

Nano-particle Characterisation: A Cautionary Tale

Introduction

Intertek MSG is using its specialised instrumentation to do some in-depth characterisation of commercially-available dispersions of nano-particles and also of filled polymer systems.

The aim is to help producers and potential end users by supplying them with accurate information to support their development projects. This might range from knowing an accurate particle size distribution of a nano particulate material that is being bought in or manufactured, right through to assessing the property benefits of a polymer filled with such a nano particulate filler.

On paper analysis might appear to be quite straightforward but in practice cross validation of measurements using a number of techniques is crucial in obtaining a full and accurate picture of material characteristics.

There are many tools available for looking at particle size distribution (PSD) of particulates, each with its own pros and cons. MSG has a good range of these and has employed them to evaluate a number of randomly selected nano particulate products that are available commercially. This note describes the analysis of just one of them.

Particle size distribution (PSD) information can be obtained by Intertek MSG using the following techniques:

- Traditional laser diffraction
- PCCS (Photon Cross Correlation Spectroscopy)
- SEM/TEM to generate images, with image analysis of them for quantification of diameters
- BET surface area
- XRD
- Disc Centrifuge (instrument due to be delivered)

The material obtained commercially was said to be alumina (Al_2O_3) and the nominal data on its composition and particle size is given below

Table 1: Nominal Data provided by the supplier

Material description	Molecular Formula given	Particle Size by BET (nm)	Particle Size by XRD (nm)	Dispersant
5% aluminium oxide dispersion in water	Al_2O_3	<50 nm	<25 nm	None

Even from this supplied data one can see that the particle size information obtained is dependent on the exact method employed. The aim of this work was to build up as full a picture of the material as possible from the wide range of methods that MSG has available. The full findings will be presented as a poster at NanoMaterials 08 in Newcastle 7-9th July (see link for more details). Although a number of different materials were obtained just one material is discussed here and that is the sample that produced perhaps the most surprising results.

Studies on the Dispersion

This first stage of analysis involved comparing the data obtained using the laser diffraction method with PCCS.

Laser Diffraction is unable to detect particles with diameters less than about 40-50 nm (using our instrumentation) so if all particles were indeed less than 25 or 50 nm then nothing would be seen using this approach. The data obtained is given below.

Fig 1a: PCCS

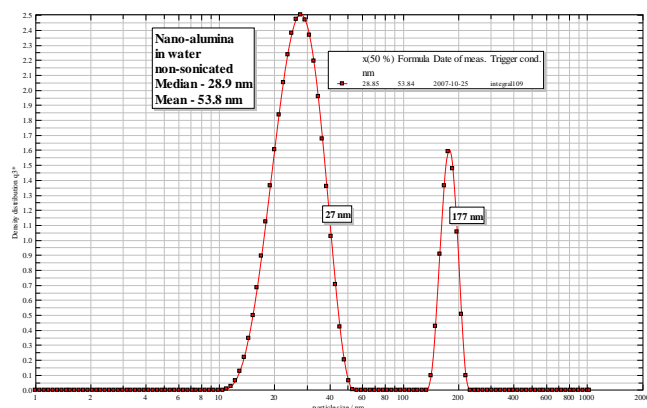
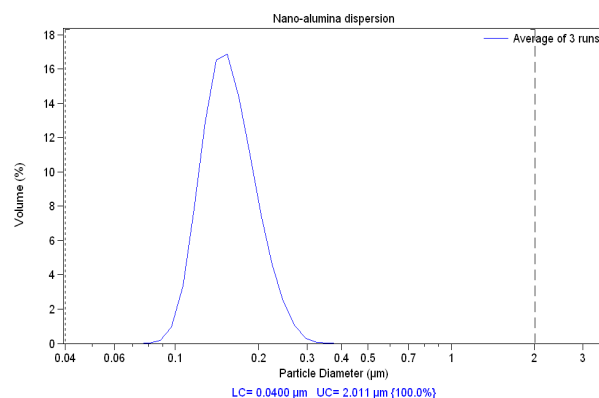


Fig 1b: Laser Diffraction



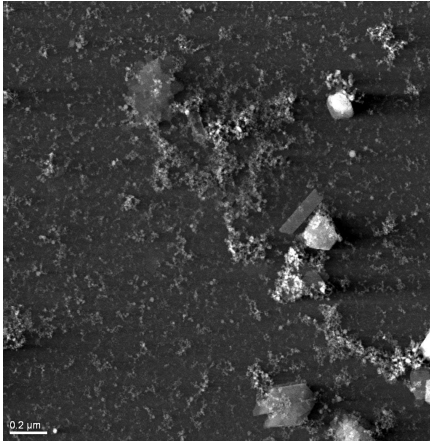
PCCS clearly suggests that there are large quantities of material with a diameter less than 50 nm which laser diffraction, as expected, just does not see. Both indicate however that there is, unexpectedly, material with a diameter of greater than 100 nm.

Studies on the Dry Powder

Imaging is a powerful method of confirming the presence of species in mixtures so SEM and TEM were employed on this alumina dispersion. Only SEM is reported here. The SEM confirmed the presence of a significant proportion of large particles, greater than 100 nm in diameter. In addition, it appeared there

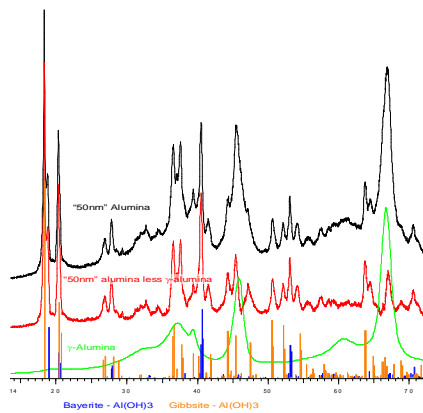
might be at least two if not three different crystal forms of the material present as seen in the large 'cubic' structures, the more plate-like ones and the very fine material in the background.

Figure 2: SEM of Dried Dispersion



Following this work it was decided to use XRD to reveal compositional information to complement the above micrographs and also to provide its' own information on crystallite size:

Figure 3: XRD Traces



The XRD showed that there were in fact 3 different crystal phases and these were assigned as:

Gamma-alumina - 68% by mass
Gibbsite - 19%
Bayerite - 13%

Both Gibbsite and Bayerite are in fact aluminium hydroxide $\text{Al}(\text{OH})_3$ not oxide adding to the picture that the material chemically is not as described by the supplier.

Gamma-alumina is always a high surface area material and therefore probably contributes most of the measured $133 \text{ m}^2\text{g}^{-1}$ nitrogen surface area. This surface area is equivalent to having 12 nm spheres if all the particles are this shape and are the same size.

This brings us to an important distinction in particle sizing: XRD measures the ultimate particle size (often termed crystallite size) of a phase and these can be much smaller than the size of dispersed particles in a fluid. In fact the dispersed particles are sometimes clusters of crystallites. It is very important for a developer to know which 'size' is relevant in the application of interest and it is easy to be misled by the various 'sizes' that can be measured.

A summary of the findings are in table 2 below

Table 2

Technique	Technique Results	Other Comments
PCCS	Peaks observed at 27 nm and 177 nm	Mean by volume is 53.8 nm
Laser Diffraction	Any material present at < 50 nm is unanalysed A peak is seen at about 155 nm	Range of size is 85 to 325 nm
Microscopy	Sub-50 nm material is present as are large cubic particles 150-200nm in diameter plus 'lath-like' large particles	TEM data will be reported later
XRD	Gibbsite and bayerite species have a wide size distribution but their mean sizes are calculated as follows: Gibbsite - 52 nm; Bayerite - 31 nm	Gamma alumina is expected to very small particle size
Surface Area	Nitrogen surface area $133 \text{ m}^2\text{g}^{-1}$.	12 nm diameter uniform spheres would give this value

Is it what it says on the tin?

The aim of this work had been to apply a range of techniques available via the NanoCentral hub in order to demonstrate the power (and sometimes the necessity) of using a multi-technique approach. The discovery that the material supplied is in fact not just an oxide but contains three phases of materials (two of which are hydroxide) is surprising but underlines the necessity for detailed analysis. Furthermore, the fact that the dispersion also contains particles with sizes significantly greater than 50 nm suggests reinforces this conclusion.

Knowledge of the detailed size distribution and the composition of a nano-material could be crucial in achieving the property enhancement desired by end users.

The good news

For manufacturers of nano-materials the good news is that there is a range of techniques available that can help characterise final products. This means that a well-defined, quality product can be developed, refined and monitored for delivery to customers and that the techniques needed to do this are available through the NanoCentral hub.

For the potential user of these materials it is clear that some analysis of what is being delivered can be important and this is available via NanoCentral. Further, it is clear that monitoring the end properties of the product (including degree of dispersion etc...) may be essential to arriving at a consistent final product.