The use of mercury intrusion porosimetry for the determination of particle size distribution on nano-particles carbon black.

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Carbon black powder is a commonly used additive in rubber and tyre industries. This material is produced by combustion processes and it can be designed in terms of particle size and shape in order to fulfil the application requirements. The effect of carbon black in rubber is related to the type of required features. This can vary from a simple colouring of the rubber (like, for instance, in the shoe's soles) to the reinforcement of tyres for normal or special use. It is well known how the properties of tyres can influence the results of a Formula 1 race!

One of the main feature of a carbon black as rubber additive is the extreme small dimension of the particle size. In addition, other parameters to be controlled and that have an influence in the rubber properties are the particle shape and the surface roughness. A number of investigation methods can be used to determine the above parameters but, as we will see, depending on the small dimensions of the particles, some methods have a lot of limitations and difficulties.
The particle size for carbon black is usually ranging between 20 and 50 nm. Particles of this size are very much aggregated. The study of such small particles is critical with conventional methods for particle sizing. Wet methods like light scattering or laser scattering analysis, sedimentation, image analysis, etc. have an important limitation related to the technique resolution in term of size and, most critical, in the powder de-aggregation. All powders, depending on their surface properties (like roughness, surface charge, zeta potential, etc.) show a certain degree of aggregation. Aggregation leads to the formation of agglomerates of larger dimension. Agglomerates should be completely "dismounted" prior the experiment because the special properties of carbon black are mainly related to the real particle size rather than the agglomerate size. The process of de-aggregation of such small particles is quite complex if the analytical technique is based on a liquid carrier, like water. The use of tensile active agents (to reduce the surface charge) and ultra-sound sometimes don't provide an acceptable solution. Small particles can be identified and measured by the use of electron microscopy technique. Electron microscopy is a reliable method but it is almost impossible to be applied in the industry for quality assurance purposes, as required by most advanced industrial processes.

Three rapid and reliable analytical methods are available from Thermo Electron for the investigation of these types of materials, mercury pressure porosimetry (Pascal series), gas adsorption (Sorptomatic) and helium pycnometry (Pycnomatic ATC).

Some physical properties of nano-powders

Any solid material can be characterized in terms of pore size (intra or inter particle), particle size, surface area, envelope (or bulk) and real density. Depending on the above parameters the properties of a solid material can vary enormously. The specific surface area of a solid or a powder is measured in square meters per gram of dry sample and it is the total available surface of the solid in contact with the fluid (usually air) in which the material itself is immersed. The surface area depends mainly on three factors:

1. the pore size, whenever present (smaller the pores higher the surface)
2. the particle size, in case of powders (smaller the particles higher the surface)
3. the surface roughness

Whenever porosity is present, generally the second and third factors give a small contribution to the total surface area. But this is not the case of nano-particles because they are not porous, thus the surface area in this case is strongly related to the particles dimensions and the surface roughness.
The bulk density is the density of material when referring to the packed particles volume. Bulk density, therefore, encloses the void space between particles and the void volume contained inside the agglomerates. For a given material, the bulk density value is in direct relation with the aggregation degree of the powder. Finally, the real density is independent on the aggregation degree, being related to the real volume occupied by the material, excluding all inter and intra particle voids contained in the pores or in the agglomerates. For a given material, therefore, the real density is only related to the material purity (if all the porosity is accessible by the measuring gas).

Available techniques from Thermo Electron for the investigation of non porous nano-powders

Mercury Intrusion Porosimetry is a well know technique based on the property of a non-wetting liquid (like mercury) of not being adsorbed on the surface of solids or inside their pores. In this type of instruments, the sample is kept in a glass cell under vacuum conditions. Vacuum has a dual role, first to dry the material from the humidity adsorbed from the environment and second to fill the cell with mercury. At the end of preparation, the cell will contain only the material under test and mercury. In these conditions of very low pressure mercury cannot enter in the pores of a substance or, in case of powders, it surrounds completely the particles and agglomerates without entering in the inter-particles voids. At this stage it is easily possible to calculate the "envelope" sample volume, that is the material external volume comprehensive of all the pores and inter-particle voids. This leads to the calculation of the bulk (or envelope) density. The instrument then generates a controlled

pressurization of the system mercury plus sample. At a certain point mercury is forced to penetrate the sample porosity or the inter-particle voids, by breaking the agglomerates. The penetration pressure of mercury is inversely proportional to the pore and particles size according to two well known calculation models, the Washburn equation for the pore size and the Mayer-Stowe method for the particle size. MIP also provides information on the surface area of the material, considering the pores as cylindrical and the particles as spherical. Besides the approximation, there can be a good agreement between the area determined by MIP and gas adsorption technique. This latter method is the most commonly used to measure the specific surfaces. It is based on the principle that when a solid sample is kept at a very low temperature (usually the liquid nitrogen boiling temperature, 77K) it can adsorb on the surface gas molecules due to very light attraction forces that are present on the surface of any solid material. The most commonly used gas is nitrogen, despite any gas in principle might be used. The molecules adsorb on the surface and inside the pores in a multi-layer way. A number of calculation models (being the most popular of them the BET model) are available to determine from the adsorption uptake the monolayer volume that is the number of molecules adsorbed on the first layer. Knowing the dimension of a nitrogen molecule is then easy to calculate the total free surface of the material. The gas adsorption technique is more reliable than MIP for the specific surface determination because it is most of the times independent from the sample nature and from the pore shape and it is sensitive also to the surface roughness, particularly important in case of non-porous powders. Finally, the real density can be measured by means of helium pycnometry. Helium is formed by a very small mono-atomic molecule, which is able to penetrate even the narrowest pores. The instrument is thus capable of measuring with a very high precision the real volume occupied by the material in the environment, excluding all the open porosity. The determination of the real volume permits the calculation of the real density, one of the most important parameters to determine easily and rapidly (the measurement lasts not more than 15 minutes) the purity of virtually any solid material.

The case of carbon black nano-particles

As already mentioned, the determination of particle size and surface area is of special importance for carbon black for a number of applications. The size of particles, the degree of agglomeration and the surface roughness directly influences important parameters of, for instance, tyres, influencing the durability, the resistance to friction, the elastic property at high temperatures, etc. The following analysis examples are related to the characterization of a carbon black used in the tyres production.

Mercury intrusion porosimetry with Thermo Pascal porosimeter series

This type of characterization provides initially a curve like the one reported in figure 1. The intruded mercury volume is referred to the sample mass unit and it is plotted versus the applied pressure in Mpa. The figure 1 is typical of the intrusion of mercury into an aggregated powder. The first part of the curve, with an apparent continuous intrusion, is due to the de-agglomeration of the particles. This phenomenon proceeds until the particles are completely separated and packed. The steep part of the curve represents the mercury penetration, in case of carbon black nano-powder, in the inter-particle voids. The analysis proceeds up the maximum selected pressure, in this case 400Mpa.

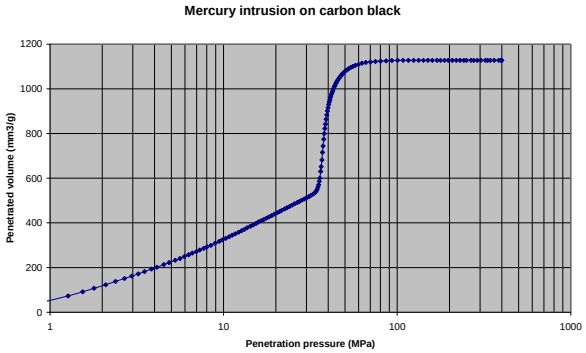

Figure 1 – Mercury intrusion curve on carbon black nano-powder

From the intrusion curve the Pascal porosimeter provides the following information on the sample:

Total cumulative volume (mm3/g) :	1127.22
Total specific surface area (m^2/g) :	105.1
Total porosity (%) :	58.97
Bulk density (g/cm3) :	0.523

Then by applying the Mayer-Stowe calculation model it is possible to compute the particle size directly from the intrusion pressure, then the particle percentage versus the particle size is easily represented.

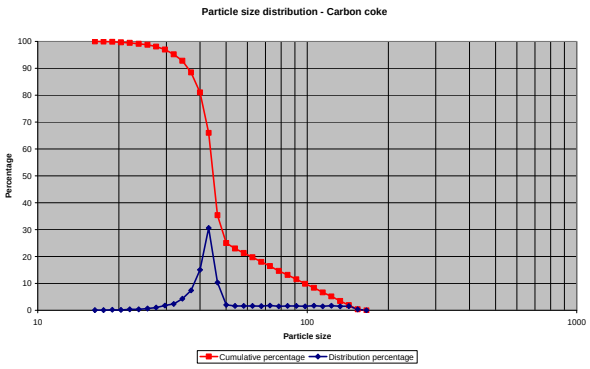

Figure 2 – Particle size distribution plot for carbon black nano-powder using kp=3,
contact angle=124°, hg surface tension=480 dyne/cm, real density=2 g/cc

Particle diameter range (nm)		Cumulative percentage (%)	Distribution percentage (%)	Specific surface area (m2/g)
159.8	148.2	0.37	0.37	0.1
148.2	137.5	1.95	1.57	0.6
137.5	127.6	3.45	1.5	1.2
127.6	118.4	5.17	1.72	1.9
118.4	109.9	6.67	1.5	2.5
109.9	101.9	8.39	1.72	3.3
101.9	94.6	9.89	1.5	4.0
94.6	87.7	11.54	1.65	4.8
87.7	81.4	13.18	1.65	5.8
81.4	75.5	14.68	1.5	6.7
75.5	70.1	16.48	1.8	7.9
70.1	65	18.05	1.57	9.0
65	60.3	19.7	1.65	10.2
60.3	56	21.35	1.65	11.6
56	51.9	23	1.65	13.0
51.9	48.2	25.02	2.02	15.0
48.2	44.7	35.36	10.34	25.7
44.7	41.5	65.99	30.64	59.4
41.5	38.5	81.05	15.06	77.2
38.5	35.7	88.46	7.42	86.7
35.7	33.1	92.81	4.34	92.7
33.1	30.8	95.21	2.4	96.2
30.8	28.5	97	1.8	99.1
28.5	26.5	98.05	1.05	100.9
26.5	24.6	98.73	0.67	102.2
24.6	22.8	99.1	0.37	102.9
22.8	21.1	99.48	0.37	103.7
21.1	19.6	99.63	0.15	104.1
19.6	18.2	99.85	0.22	104.6
18.2	16.9	99.93	0.07	104.8
16.9	15.7	100	0.07	105.1

The Pascal mercury porosimeters have carried out the above measurements in a total analysis time of about 90 minutes. The analysis, apart from the sample holder assembling and weighing operations, is performed in a complete unattended way. The particle size distribution result show that this powder features about 68% of the particles in a range between 33 and 48 nm with a peak at 43.1 nm. This result has been confirmed by electron microscopy. Pascal porosimeters also provide a measure of the specific surface area. This model is usually an approximation because it cannot detect the particles surface roughness and the particles are simply considered of spherical shape. But the main limitation of mercury porosimetry related to the determination of the surface area is due to the possible sample compression at high pressure. To overcome this issue or to confirm the results of porosimetry, a gas adsorption experiment was carried out on the sample by using the Thermo Sorptomatic Unit.

Gas adsorption tests on carbon black with Thermo Sorptomatic Unit

The Sorptomatic provides the curve represented in figure 3, named adsorption isotherm. In the isotherm the amount of nitrogen adsorbed per sample mass unit is plotted versus the relative pressure of adsorption, giving the following plot:

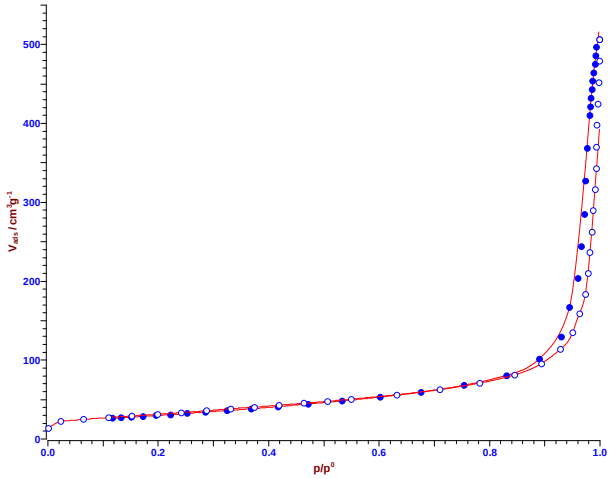

Figure 3 – Adsorption isotherm on carbon black

The amount of nitrogen adsorbed at the beginning of the isotherm, up to about 0.33 p/po, contains the monolayer uptake, from which it is possible to compute the total specific surface area, by applying the BET equation:

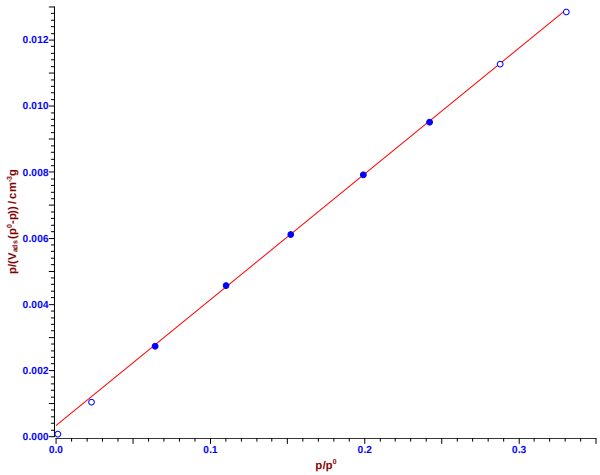

Figure 4 – BET plot for carbon black

The surface area measured with the Sorptomatic is about 113 m2/g and shows that the sample is formed by very small particles and that microporosity (0 to 2 nm size) is not present. The hysteresis and the capillary condensation at high relative pressures is occurring in the porosity between the particles, therefore also mesopores (from 2 to 50 nm) are not present in the

particles themselves, that is the surface area is controlled only by the external surface of the small particles and their roughness. The BET surface area is slightly larger than the one measured by mercury porosimetry, but this is understandable (and usual) because porosimetry cannot determine the surface roughness and uses a more simplified calculation model.

Last test with Thermo Pycnomatic ATC for real density determination

Finally, the sample was tested using the Thermo Pycnomatic ATC to measure the real density of carbon black. The sample was degassed in an oven at 120°C during 1 hour to dry it. The results are confirming the density of pure carbon:

Test #	Density (g/cc)	Standard Deviation (g/cc)
1	1.9992	+/- 0.0028
2	1.9997	+/- 0.0019
3	2.0001	+/- 0.0008

Average value
1.9996 g/cc (average on 3 tests)
+/- 0.0005 g/cc (standard deviation on 3 tests)
+/- 0.02 %

Conclusions

A number of industries both producing carbon black and purchasing for the rubber and tyre manufacturers have chosen Thermo Electro as the instrument supplier. The main feature of the Pascal porosimeter and Pycnomatic ATC are related to the high degree of accuracy combined with speed of analysis. In addition, the ease of use is an important added value from our products as often required in the quality assurance labs. Mercury porosimetry is therefore a valid alternative if not essential, for the rapid and reliable determination of nano-particle size distribution, as other most common methods for powder sizing fail due to the very small size or sample preparation issues. In case of mercury porosimetry, the sample prep is limited to drying the material prior to the experiment for proper weighing. Whenever required, Sorptomatic for surface area determination provides additional information related to the carbon black characterization.

Instrument presentation – Pascal Mercury Porosimeters

The **Pascal 140** has a dual role: it prepares the sample and the dilatometer for the analysis and carries out low pressure porosimetry measurements.
Operations are done automatically thus freeing the operator for other tasks. Thanks to its modular concept, it can be used by itself or together with other Pascal porosimeters, thus modularity of the Pascal system features “buy what you need” approach. Data from the low pressure intrusion can be combined with data from the other high pressure modules (240 or 440) to get a complete porosity spectrum of the sample.

The **Pascal 240** and **Pascal 440** high pressure porosimeters take over where the Pascal 140 leaves off to measure pores down to the lower mesopore region. They incorporate a new pressurization system, developed to meet the sophisticated analytical requirements of laboratories working with modern materials. The pressurization system uses a reversible pump operating continuously, which permits a perfect control in increasing/decreasing the pressurization speed, and a new type of pressure multiplier. The key features of this system are the extremely high maximum speed of pressurization and the immediate acceleration or deceleration response permitting the optimal application of the Pascal system during the analysis. The easy-to-use control panel with liquid crystal display permits the unit to be operated also without a PC. It lets the operator program the analysis or the calibration and provides a useful guide to operate correctly. It shows the analysis status in real time and indicates incorrect operations by means of error messages. The Pascal 240 porosimeter operates up to the maximum pressure of 200 MPa. Its large autoclave together with the special electrode system makes it an extremely versatile porosimeter as it can measure a wide range of solid materials: homogeneous, heterogeneous, low and high porosity. The accuracy

and reproducibility are the utmost thanks to the proprietary Pascal system. The Pascal 440 is not only the highest pressure model but it also offers the highest speed of the series. It reaches its maximum pressure of 400 MPa in the same time as the Pascal 240 reaches its maximum of 200 MPa. It is particularly suited for ceramics, sintered metals, very hard materials or nano-particles size determination and, in general, for all the solids which have a porosity approaching the micropore region. Thanks to its high pressurization speed, it is highly recommended in QA labs where short run times and productivity are the priorities combined with ease of use.

Pycnomatic ATC, the unique real density analyzer with built-in temperature control

Pycnomatic is the ultimate development for density measurement of solid materials and powders available from Thermo. Based on the technique of gas displacement to measure real density of solids and powders, Pycnomatic delivers unrivalled fast and accurate results. Once the sample is placed in the analysis chamber, the Pycnomatic completes the experiment in a matter of minutes and prints out the results completely unattended or transfer to a pc in electronic format. Pycnomatic can also perform repeat analyses and use them for statistical data evaluation.