheres, ρ_{part} is constant as the Df is 3. For increasingly more complex structured and more open particles (Df < 3) , the ρ_{part} decrease with an increase in particle size. The more "open" the structure is, the more pronounced the decline ρ_{part} gets, which is equal an even lower Df.

When comparing the theoretical ρ_{part} curves with the measured curves (grey lines in Fig. 2), one can see that the aggregates have a higher ρ_{part} and higher Df of 2.86 which makes them more spherical than the more loosely packed agglomerates with a Df of 2.58. It is noteworthy that the density curve for the agglomerates is independent of the intensity of the dry dispersion. The correlation between mass, diameter and density can be considered as an intrinsic property of the Printex 90 agglomerates.

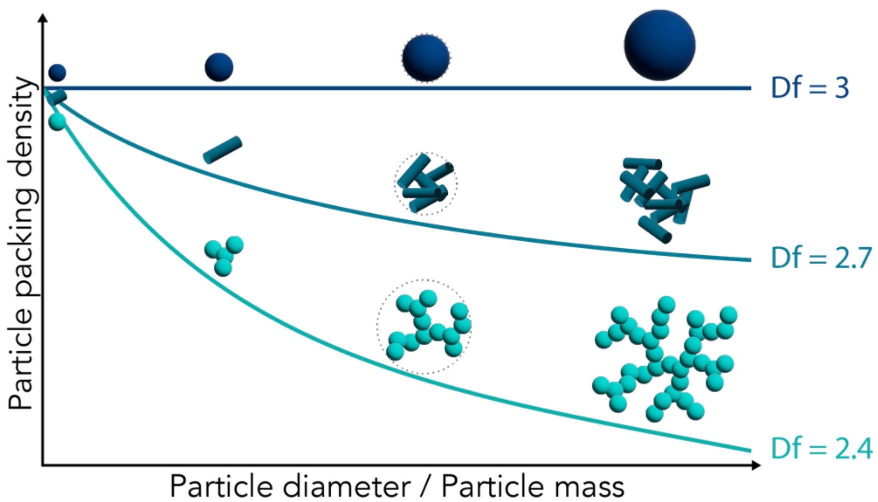

Figure 3: Illustration of the change in the particle packing density for different particle structures.

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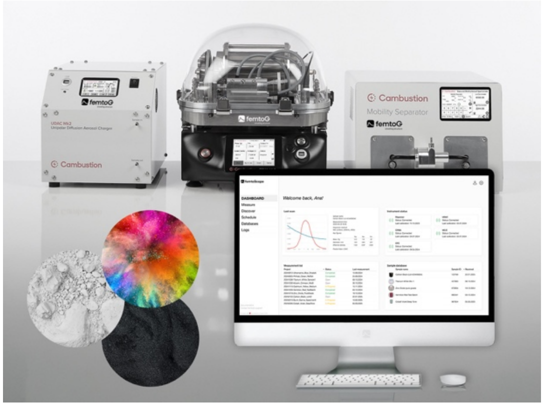

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