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Dispersion of TiO_2 nanopowders to obtain homogeneous nanostructured granules by spray-drying

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Abstract

This work deals with the dispersion and stabilisation of nanosized TiO_2 particles in an aqueous medium as a first step in the preparation of spray-dried nanostructured powders.

A colloidal route leading to the production of titania nanostructured feedstocks to obtain nanostructured powders was developed. The process was based on the production of homogeneous and concentrated TiO_2 nanosuspensions dispersed in deionised water with a suitable control of pH and the use of an appropriate anionic dispersant. Concentrated suspensions could be obtained by mixing with an ultrasounds probe at different times depending on the dispersing conditions.

Homogeneous suspensions prepared were then reconstituted by spray drying into free-flowing powders with an adequate granule size distribution for diverse purposes, such as atmospheric plasma spraying coatings.

Keywords: TiO_2; Dispersion; Suspensions; Rheology; Drying

1. Introduction

Nanoparticles and nanostructured-materials study has revolutionized a number of areas in engineering and life sciences in the last years. Nowadays, recent advances in the synthesis and investigation of functional nanostructured materials have been carried out.[1]

Coatings with photocatalytic properties have a series of functionalities of wide interest and applicability such as: self-cleaning, anti-fogging, biocide and air purification. There are many photocatalysts, such as ZnO, CdS and WO_3, although TiO_2 is known to be the best photocatalyst in terms of its chemical stability, low cost and lack of toxins.[2]

Thermal spray is one of the most economical and viable processes to obtain coatings at an industrial scale, given its high deposition rates and that there is no need for special atmospheric or chemical chambers. Additional advantages are the durability and high bond strength of the coatings, which give thermal spraying a technical advantage for the application in self-decontamination surfaces.[3]

It is believed that the use of nanostructured materials could provide enhanced properties if the nanostructure is preserved in the final coating. The manufacture of nanostructured coatings by atmospheric plasma spraying (APS) requires the reconstitution of starting nanopowders into a sprayable size since nanoparticles could not be directly deposited because of their low mass and their poor flowability. A suitable method to reconstitute the nanoparticles is spray-drying. Moreover, the possibility to prepare nanoparticle granules by spray-drying that have a good flowability and a size that minimize respiratory intake without inducing additional hard agglomerates could provide a route to safe handling of nanoparticles.[4]

In the spray-dryers, a suspension is fed into the drying chamber, then the slip is atomized by pumping it at high pressure through a multi-nozzle array, after that the upward spiralling droplets encounter hot air and fed through a diffuser into the chamber (countercurrent to the droplets).[5] This makes it necessary to prepare and optimise the nanopowder suspensions in order to obtain homogeneous spray-dried granules[6] with high apparent density.

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Table 1
Commercial nanoparticles characterisation of TiO_2 AEROXIDE® P25 (information provided by the supplier).

Average primary particle size (nm)	21
Specific surface area (m^2/g)	50 ± 15
pH in 4% dispersion	3.5–4.5
Purity (wt%)	99.5

Most studies concerning the dispersion and stability of TiO_2 suspensions have been carried out using submicrometer and micrometer sized particles.[7,8] However, some recent studies have been carried out with TiO_2 nanoparticles. On one hand, Fazio et al.[9] reported the dispersion and stabilisation of two commercial nanopowders which were an anatase and a rutile titania. Large zeta potentials were obtained for these commercial nanopowders dispersed with a polyelectrolyte. On the other hand, Faure et al.[4] evaluated and optimised the stability of an anatase–rutile nanotitania suspension in terms of dispersing agents concentration and pH by measuring the rheological properties of differently prepared suspensions. In this case, 25 wt% solids content nanosuspensions were used for spray-drying. It is therefore clear that research on the dispersion and stabilisation of nanosuspensions in general and nanotitania suspensions in particular is still incipient. Further research is then necessary for obtaining stable high solids content nanosuspensions[10,11] to be used in subsequent processing steps such as spray-drying of powders to produce granules with improved flowability and uniformity for different applications, such as the coating by plasma spraying.

The aim of this work was to study and optimise the dispersing conditions of aqueous suspensions of a commercial nanopowder of TiO_2 and to characterise the subsequent spray-dried powder obtained from one of those nanosuspensions. The results demonstrate that this procedure is a suitable method to prepare reconstituted granules of nanostructured powders to be used, in the near future, in atmospheric plasma spraying.

2. Experimental

2.1. Starting raw material characterisation

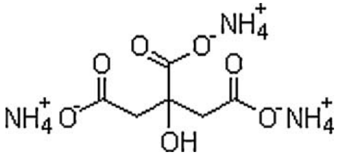
A commercial nanopowder (Aeroxide® P25, Degussa-Evonik, Germany) was employed in this study. The main physicochemical characteristics as provided by the supplier are shown in Table 1

P25 nanopowder is a reference TiO_2 standard material that has been widely used in many studies. It contains anatase and rutile phases in a ratio of about 3:1.[12] It was characterised by transmission electronic microscopy, TEM (H7100, Hitachi, Japan and CM10, Philips, Netherlands) and specific surface was determined using the single-point BET method (Monosorb, Quantachrome Co., USA).

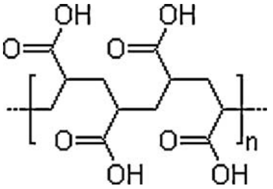
2.2. Colloidal behaviour characterisation

The colloidal behaviour of nanopowders in water was studied through zeta potential measurements. The efficiency of polyacrylic based polyelectrolytes and basic citrates in the dispersion of nanosized ceramic suspensions has been reported elsewhere.[4,9] Accordingly, the following dispersants were used

- *TAC*: Ammonium citrate tribasic anhydrous ($C_6H_{17}N_3O_7$, Fluka, Germany). It is a short molecule with a molecular weight of 243.2 and it is very spherical in shape due to the ammonium groups, as shown below:[13]



- *PAA*: Commercial salt of polyacrylic acid-based polyelectrolyte (DURAMAX™ D-3005, Rohm & Haas, USA). It is provided as a solution with 35 wt% active matter of PAA ($(C_3H_4O_2)_n$) and it has an average molecular weight of 2400. The chemical structure is:[13]



The colloidal stability of TiO_2 nanopowders was studied measuring the zeta potential as a function of deflocculant content and pH using a Zetasizer NanoZS instrument (Malvern, UK), based in the laser Doppler velocimetry technique. Different TiO_2 dilutions were tested to measure zeta potential with the best accuracy, which was reached for a concentration of titania of 0.005 wt%, using KCl 0.01 M as inert electrolyte. pH values were determined with a pH-meter (716 DMS Titrine, Metrohm, Switzerland) and were adjusted with HCl and KOH solutions (0.1 and 0.01 M). To improve the dispersion state, some sonication times were tested using an ultrasounds probe (UP 400S, Dr. Hielscher GmbH, Germany) in order to avoid agglomerates. A sonication time of 30 s was found to be the optimum time for the preparation of diluted suspensions for zeta potential measurements. These diluted aqueous suspensions were also used to determine the particle size distribution by dynamic light scattering using the same equipment as that used for zeta potential measurements.

2.3. Rheological study

First of all, nanoparticles suspensions were prepared by adding titania nanoparticles in dispersing medium (optimal quantity of dispersant into water) using a blade-stirrer. Preliminary test showed that these "stirrer conditions" are insufficient to completely deagglomerate the powder for high solids content suspensions. In order to break down any agglomerates present, the suspensions were dispersed with the ultrasounds probe. Different periods of ultrasounds (US) exposure were investigated, from 0 to 5 min. Note that the ultrasounds were applied to 20-mL aliquots of every nanosuspension and using an ice bath to avoid excessive heating.

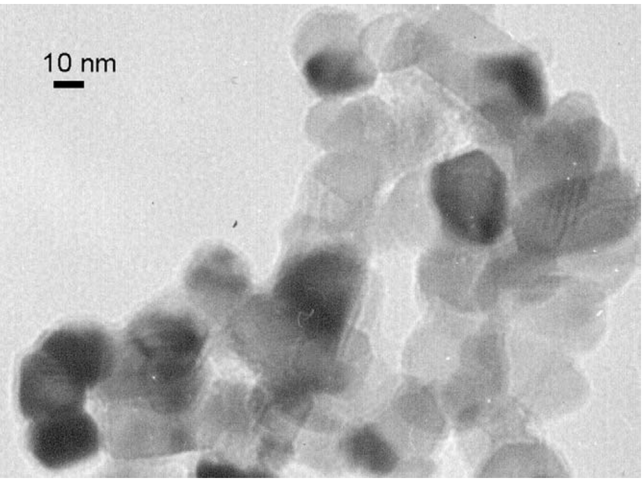


Fig. 1. TEM micrograph of TiO_2 nanoparticles (AEROXIDE® P25).

TiO_2 nanosuspensions were prepared to solids loadings of 5, 10, and 20 vol.% by dispersing the powder in deionised water using the optimum dispersant content and applying different sonication times.

The rheological behaviour of all nanosuspensions was determined using a rheometer (Haake RS50, Karlsruhe, Germany) operating at controlled shear rate (CR) by loading the shear rate from 0 to 1000 s^{-1} in 5 min, maintaining at 1000 s^{-1} for 1 min and uploading from 1000 to 0 in 5 min. The measurements were performed at 25 °C using a double-cone and plate system.[11]

2.4. Spray-drying

Spray-dried granules were obtained from 10 vol.% suspensions in a spray-dryer (Mobile Minor, Gea Niro, Denmark) with a drying capacity of 7 kg water/h.[14] Granule size distribution was measured by laser diffraction (Mastersizer S, Malvern, UK). Agglomerate apparent density was calculated from powder tapped density by assuming a theoretical packing factor of 0.6, which is characteristic of monosize and spherical particles.[15] Granules flowability was evaluated in terms of Hausner ratio, which is determined by directly dividing the powder tapped density and the loosely powder bed density. Finally, a stereoscopic microscope (SMZ-U, Nikon, Japan) and a field emission environmental scanning electron microscope (QUANTA 200FEG, FEI Company, USA) equipped with an energy-dispersive X-ray spectrometer (EDAX Genesis) were used to study the feedstock microstructure.

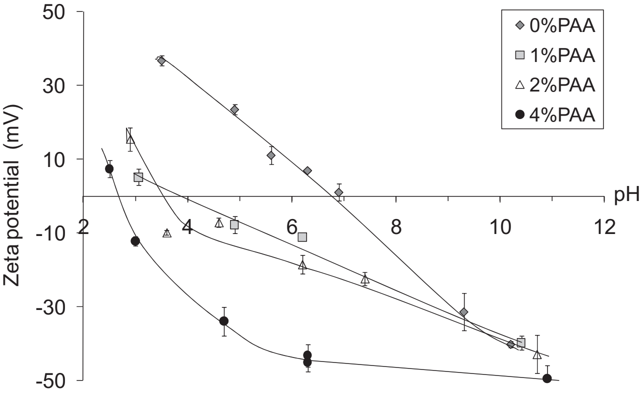


Fig. 3. Effect of PAA addition in evolution of zeta potential vs pH.

3. Results and discussion

3.1. Starting raw material characterisation and its colloidal behaviour

The microstructural observation of the P25 nanopowder, made by TEM, shows that the particles are agglomerated and primary particles are approximately 40 nm in diameter (Fig. 1). P25 specific surface area is 48.5 m^2/g.

It is necessary to deagglomerate and then stabilise titania nanoparticles in water and two different dispersants were tried. Fig. 2 shows the evolution of zeta potential of the titania nanopowders as a function of pH for suspensions without and with 1 and 2 wt% TAC. The IEP of this powder occurs at pH around 7, in good agreement with the values typically reported in the literature.[9,16,17] The evolution of zeta potential with pH does not depend on the dispersant concentration which shifts the isoelectric point (IEP) very slightly, thus meaning that it does not adsorb on the particles surface or adsorption is small. However, high zeta potentials are obtained, especially at basic pH, due to the dissociation of TAC (occurring at alka-

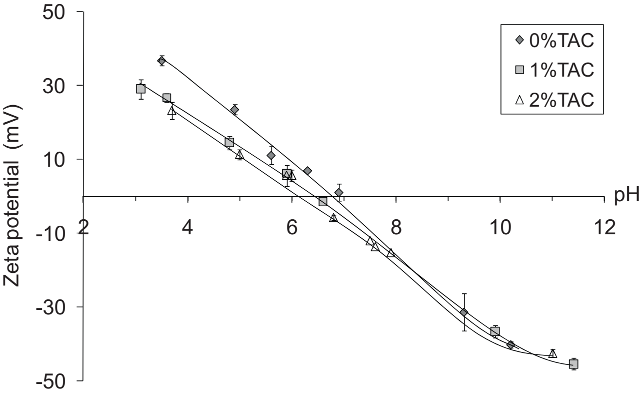


Fig. 2. Effect of TAC addition in evolution of zeta potential vs pH.

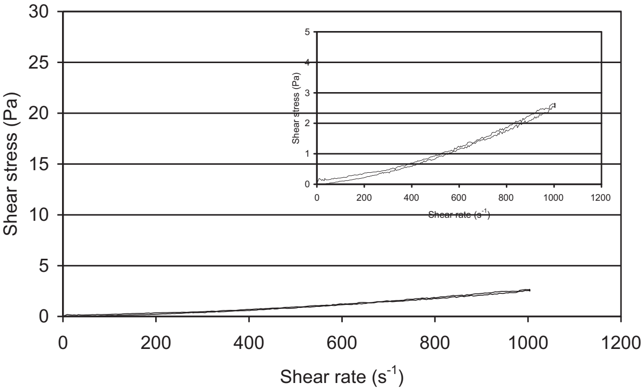


Fig. 4. Flow curve of dispersed 5 wt% (1.4 vol.%) TiO_2 suspension.

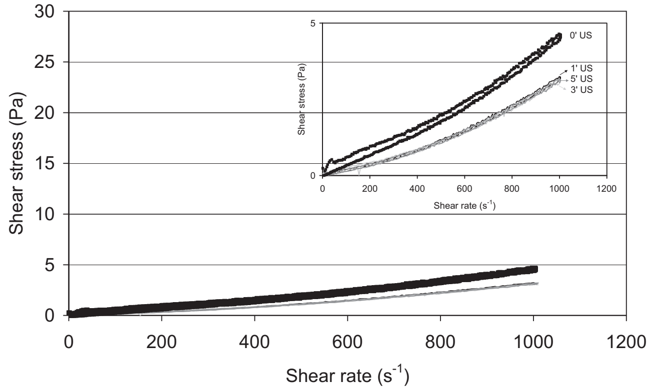


Fig. 5. Effect of ultrasound time on the flow curves of dispersed 5 vol.% TiO_2 suspensions.

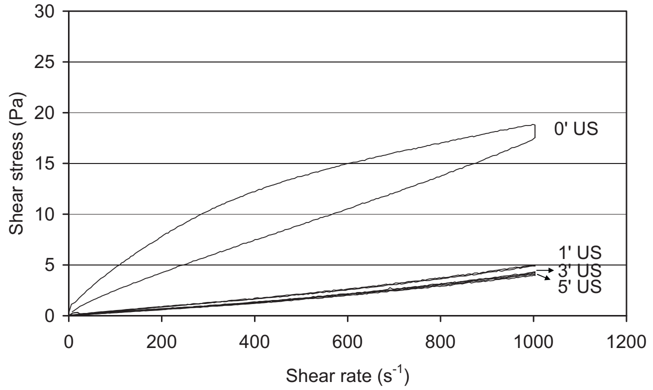


Fig. 6. Effect of ultrasound time on the flow curves of dispersed 10 vol.% TiO_2 suspensions.

line pH), but the presence of potential determining ions (protons at acidic conditions and hydroxyls at basic pH) is the responsible for pure electrostatic charging. The poor adsorption of TAC could be related to the relatively large sphericity of the molecule which does not allow proper coverage at the surface because of a volume exclusion problem. This suggests that TAC is not a suitable electrosteric deflocculant for this raw material although it could provide electrostatic stabilisation when dissociated at basic pH. To demonstrate this fact, the rheological behaviour of concentrated suspensions should be studied.

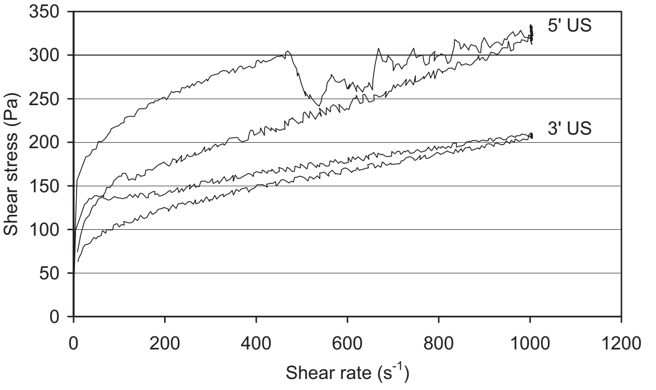


Fig. 8. Effect of ultrasounds time on the flow curves of dispersed 30 vol.% TiO_2 suspensions.

Then, another dispersant (an ammonium polyacrylate, PAA) was tested. The results obtained with this second dispersant are shown in Fig. 3 In this case, the IEP shifts to acidic pHs as the concentration of PAA increases until a value of the IEP of ~2.7 is reached when 4 wt% PAA is added. This demonstrates that PAA specifically adsorbs and leads to well dispersed suspensions above pH 5. In this case we can assume that effective electrosteric stabilisation occurs at basic pH, where dissociation of PAA occurs. At basic conditions, the zeta potential maintains a constant value for PAA contents ≥4 wt%, the amount of adsorbed deflocculant being by 0.8 mg/m^2.

The particle size distribution of TiO_2 P25 was measured on diluted suspensions and the mean particle size was found to be by 40 nm. This value agrees with TEM observations (Fig. 1).

3.2. Rheological study

The effect of sonication time, pH, solids loading and ageing time on the rheological behaviour of concentrated nanotitania suspensions was studied.

3.2.1. Ultrasounds

Sonication application plays a key role on the dispersion of nanoparticles.[18,19] Short times might not be enough for the preparation of homogeneous suspensions and long times might produce agglomeration. Because of that, the sonication

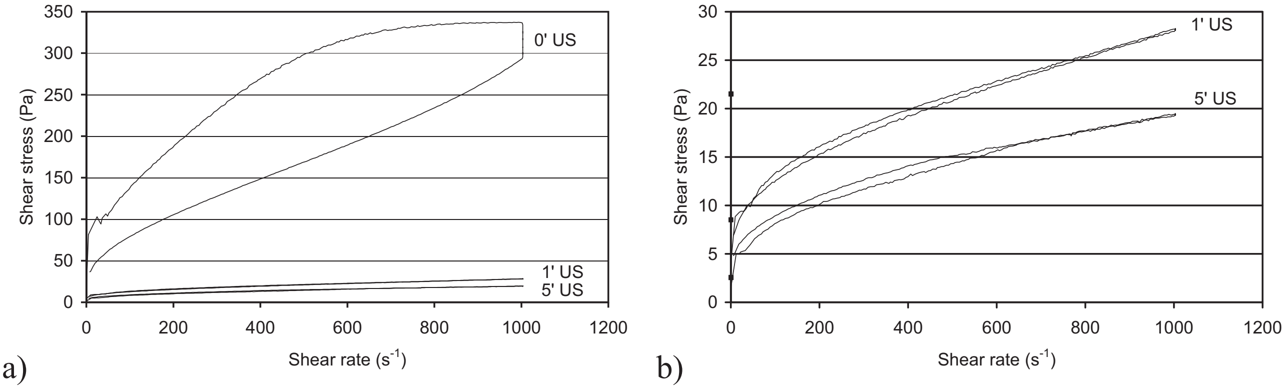


Fig. 7. Effect of ultrasounds time on the flow curves of dispersed 20 vol.% TiO_2 suspensions; (a) complete curves and (b) reduced *Y*-axis scale curves.

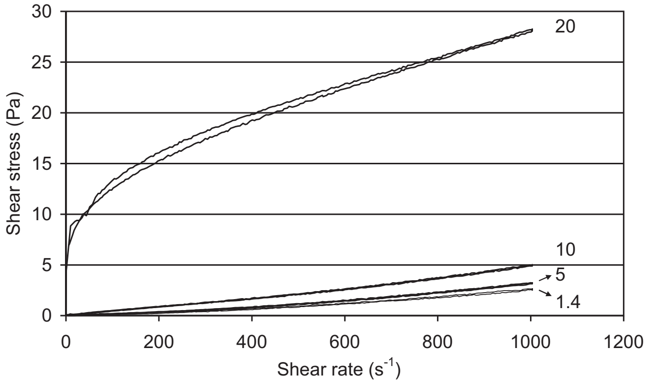


Fig. 9. Effect of solids content (vol.%) using 1 min of ultrasounds time.

time needs to be optimised for each system. Fig. 4 shows the rheological behaviour of 5 wt% (∼1.4 vol.%) solids content suspensions. In this case, sonication was not necessary because of the very low viscosity of that nanosuspension. Fig. 5 shows the rheological behaviour of 5 vol.% (∼16.5 wt%) solids content P25-suspensions just as prepared and after exposure to ultrasounds for 1, 3 and 5 min. As expected, it can be observed that sonicated suspensions show lower viscosity and no thixotropy. On reducing *Y*-axis scale, 1, 3 and 5 min of sonication time can be distinguished and the optimal sonication time for 5 vol.% nanosuspension was 3 min.

Fig. 6 shows the rheological behaviour of 10 vol.% (∼29.5 wt%) solids content suspension revealing that a broad thixotropic cycle appears when there is no sonication. The suspensions sonicated to different sonication times are rather similar, and display a Newtonian behaviour with very low viscosities.

Flow curves of 20 vol.% (∼48.5 wt%) nanosuspensions are shown in Fig. 7a. In this case, a broad thixotropic cycle is also observed for non-sonicated suspensions due to the much higher solids loading. The thixotropic cycle strongly increases with the solids content of the suspension, being 106, 226, 3 515, and 96 400 Pa/s for suspensions with solids contents of 1.4, 5, 10, and 20 vol.% respectively. Fig. 7b reveals that the optimum sonication time was 5 min.

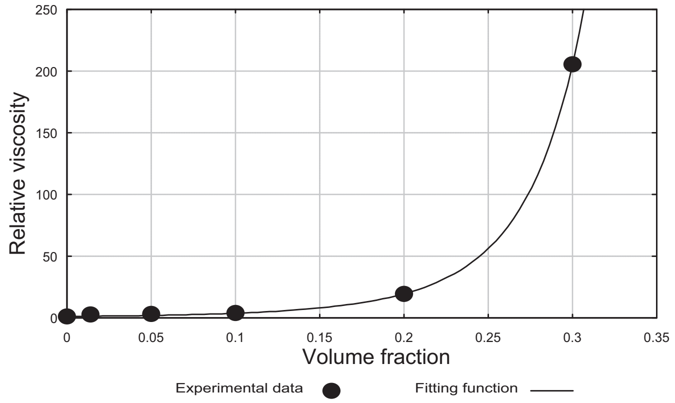


Fig. 10. Relative viscosity (measured using optimal ultrasounds time) vs volume solids content fitting to the Krieger–Dougherty equation.

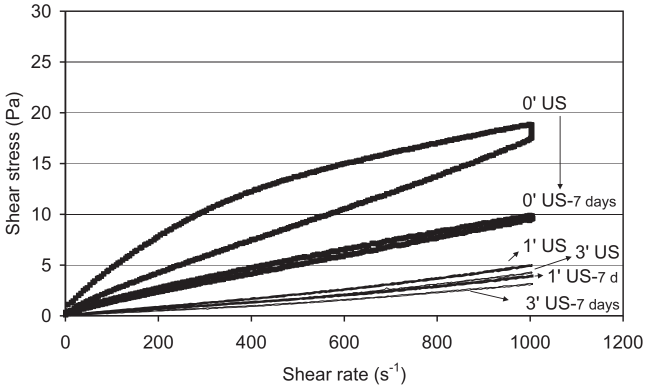


Fig. 11. Effect of ageing in 10 vol.% TiO_2 suspensions.

In the case of 30 vol.% (∼61.7 wt%) P25-nanosuspension, the curve obtained without ultrasounds could not be prepared due to its excessively high viscosity. However, the curve obtained with 1 min of sonication time could be prepared but not measured since it had still too high viscosity and the torque exceeded. Nevertheless, suspensions prepared with 3 and 5 min of sonication were measured and the minimum viscosity was obtained for 3 min sonication, as observed in Fig. 8 The further increase of viscosity with sonication time could be related to a re-agglomeration effect of the more active surfaces as a consequence of the reduction of interparticle distances that cannot overcome strong overheating.

Summarising the above results, the viscosity decreases when sonication time increases until an optimum time from which viscosity increases again. The best dispersion is achieved with 3 min ultrasounds for suspensions of up to 5 vol.% solids, whereas 5 min US are needed for higher solids content, excepting that of 30 vol.% due to its strong tendency to overheating and re-agglomeration.

3.2.2. *Solids content*

Fig. 9 compares the flow curves of suspensions with solids loadings ranging from 1.4 vol.% to 20 vol.% solids content in P25-suspensions. It is obvious from the plot that 20 vol.% solids content nanosuspension yields a very considerable vis-

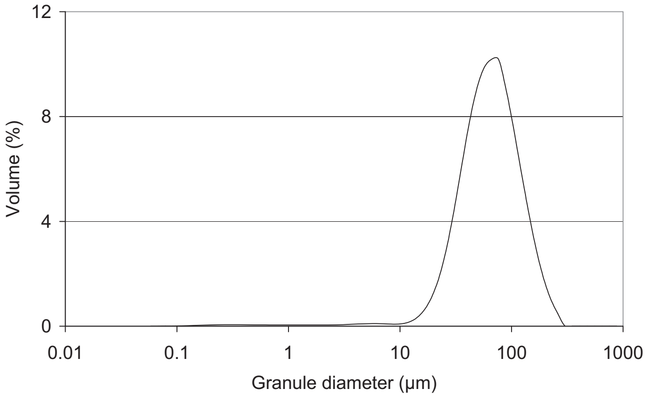


Fig. 12. Granules size distribution of spray-dried powder.

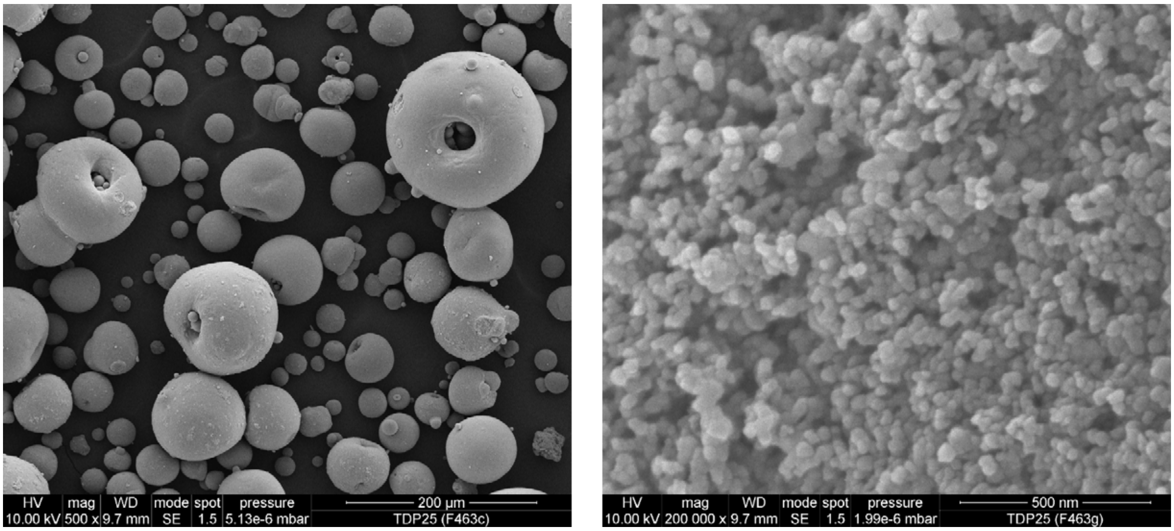


Fig. 13. FEG-ESEM micrographs of spray-dried granules (left) and higher magnification inside a granule (right).

cosity increase, as predicted for concentrated suspensions by the Krieger–Dougherty model[20], among others

Fig. 10 shows the evolution of relative viscosity with solids content using optimum ultrasounds times. The viscosity values were all taken from the downward flow curves at a shear rate of 1000 s^{-1} as an estimate of the limit viscosity (η_∞, that is, the viscosity obtained when extrapolating the shear rate to infinity). This parameter was used to calculate the variation of viscosity as a function of the volume fraction of solids by fitting the experimental points to the Krieger–Dougherty equation. As it can be observed, the experimental data fit quite well the model. The fitting parameters were maximum volume fraction of $\Phi_m = 0.50 \pm 0.03$ and intrinsic viscosity of $[\eta] = 11.6 \pm 0.9$. The intrinsic viscosity was much higher than the value of 2.5 theoretically predicted for hard spherical particles suggesting the agglomeration of nanoparticles into irregular shaped agglomerates.

3.2.3. *Ageing*

To study the effect of ageing on nanosuspensions, they were maintained at low speed agitation in a closed flask into a horizontal shaker for later measurements.[18,21] The rheological behaviour of the nanosuspensions was checked for ageing times up to 7 days. This study was carried out in all the samples (different sonication time, pH, solids content) although it is only shown the ageing behaviour of 10 vol.% nanosuspensions. Fig. 11 shows the effect of sonication on the flow curves of fresh and 7 days-aged suspensions. The viscosity of the as-prepared suspension strongly decreases with sonication time for 1 min, but further sonication up to 3 min produces a very small reduction. What is more surprising is that after one week the viscosity of non-sonicated suspension strongly decreases too. However, the viscosity is much lower for sonicated suspensions and their stability is maintained for several days without reagglomeation. This is an important issue, since many suspensions prepared from nanosized powders usually become gel in hours or even in minutes.[18]

3.3. *Reconstitution of nanopowders by spray-drying*

The 10 vol.% TiO_2 nanosuspension was spray-dried. This suspension was chosen due to its suitable characteristics to be spray-dried in the pilot equipment set out above.

Granule size distribution (Fig. 12) measured by laser diffraction, confirmed the micrometer range of the spray-dried agglomerate size. Agglomerates displayed a monomodal granule size distribution and the mean size was 60 µm. This agglomerate size distribution is adequate for using this powder in APS as reported elsewhere.[8,14,22]

In addition, agglomerate apparent density was 1335 kg/m^3. Fauchais et al.[23] reported that the apparent density of the agglomerates of APS spray-dried powders can widely range from 1000 to 2000 kg/m^3.

High powder flowability is also required for homogeneous feeding of the feedstock into plasma flow in order to produce a continuous and constant powder mass flow. Hausner ratio of spray-dried granules is 1.15 ± 0.03 which confirms the good flowablity of the obtained powder since free-flowing powder is considered when Hausner index is <1.25.[24]

FEG-ESEM micrographs (Fig. 13) reveal that granules are highly spherical and at high magnifications, it can be confirmed that the granules are built of glued nanoparticles. Typical doughnut shaped of spray-dried granules are clearly observed.

4. Conclusions

The colloidal stabilisation of a commercial (P25) nanosized titania suspension has been studied, as well as their rheological behaviour at different solids content. Aqueous titania nanosuspensions have been stabilised by means of electrosteric mechanism using a polyacrylic based (PAA) polyelectrolyte at controlled pH. This makes the isoelectric point to shift down from pH 7 to 2.7 when 4 wt% PAA is added thus demonstrating that it specifically adsorbs.

Concentrated suspensions were prepared in water at the optimised dispersing conditions by homogenising with an ultrasounds probe which allowed the preparation of up to 30 vol.% solids loadings. The viscosity increases with volume fraction of particles exponentially and measured values can be fitted to the Krieger–Dougherty equation leading to a maximum packing fraction of 0.50, which is a high value for nanosized suspensions.

The use of stable nanoparticle suspension for the spray-drying reconstitution process allows us to obtain nanostructured micrometric-size, spherical and free-flowing spray-dried powders which are in principle suitable for further atmospheric plasma spraying.

Acknowledgements

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