PARTICLE SIZE CHARACTERIZATION: COMPARISON OF LASER DIFRACTION (LD) AND SCANNING ELECTRON MICROSCOPY (SEM)

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ABSTRACT

Two of the most significant properties of particles are size and shape; they often have direct influence on the materials behavior. Since the particulate systems are constituted by 3D particles of different size, the characterization of this property has to be given by a particle size distribution (PSD). Among the most popular techniques for PSDs measurement, the image analysis (IA) presents some disadvantages: sampling errors, the analysis of only hundred or a few thousand particles to represent the whole population, the use a 2-D projected image of a 3-D particle and long analysis times. In contrast, the laser diffraction technique allows fast particulate systems characterization, processes a high number of particles per assay and provides highly reproducible results. However, LD provides no details about the particle morphology. Both techniques can be considered complementary, however several data interpretation problems appear when the results are compared. To do so, it is necessary to understand the meaning of the size descriptors given by each technique and under which conditions the comparison of results from different size analyzers can be done. In this sense, this work explores first the number of particles required to obtain reproducible PSDs by SEM. Then, it presents a comprehensive characterization of PVC particles by assessing a set of size and shape descriptors. The PSDs obtained by IA-SEM and LD were mathematically transformed to be compared. Finally, IA-SEM data was used to evaluate the convenience of using more than one size descriptor to represent the particles volume.

Keywords: Laser Diffraction Analyser, SEM, particle characterization.

CARACTERIZACIÓN DE TAMAÑOS DE PARTÍCULA: COMPARACIÓN ENTRE DIFRACCIÓN LASER (LD) Y MICROSCOPÍA ELECTRÓNICA DE BARRIDO (SEM)

RESUMEN

El tamaño y la forma son propiedades muy importantes de las partículas por su influencia directa sobre el comportamiento de los materiales. Dado que los sistemas particulados están constituidos por partículas 3D de diferentes tamaños, ellos deben ser caracterizados por distribuciones de tamaño de partículas (PSDs). Entre las técnicas más populares para establecer PSDs, el análisis por imágenes (IA) presenta algunas desventajas: es muy sensible a la técnica de muestreo, se evalúa sólo cientos o unos pocos miles de partículas para representar a toda la población, se utilizan imágenes proyectadas 2D para representar partículas 3D y se requiere de largos tiempos de análisis. En contraste, la técnica de LD permite la caracterización rápida de sistemas particulados, se procesa un gran número de partículas por ensayo y proporciona resultados altamente reproducibles. Sin embargo, la LD no proporciona detalles sobre la morfología de las partículas. Ambas técnicas pueden considerarse complementarias, sin embargo, suelen surgir problemas de interpretación cuando los resultados son cotejados. Para una apropiada comparación, es necesario entender el significado de los descriptores de tamaño determinados por cada técnica y bajo qué condiciones puede realizarse. Este trabajo explora el número de partículas necesarias para obtener PSD reproducibles por SEM. A continuación, se presenta una caracterización exhaustiva de partículas de PVC mediante la evaluación de un conjunto de descriptores de forma y tamaño. PSDs obtenidas por IA-SEM y LD se transforman matemáticamente para su comparación. Por último, los datos IA-SEM se utilizan para evaluar la conveniencia de usar más de un descriptor de tamaño para representar el volumen de las partículas.

Palabras claves: Difracción Laser, SEM, caracterización de partículas.

INTRODUCTION

The irregular shape of the particle presents a problem in particle size analyses. Sphere is the particle shape which size can be described by a single number (diameter). Equivalent particle sizes are therefore required to represent irregular particle sizes and the particle size distributions [1, 2].

In the late 1940's, Heywood [3] reported the results of particle sizing as being "somewhat dependent on the physical principles employed and the assumptions or conventions involved". He indicated that the available techniques those days were "only able to measure and classify particles if the particles under test were imagined as spheres having some property equivalent to the test material". Essentially, things are very similar today [4] and the particle size distribution of a system constituted by irregular particles obtained from different techniques are still difficult to understand and even more to compare.

There are many techniques to evaluate particle size distributions. This work is particularly focused on understanding the output results given by image analysis (particularly SEM) and LD.

SEM is a powerful technique for observation and characterization of surfaces materials on a micro area. Topographic characteristics are viewed from above but there is little indication of particles height, basically the particles are observed as 2D objects.

In order to register details of interest digital images are acquired from SEM. Contrast, focus, SEM operations conditions (accelerating voltage, working distance, magnification, spot size, apertures, tilt, etc) and image resolution will determine the quality of images [5]. Depending on the particles shape and the detector location, the images may show different contrast requiring image processing and analysis. These are different digital image operations. Image processing turns one image into another (filters application) that can be used for IA. Images analysis from SEM involves the quantification of particle shape and size descriptors from the 2D particles image (e.g., circularity, convexity, equivalent diameters, projected areas, perimeters, etc.) [6].

For particle size characterization an adequate number of SEM images have to be processed by using appropriate software. To finally traduce the pixels to a reference length, an image calibration has to be done before image analysis.

The LD technique is based on the optical properties of the particles. Particle suspension flows through the beam of laser light and the scattered light is collected by the photo detectors [7]. The particle size affects to the angle of scattering and also to the intensity of scattered light. Small particles scatter the low intensity light at wide angles and large particles scatter the high intensity light at narrow angles. To provide a PSD the scattered light distribution is processed and compared to the scattering models. In the case of laser diffraction, the particles under test are imagined as spheres that scatter light in the same manner as do the particles of the test material.

Considering this assumption, it is possible to traduce intensities to particle volumes, for this reason LD is known as volume-based technique [8].

Laser diffraction represents a rapid, robust method for measuring the bulk properties of powders, emulsions and suspensions. It is an ensemble technique that measures millions of particles during any measurement. In contrast, IA offers a high-resolution technique for particle characterization, and multiple size and shape parameters can be extracted for single particles. As imaging is a number based technique, it is very sensitive to the presence of fine particles which are often in significant numbers. Table 1 compares the IA and LD techniques [8].

Techniques for particle size analyses measure different dimensions of the particle and the results are not directly comparable when irregular particles are studied. This work explores the conversions of PSDs and possible strategies for comparison of data obtained from different techniques.

Table 1. Comparison of IA and LD techniques. [8]

IA	LD
Provides number distributions	Provides volume distributions
High sensitivity to small particles	High sensitivity to over-sized material
Specific particle properties	Bulk material properties
Resolves precise morphological information	Resolves broad size distributions
Presents detailed sample information	Provides rapid particle characterization
Research and diagnostic tool	Routine sample analysis tool
High resolution and sensitivity	Robust, reproducible measurements
Samples: small amount of material	Samples:relatively large amount of material

MATERIALS AND METHODS

The powder used in the present study was Polyvinyl Chloride (PVC) resin. Prior the IA-SEM and LD assays, the material was sieved, the mass fraction between 105-149 µm (-100 +140 ASTM Mesh) was reserved for analyses.

For the IA by SEM, the PVC particles were dispersed over 3M ® aluminium conductive tape sticked onto stubs by using an air flow. Samples were coated with gold in a sputter coater SPI, and observed in a LEO 40X-VP Scanning Electron Microscope, operated at 10 kV. Topographical characteristics of particles were obtained from secondary electron signal. A set of digital images of PVC particles were taken in order to study the required number of particles to be analysed in order to obtain representative results for the whole powder population.

Images processing and analysis was carried out with AnalySis Pro software. Figure 1 shows a PVC particles image (up) obtained by SEM and the corresponding processed image (down). The mentioned software allows evaluating many equivalent diameters and size descriptors, Figure 2 shows the selected ones for this study.

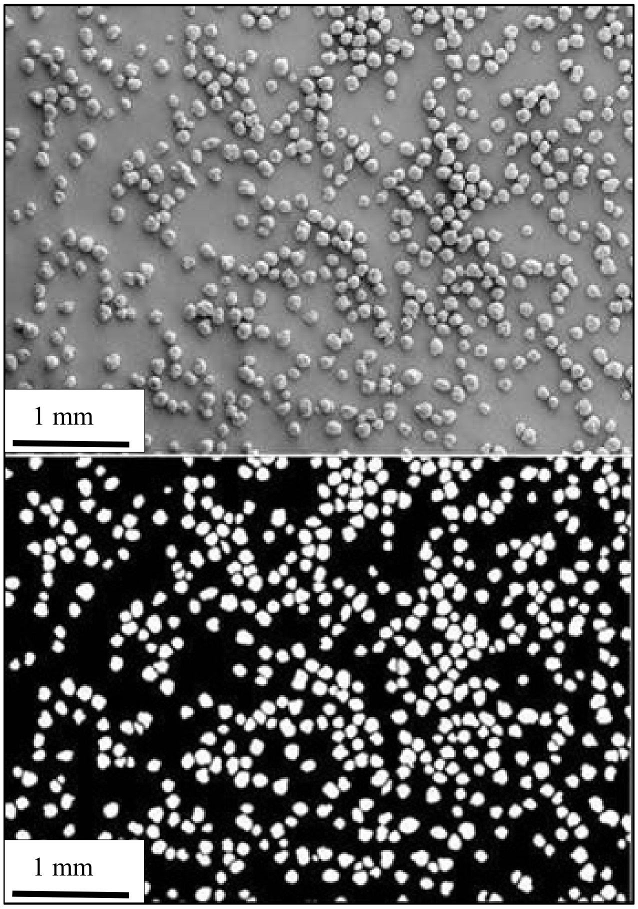


Fig. 1. SEM image and binarized image.

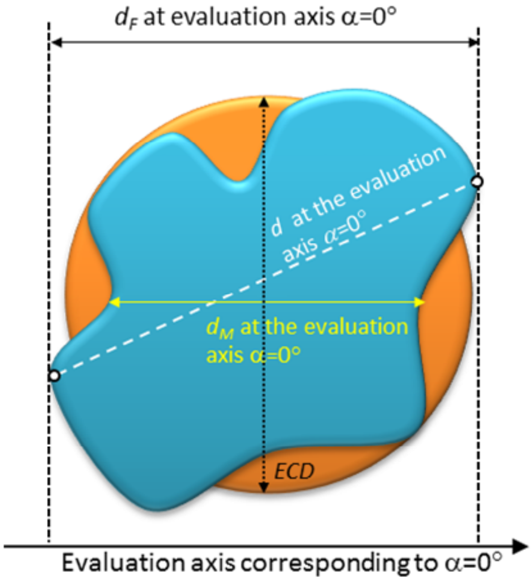


Fig. 2. IA-SEM: Size Descriptors.

Table 2 lists the definitions of the size descriptors calculated for each particle.

The Horiba Partica LA-950 Laser Diffraction Particle Size Distribution Analyzer was employed for the LD assays. The sample was fed by using the module for dry measurement (Powder Jet Dry Accessory). Sample flows along a vibratory feeder before falling into the dispersion chamber. There, the sample flows through a Venturi nozzle where any agglomerates are dispersed using 360° compressed air (2 bar). The powder is measured and then evacuated through the bottom of the system automatically by vacuum. The out up reports give the PSDs expressed either as volume or number %, the last one obtained by mathematical transformations.

Table 2. IA-SEM size descriptors.

Descriptor	Definition
d	Distance between two parallel lines tangent to the particle, which are perpendicular to the evaluation axis.
d_{min}	Minimum value found analyzing all the evaluation axes.
d_{max}	Maximum value found analyzing all the evaluation axes.
d_{mean}	Mean value for all the evaluation axes.
d_F	Feret diameter.
d_{Fmin}	Minimum value found analyzing all the evaluation axes.
d_{Fmax}	Maximum value found analyzing all the evaluation axes.
d_{Fmean}	Mean value for all the evaluation axes.
d_M	Martin diameter.
d_{Mmin}	Minimum value found analyzing all the evaluation axes.
d_{Mmax}	Maximum value found analyzing all the evaluation axes.
d_{Mmean}	Mean value for all the evaluation axes.
A	Projected particle area.
ECD	Equivalent Circle Diameter: Diameter of a circle that has equal A than the analyzed particle (single value).
P	Particle perimeter
P_{ch}	Convex hull perimeter (elastic band around the particle edge).

RESULTS AND DISCUSSION

Figure 3 shows a SEM image of some particles, while Table 3 lists shape factors and material properties calculated from the IA-SEM.

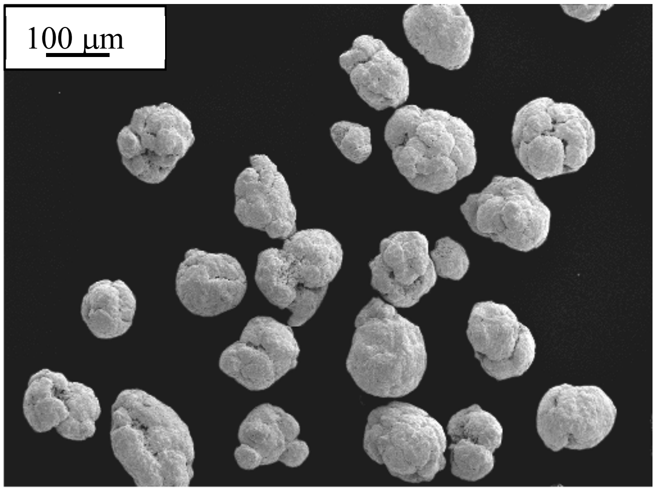
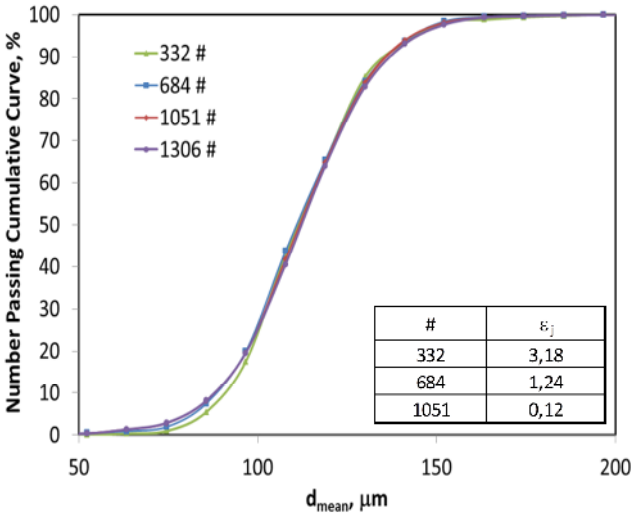


Fig. 3. Micrograph of the PVC particles.

Table 3. Shape factors calculated by IA-SEM.

Shape factor	Mean value (1306 particles)
Circularity, $4\pi A/P^2$	0.89
Convexity, P_{ch}/P	0.95
Aspect Ratio (AR), d_{Fmin}/d_{Fmax}	0.79
Elongation, $1\text{-}AR$	0.21
d_{Fmean}/d_{Mmean}	1.13

As shown in Table 3, the relative high circularity of the particles (as confirmed by visual observation of Figure 1) indicates that they are highly regular and the shape does not strongly deviate from circles. The mean particle convexity points out a low surface roughness given by the close values found for the convex hull and the real particle perimeters. The mean aspect ratio indicates that the particles are relatively symmetrical in all the axes, and therefore they are not very elongated. The relationship d_F/d_M is described as a parameter that characterizes the materials; Allen [9] reported that this ratio has to be practically constant for a given powder. That relationship was evaluated for the PVC particles using the mean Feret and Martin diameters for each particle. The results indicate that the mean ratio is about 1.13, while the 98% of the particles present d_F/d_M between 1.1-1.3.



#	ε_j
332	3,18
684	1,24
1051	0,12

Fig. 4. IA-SEM. Influence of the analyzed particles number on the number passing cumulative particle size distribution.

The IA analysis allows calculating the size descriptors defined in Table 2 for every particle. From the raw data, the frequency of the counted particles within a give size range can be easily calculated. The particle size distributions can be expressed in different ways, particularly the passing cumulative distributions are often used to characterize particulate systems. The number passing cumulative function can be calculated knowing the number of particles that are present in each size class, answering "how many particles are smaller than?". The number that constitutes the answer is y-axis value, while the size mentioned in the question represents the x-axis value of the number passing cumulative distribution. It can be built as many PSDs as the number of the analyzed size descriptors.

Figure 4 shows the number passing cumulative PSD based on the mean diameters (d_{mean}) estimated by IA-SEM and employing an increasing number of images, in other words increasing the number of particles analyzed. Since the IA-SEM technique is highly sensitive to small particles (Table 1), the higher errors between the PSDs are found for low values of d_{mean}. In Figure 4 is also included a table reporting errors based on the differences found between the cumulative numbers estimated by using different number of particles and the cumulative numbers found for 1306 particles. The error ε_j is defined as follows:

$$\varepsilon_j = \sum_{i=1}^{N_{class}} \left[\frac{(F_i^j - F_1^{1306\#})}{F_1^{1306\#}}\right]^2 \qquad (1)$$

where j represents the particles number used for IA, i the class number, $F_i^{\,j}$ the cumulative number passing function (for j particles) evaluated at class i and $F_i^{\,1306\#}$ the cumulative number passing function (for 1306 particles) evaluated at class i. As it can be seen in Figure 4, the sum of the squared relative errors using 1051 particles is very low. Based on these results, 1306 particles where used to compare PSDs obtained by SEM and LD.

The IA-SEM number data can be transformed to volume data assuming that the volume of the irregular particles can be calculated using the size descriptors that the technique provides. Also, the LD volume PSD can be converted to number distributions if the particles are assumed to be spheres. Therefore, any numerical transformation to compare PSDs obtained from different techniques involves assumptions that we should deal with.

Figure 5 shows the number cumulative distribution for different size descriptors evaluated by IA-SEM and the number PSD obtained by numerical transformation of the LD volume PSD. As it can be seen the number cumulative PSDs based on the Martin and ECD diameters do not match the LD results. However, the number PSDs calculated from the d_{mean} and d_{Fmean} can follow the trend exhibited by the LD number PSD. The higher differences between the d_{mean}, d_{Fmean} and LD PSDs are found for the small and big particle sizes. This result is in agreement with the fact that IA-SEM is very sensitive to the small particles, while the LD technique shows high sensitivity for over-sized material. The LD PSD indicates that there are less small and more big particles respect to the prediction given by the d_{mean} and d_{Fmean} PSDs.

Figure 6 shows the PSDs expressed in terms of volume, in this case all the number PSDs obtained by IA-SEM (i.e., for all the studied size descriptors) where transformed to volume PSDs assuming that the particles can be idealized as spheres. The results indicate, as it happened for the number PSDs, that the volume PSDs calculated from the d_{mean} and d_{Fmean} are quite close to the volume LD PSD. Eventhough, the d_{mean} and d_{Fmean} PSDs are in good agreement with the LD data for the studied powder; this result cannot be extrapolated to other systems. This study shows that the comparison of PSDs between techniques is not simple and that the use of different descriptors can give completely different results.

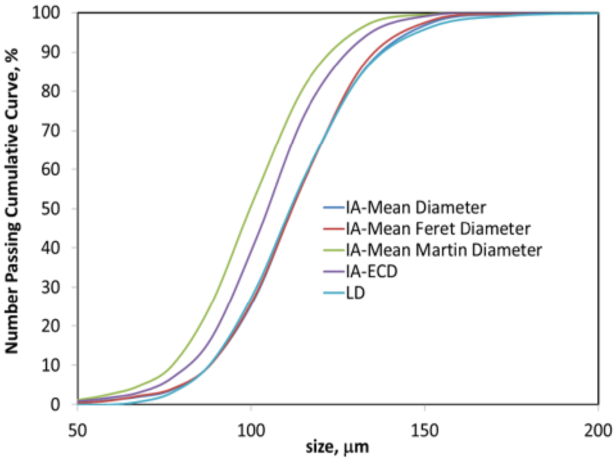


Fig. 5. Comparison of number passing cumulative functions obtained by IA-SEM and using different size descriptors with the number distribution calculated from LD data.

The transformation of the IA-SEM number PSDs to volume distributions involves the assumption of a given geometrical form. Figure 6 shows the IA-SEM volume PSDs obtained assuming that the particles are spheres. Even though, d_{mean} and d_{Fmean} volume PSDs are the ones closer to the LD data, higher deviations are noticed for large particles. This is an expected result, since small differences in number PSDs for over-sized material are magnified when volume based PSDs are compared.

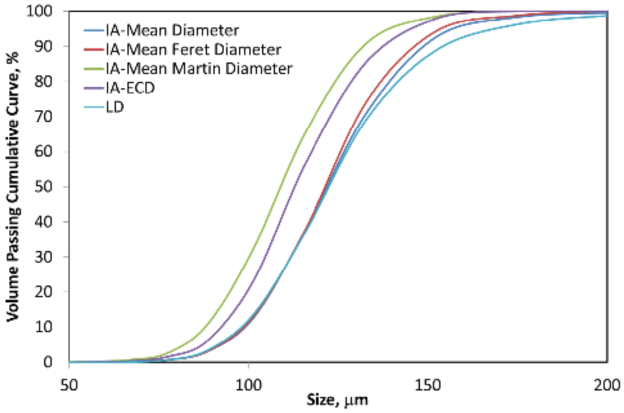


Fig. 6. Comparison of volume passing cumulative functions derived from IA-SEM data (for different size descriptors) with the volume distribution given by LD technique.

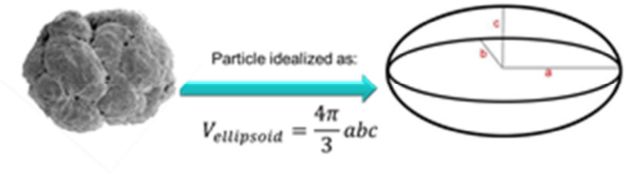


Fig. 7. The particles are idealized as ellipsoids to build volume distributions based on shapes other than spheres.

Table 4. Volume calculation of ellipsoidal particles employing different size descriptors base on the length *d* (see Table 2).

Formula
$V_1 = \frac{\pi}{6} d_{min}^2 d_{max}$
$V_3 = \frac{\pi}{6} d_{min} d_{max} d_{mean}$
$V_2 = \frac{\pi}{6} d_{min} d_{max} (d_{min} + d_{max})/2$
$V_4 = \frac{\pi}{6} d_{mean}^3$

The IA gives detailed information of the particles size; therefore the particle volume calculation can be based on shapes other than spheres. Taking into account the calculated shape factors (Table 3) and the micrographs (Figure 1), the particles volume were idealized as ellipsoids (see Figure 7). As d_{mean} showed to be a size descriptor that well predicted the LD data, different dimensions (but all based on the size descriptor *d,* see Table 2) were selected to calculate the ellipsoids volume.

Table 4 shows the expressions used to calculated the volume of each individual particle, to finally estimate the volume cumulative distribution.

Figure 8 compares the volume distributions calculated from the IA-SEM data (considering the expressions given in Table 4 for volumes calculations) with the LD volume PSD. The sphere conceptualization of particles volumes is the better representation to match the LD volume PSD. For the explored material, it is not necessary the use of multiple size descriptors to calculate the particles volume.

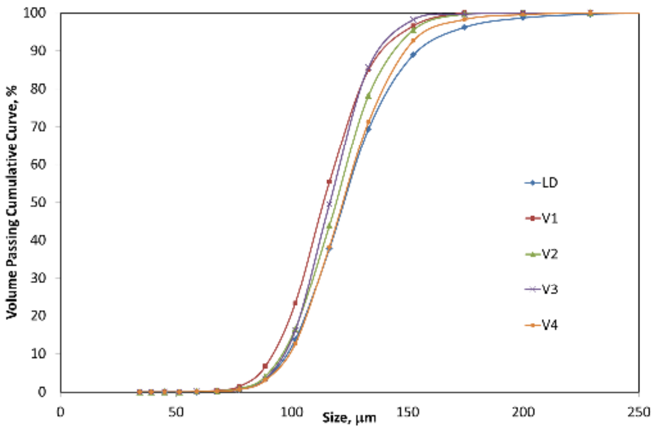


Fig. 8. Comparison of volume passing cumulative functions derived from IA-SEM data (considering that the particles are ellipsoids and that their dimensions can be represented by different size descriptors) with the volume distribution given by LD technique.

CONCLUSIONS

This study is based on the analysis of particles that are relatively symmetrical in all the axes. Therefore the findings of this work should not be extrapolated to different kind of materials.

As the number of particles analysed were increased, the number PSDs obtained by IA-SEM tend to be equal. Samples about 700 particles give good PSDs, however more than 1000 particles are needed to ensure that the obtained PSD is a good representation of the whole particulate system.

Assuming spheres, the mean diameter was the size descriptor that better allowed reproducing the LD data. The idealization of the particles volume as ellipsoids of different size did not give overwhelming results respect to the ones obtained assuming spheres.

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