

# Production of Nanoparticle Assemblies by Electro-Spraying and Freeze-Drying of Colloids: A New Method to Resolve Handling Problem of Nanoparticles

**Samimi, Abdolreza\*<sup>+</sup>**

*Department of Chemical Engineering, University of Sistan and Baluchestan, Zahedan, I.R. IRAN*

**Ghadiri, Mojtaba**

*Institute of Particle Science and Engineering, University of Leeds, Leeds, UK*

**ABSTRACT:** *To resolve handling problem of nanoparticles, due to their small size, a new methodology of electro-spraying and freeze-drying was developed for colloidal nanoparticles of silica and titania to transform them to solid macro-scale nanoparticle assemblies. The assemblies were then redispersed in an aqueous system to investigate the effect of formulation of original solutions and the process parameters on reversibility of the system to a stabilised colloidal condition. The electro-spraying was employed to control the size of droplets and consequently the size of nanoparticle assemblies in the freeze-drying. High speed digital video recording of the spray process revealed that within a narrow range of voltage, the size of droplets reduced sharply to a minimum value, where a narrow size distribution was obtained. Non-destructive structural analysis of the freeze-dried nanoparticle assemblies using X-ray micro-tomography represented different structures of the nanoparticle assemblies depending on type of nanoparticles. The stability analysis of redispersed nanoparticles in water (using centrifugal stability analyser) and their size distribution (obtained by nano-sizer) showed different stability conditions. These conditions were affected by physicochemical properties of nanoparticle assemblies and process parameters. In terms of titania, it was found that with an appropriate formulation of PEG solution (as binder of assemblies) and optimum size of the nanoparticle assemblies it was possible to produce assemblies having adequate strength and good re-dispersion properties.*

**KEY WORDS:** *Electro-spray, Freeze-drying, Nanoparticle assemblies, Colloids, Redispersion.*

## INTRODUCTION

Nanoparticles are important to a number of industrial sectors including ceramic-processing, coating, paints, inks, drug delivery and food processing due to their

unique characteristics. However, they present great difficulties for handling and processing especially during production at industrial scale due to their small size.

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\* To whom correspondence should be addressed.

+ E-mail: a.samimi@hamoon.usb.ac.ir

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To resolve the problem, one approach is to transform the nanoparticles in colloidal form into solid nanoparticle assemblies, sufficiently strong during handling, and to redisperse them reversibly to the colloidal form when is required. The challenging task in this regard is to produce the nanoparticle assemblies with a view to break them apart into the individual and stable nanoparticles in the redispersion process.

The redispersion mechanisms of nanoparticle assemblies in a liquid medium often consist of wetting, immersion and disintegration of the assembly structure into the primary nanoparticles. The final step is a difficult job that might not be fully achieved due to partial disintegration of the assemblies to the clusters or re-aggregation of the nanoparticles in the liquid. The behaviour of a nanoparticle assembly during redispersion can mainly be controlled by physicochemical properties of the nanoparticles and structure of the assembly as well as mechanical energy applied to the dispersion system. The physicochemical properties may depend on the force acting between the nanoparticles in the assembly, where the attractive force may be as a result of van der Waals force [1-3], capillary (i.e. liquid binder) [4] or solid bridge binder [5].

To overcome these forces, stresses need to be applied to the interparticle contacts. The stresses to break up the assembly structure might be a result of an external mechanical energy source such as milling or ultrasonication and/or due to the physicochemical energy of the wetted system [6]. The latter energy is employed when the nanoparticle assembly contains a soluble polymeric binder whereby an osmotic pressure is developed in the assembly due to the wetting of particles and binder in a dispersant agent [7]. A suitable formulation of binder along with a proper structure of nanoparticle assembly can optimise the effects of physicochemical energy for good redispersion of the assembly to a stable colloidal form. This is interesting in processes in which the mechanical energy is not feasible or minimum mechanical energy is available.

Polymers are usually added to the initial colloidal systems to improve the stability of nanoparticles in the system. However, in this work these materials should also behave as the binder for agglomerating of the nanoparticles. The presence of a polymer such as polyethylene glycol (PEG) in the assembly pore structure and its dissolution

during redispersion can produce a powerful pore osmotic pressure [7, 8] leading to an extensive internal stress distribution within the structure. The stress distribution inside the assembly should be higher than the bond strength between the primary particles to disintegrate the assembly. PEG is an excellent polymer in this regard as it is inexpensive, is available in a wide range of molecular weight and is widely used as a binder in the agglomeration processes [9].

In this study a combined method of electro-spraying and freeze-drying was employed for the production of nanoparticle assemblies using three types of stable colloidal solutions of latex, silica and titania as input materials. A high DC electric field was applied to the spray system to produce mono-sized colloidal droplets with a desired size. The idea of using an electrostatic field between a capillary tip such as nozzle and a flat counter electrode was initially used to reduce the diameter of droplets by applying an additional force (i.e. electric force) in the direction of gravitational force [10, 11]. This was done to overcome the upward capillary force of liquid on the tip of nozzle and hence reducing the droplet size. Freeze-drying or lyophilisation has been used as a method for drying of heat-sensitive food and pharmaceutical materials with various applications such as drug delivery [12, 13]. In most of the cases, the materials were initially frozen in liquid nitrogen for fast freezing and then the frozen materials were transferred to the vacuum freeze-dryer. The process of freeze-drying usually involves three main stages: freezing, primary drying and secondary drying [14]. The primary drying includes ice sublimation and the secondary drying involves removal of the water from the solid structure by desorption.

The objectives of this paper are to analyse the effects of combined process of electro-spraying and freeze-drying, and formulation of the original colloids on the size and the structure of produced nanoparticle assemblies and their behaviour in the redispersion. The redispersion is carried out to investigate the reversibility of the system to stabilised colloidal liquids.

## MATERIALS AND METHOD

### *Preparation of initial colloidal solutions*

The colloidal nanoparticles of latex, silica and titania were used as initial materials for production of

nanoparticle assemblies. The latex (360 nm) and silica nanoparticles (10-20 nm) were supplied as concentrated stable colloidal solutions. Both samples were diluted to about 6.0 wt % solutions before being used in the next process. The rutile  $\text{TiO}_2$  (30-50 nm) was supplied as dry nanoparticles whereby a 5 wt % colloidal solution was made by dispersing the powders in a demineralised water for 12 h using a high shear mixer (model; Ultra-Turax, IKA-WERKE). Two molecular weights of 1500 and 20000 of PEG were employed in the production of colloidal  $\text{TiO}_2$  solutions, each having 3 wt % and 7 wt % concentrations of PEG. An additional 5 wt %  $\text{TiO}_2$  solution was prepared with no PEG for comparison. The PEG polymer was used for titania system to study the effect of its molecular weight and its concentration on the stability of redispersed nanoparticles and also on the interparticle bond strength of the assemblies.

The pH of aqueous  $\text{TiO}_2$  has a significant effect on its stability as according DVLA theory repulsive surface potential is required to hinder the particles from agglomeration. This is achieved by establishing electrical double layer over the surface of nanoparticles using  $\text{H}^+$  or  $\text{OH}^-$  ions [15]. The dispersion of  $\text{TiO}_2$  nanoparticles in an aqueous system was initially led to a pH of about 3. Titration tests were carried out to investigate the effect of pH on zeta potential of the solutions by using a zeta potential meter model; Colloidal Dynamic, Zeta Probe. Fig. 1 illustrates two typical graphs of  $\text{TiO}_2$  solutions with and without PEG. As it is seen, with increasing pH, the positive zeta potential decreases to zero at IEP and then increases negatively at the pHs higher than 6.0 and 6.5 for the solutions with PEG and without PEG, respectively. Both acidic (pH=3) and basic (pH=11) solutions may show stable behaviour as in both cases sufficient repulsive potential is developed on the surfaces of the nanoparticles. Furthermore, addition of 3 % PEG improved the zeta potentials negatively at high pHs (i.e. from -40 to -70 at pH=11) as compared to the system without PEG, while it reduced the positive zeta potentials at low pHs (i.e. from 60 to 45 at pH=3). Considering these effects, in this work all the  $\text{TiO}_2$  solutions were made at pH of 11, where more stable initial solutions were obtained.

#### Experimental processing methods

A prototype experimental unit was set up for the manufacturing of nanoparticle assemblies from the

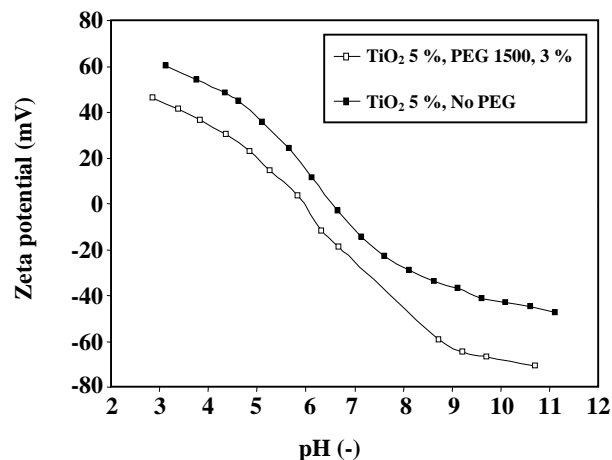


Fig. 1: Effect of pH on interparticle potential of solutions made with and without PEG shown as zeta potential vs pH.

colloidal solutions. The process included two stages of electro-spraying of the colloidal droplets and consequently their freeze-drying. Fig. 2 illustrates the schematic diagram of process in which the colloidal solution is pumped into a nozzle charged by a high DC electric field using a syringe pump. A flat annular and earthed electrode was set at a certain vertical distance under the nozzle. As a result, a capillary liquid was formed on the tip of the nozzle where it was then broke up to a droplet with a certain size at a distance from the nozzle. The droplet size depended on its viscosity, its surface tension as well as the flow rate of the liquid and the applied voltage. The formed droplets were then allowed to drip into the liquid nitrogen for rapid freezing. The frozen droplets were collected in the stainless steel containers and the containers were then transferred to a laboratory freeze-dryer model SB4 where it had already been set up at a very low pressure and temperature (i.e. 1 mbar absolute and  $-30\text{ }^{\circ}\text{C}$ ). The drying process was carried out at low pressure and temperature for 24 h to sublime the ice during primary drying and then at low pressure and room temperature for further 24 h to complete the secondary drying process. The dripping of the droplets was recorded at the speed of 5000 fps using a high-speed digital camera model; Red Lake Motion, Xtra HG-100K. The illumination of the spraying event was made using two halogens lamp, 500 W each, which provided a continuous light. The recorded images were downloaded into a PC and were processed by an automatic image analyser model Motion Central V2.5.7 to observe the patterns of dripping and to find out the average size of the droplets.

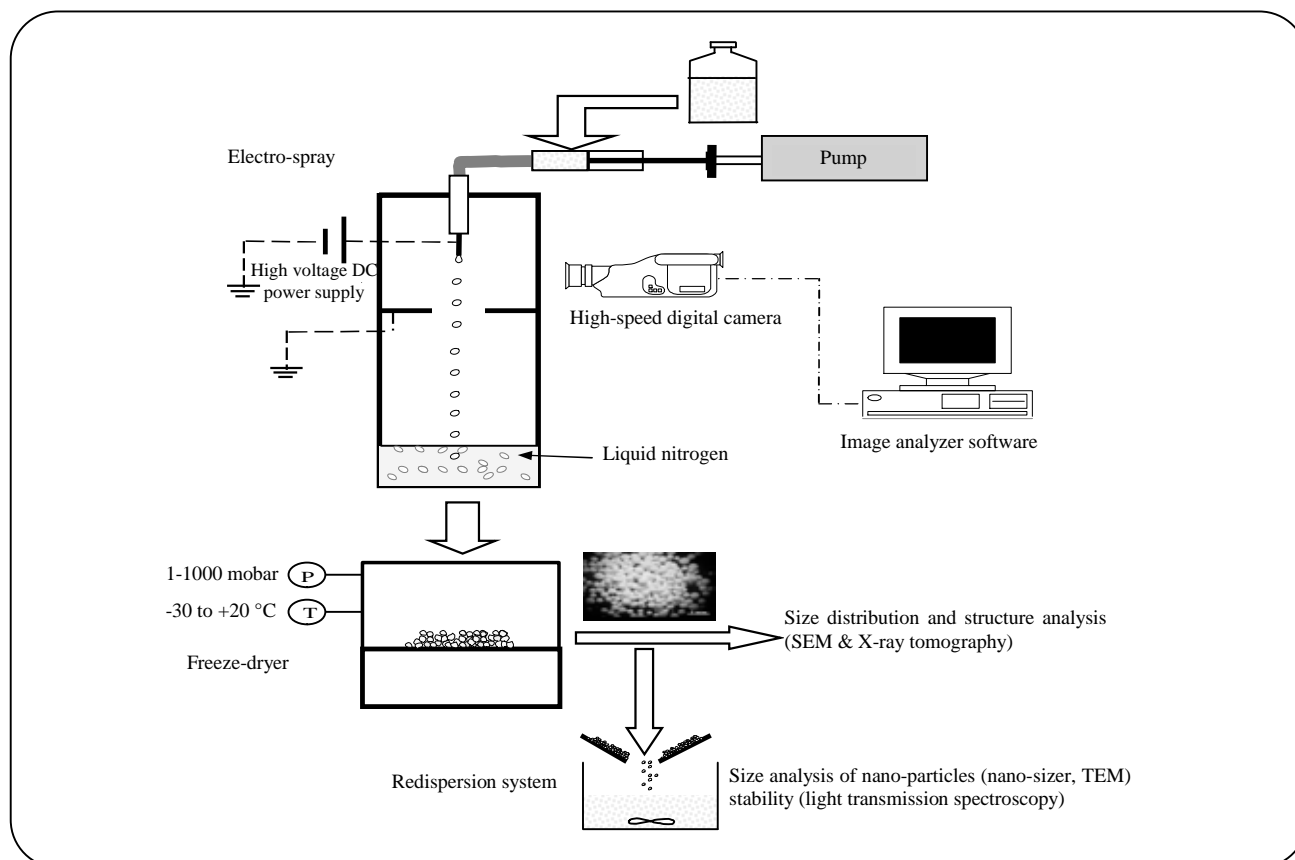


Fig. 2: Schematic drawing of combined process of electro-spraying and freeze-drying.

A part of dried nanoparticle assemblies was kept for size and structural analysis using SEM and X-ray microtomography (model; Skyscan 1072). X-ray tomography was employed as a non-destructive imaging technique whereby cross-sectional structures of the particles were obtained without their physically slicing up in a resolution of more than 4 micron per pixel. The second part of the nanoparticle assemblies was used in the redispersion experiments. In all experiments the concentration and pH of the redispersed particles in the aqueous system were kept constant at 1.5 wt % and 11, respectively, to compare the other parameters. The redispersion tests were carried out using a low shear magnetic mixer where the rate and duration of mixing was kept constant (i.e. 1 h mixing at the rate of 300 rpm). The stability of redispersed solutions was investigated using a centrifugal stability analyser (model; Lumi Fugi 114) and the size distribution of nanoparticles was analysed using Malvern Nanosizer (model Nano-zs).

The centrifugal stability analyzer was operated by

continuous scanning of light transmission along the height of solution in a small vial when the solution inside the vial was subjected to a centrifugal force under a rotational speed of 300 rpm. As a result of centrifugal force the unstable solids sediment in the vial causing the light transmission increase along the height. In some cases, TEM of the colloidal solutions was also carried out to observe the condition of nanoparticles in the dispersed system whether they are individual or clustered.

## RESULTS AND DISCUSSION

### *Electro-spraying of colloidal solutions*

Figs. 3 shows the effect of DC voltage on average size of droplets made of three colloidal solutions of titania, silica and latex using  $10 \text{ ml h}^{-1}$  flow rate and 1mm (ID) nozzle. As it is seen, the average size of droplets reduces with increasing voltage. However, there was a range of applied voltage, termed as transition zone, within which the droplet size decreased significantly and the pattern of spraying shifts gradually from dripping mode to jet mode.

The threshold voltage above which the droplets size varied within a minimum range without an extensive size reduction was termed as critical voltage [16] (Fig. 3). At the critical voltage, uniform pattern of spraying and consequently a narrow size distribution of droplets were developed. Fig. 3b shows three typical photos of latex droplets captured by high-speed digital camera at three voltages of 0, 4 and 10 kV, photographs 1, 2 and 3, respectively. The photos show clearly the effect of voltage on the size reduction, where photograph 2 illustrates the spray at the critical voltage. At high voltages (i.e. 10 kV, photo 3) an angular oscillating jet mode dominated and as a result of high electric field the small droplets were broken up to the secondary fine droplets.

In Fig. 3a, the surface tension of colloids used in this study are also shown. The surface tensions were measured using a mechanical tenso-meter. As it is seen, a significant reduction of surface tension from silica and titania to latex leads to a major decrease in the critical voltages (i.e.  $\sim 65 \text{ N m}^{-1}/8 \text{ kV}$  for silica and titania to  $30 \text{ N m}^{-1}/4 \text{ kV}$  for latex). Furthermore, the lower the surface tension the smaller the droplets produced at the voltages less than the critical voltage. Decreasing the surface tension in fact reduced the upward capillary force on the tip of nozzle enhancing the pulling effect of electric field force in the direction of gravity.

Fig. 4 illustrates the size of droplet versus voltage for silica and titania at two flow rates of 10 and  $100 \text{ ml h}^{-1}$ . As it is clear from the figure, increasing the flow rate increases the size of droplets at a certain voltage. Three regions of dripping, transition and jet modes of spraying are also recognisable from the figure.

#### Freeze-dried nanoparticle assemblies

Fig. 5 shows the images of SEM and X-ray tomography of nanoparticle assemblies produced by the combined process of electro-spray and freeze drying. As it is seen, rapid freezing of the droplets in the liquid nitrogen caused the spherical assemblies to be shaped. For the latex solution applying the voltage led to a change in the surface characteristics of nanoparticle assembly along with decreasing the size. The effect of voltage is noticeable by comparing Figs. 5a and 5b, where extensive cracks on the surface of assembly at zero voltage has changed to a shrunken and wrinkled particle at 8 kV.

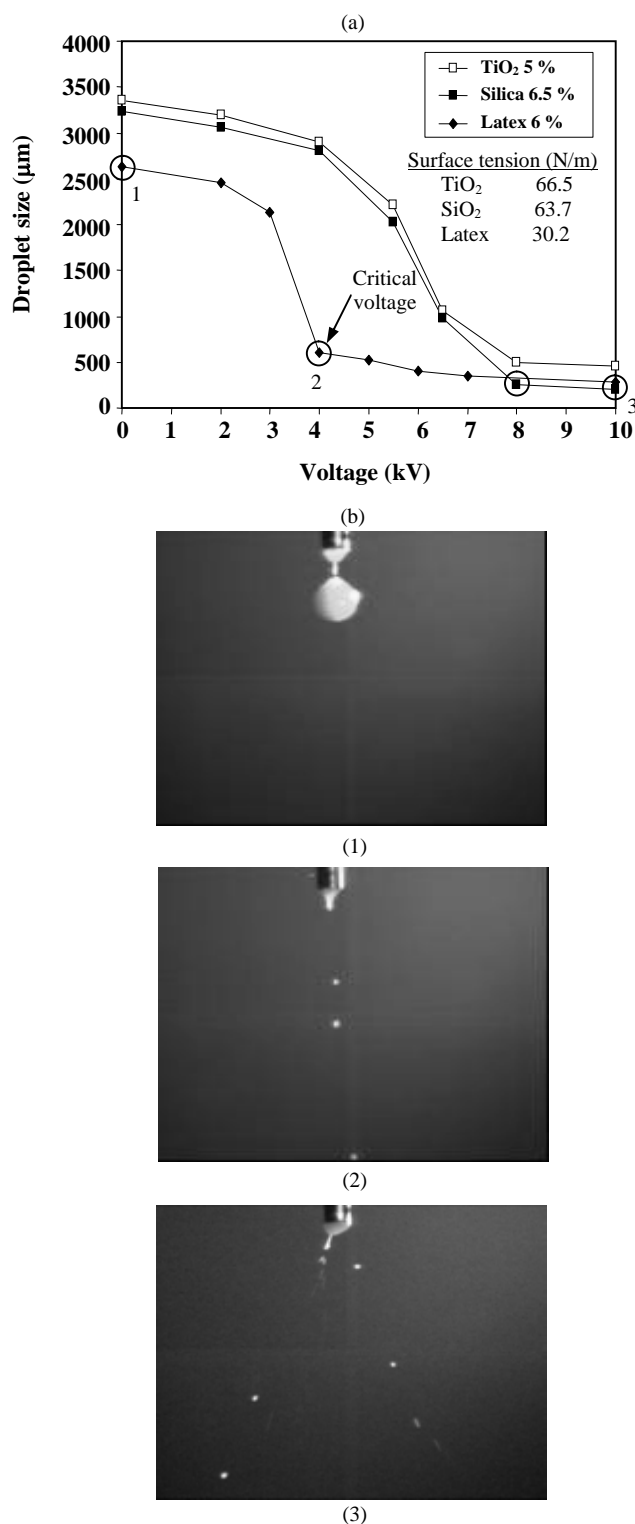


Fig. 3: Effect of DC electric field on size of droplets and pattern of spraying (a) graphs of droplet size versus voltage (b) images of spraying droplets at different conditions acquired by high-speed digital recordings of 1) no voltage, 2) 4 kV, and 3) 10 kV.

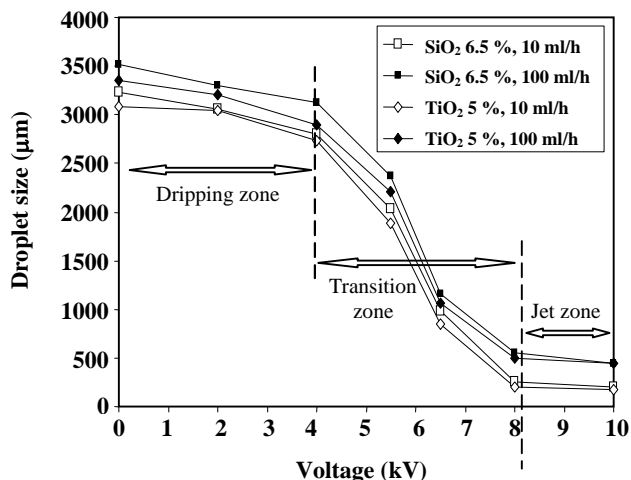


Fig. 4: Effect of DC voltage on droplet size of silica and titania at two different flow rates.

This effect was not observed for two other samples of silica and titania as both nanoparticle assemblies showed a same surface characteristics at different applied voltages. Figs. 5c and 5d illustrate the SEM images of freeze-dried silica and titania ( $\text{TiO}_2$  5 %, PEG 1500 7 %) assemblies at 0 kV and 4 kV, respectively.

The X-ray tomography of the nanoparticle assemblies of latex, silica and titania are presented in Figs. 5e, 5f and 5g, respectively. Each of the images from the left includes; i) X-ray of whole assembly (left image), ii) a cross sectional view of the assembly (middle image) corresponding to the position indicated by the line in the left image (view i) and iii) the structural information (right image) along the line in the middle view. The line profiles in the images of view (iii) represent an indication of porosity distribution. Comparing three tomography images reveals different structures of the nanoparticle assemblies obtained at almost the same processing conditions. The latex assembly obtained non-uniform porosity distribution with large internal cavities whilst the silica assembly represented the most uniform porosity distribution as compared to the latex and titania.

Fig. 6 illustrates the magnified SEM image of  $\text{TiO}_2$ , representing a porous structure of the assembly produced from  $\text{TiO}_2$  colloidal solution containing 7 % PEG. It should be noted that for titania without PEG the product was disintegrated after freeze-drying and no nanoparticle assemblies could be made. This was for the reason that for the latter case, the interparticle surface energy of the assembly after freeze-drying was much less than the

minimum value to keep the structure in an agglomerated shape. However, this was not the case for the silica after freeze-drying as even without the PEG binder, the solid hydroxide bridges formed at the interparticle contacts kept the nanoparticles in a self-assembly structure.

### Redispersion of nanoparticle assemblies

Following the methodology described in section 2.2, in this section the redispersion test results of silica and titania nanoparticle assemblies are presented. The redispersion of latex nanoparticles was not possible as no disintegration was essentially observed for this sample in an aqueous system. This was due to an irreversible change in the properties of the latex nanoparticles during the freeze-drying.

Fig. 7 illustrates the stability analysis of the re-dispersed solutions of titania (containing 7 % PEG of two molecular weights of 1500 and 20000) and silica (without PEG) using a centrifugal light transmission instrument. The tests for all the samples were carried out under the same operating conditions (i.e. continuous light transmission scanning along the solution height in the vials for 600 seconds at rotational speed of 300 rpm). Furthermore, all the colloidal solutions were obtained by dispersing 1.5 % nanoparticle assemblies in an aqueous system using a same size of nanoparticle assemblies (425-500  $\mu\text{m}$ ) of titania and silica.

Each curve in Fig. 7 corresponds to the light transmission along the solution height in the vial at a certain time; therefore, the thickness of a set of curves represents the extent of sedimentation during 600 seconds centrifugation. The thicker the band the larger extent of sedimentation was observed, showing the lesser stability.

Comparing the Figs. 7a, 7b and 7c reveals that the best stability is detected for the redispersed system of  $\text{TiO}_2$  7 % PEG 1500 (Fig. 7a) and the worse one for  $\text{TiO}_2$  7 % PEG 20000 (Fig. 7b) and stability of silica colloids is located between them. As it is seen in Figs. 7a and 7b, the titania assemblies make a solution with less initial light transmission and therefore a more turbid solution at the same concentration (1.5 wt %) as compared to the silica redispersion (Fig. 7c). A large difference is seen between the stability of  $\text{TiO}_2$  systems using PEG with two molecular weights of 1500 and 20000. Comparing Figs. 7a and 7c reveals that  $\text{TiO}_2$  nanoparticle assemblies containing 7 % PEG 1500 redispersed and stabilised

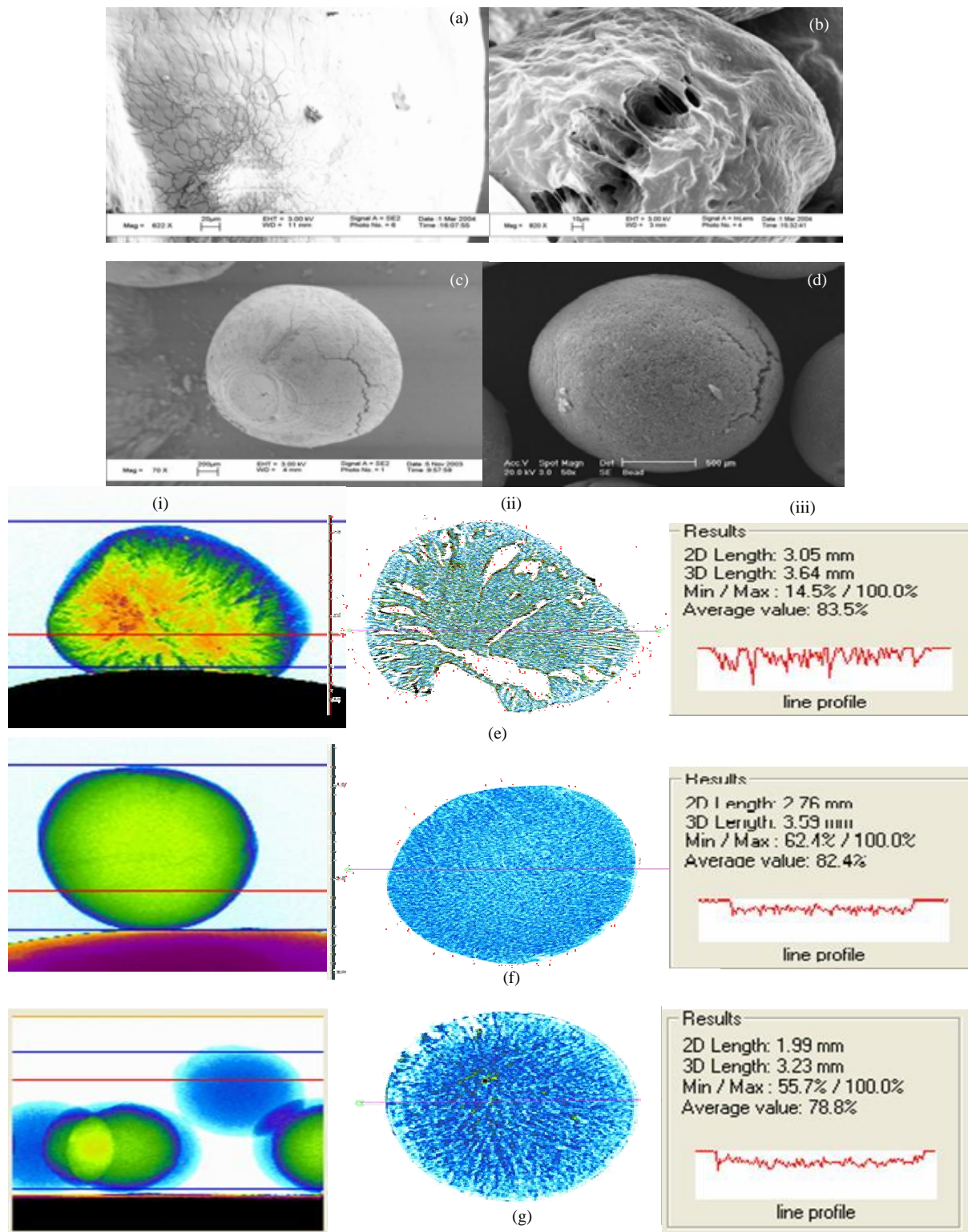


Fig. 5: SEM and X-ray tomography images of nanoparticle assemblies produced by freeze drying at different voltages. SEM images are: a) latex, 0 kV; b) latex, 8 kV; c) silica, 0 kV; d) titania with 7 % PEG, 4 kV; and X-ray tomography images are: e) latex 0 kV; f) silica 0 kV; and g) titania 4 kV.

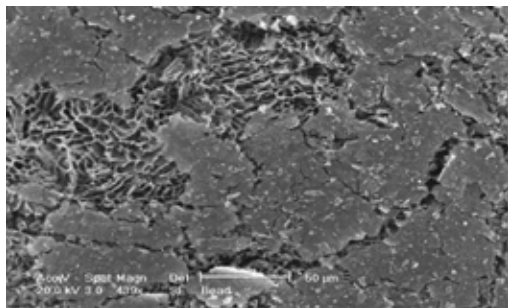


Fig. 6: SEM image of surface of a freeze-dried  $\text{TiO}_2$  nanoparticle assembly using initial colloidal solution of 5 %  $\text{TiO}_2$  and 7 % PEG 1500.

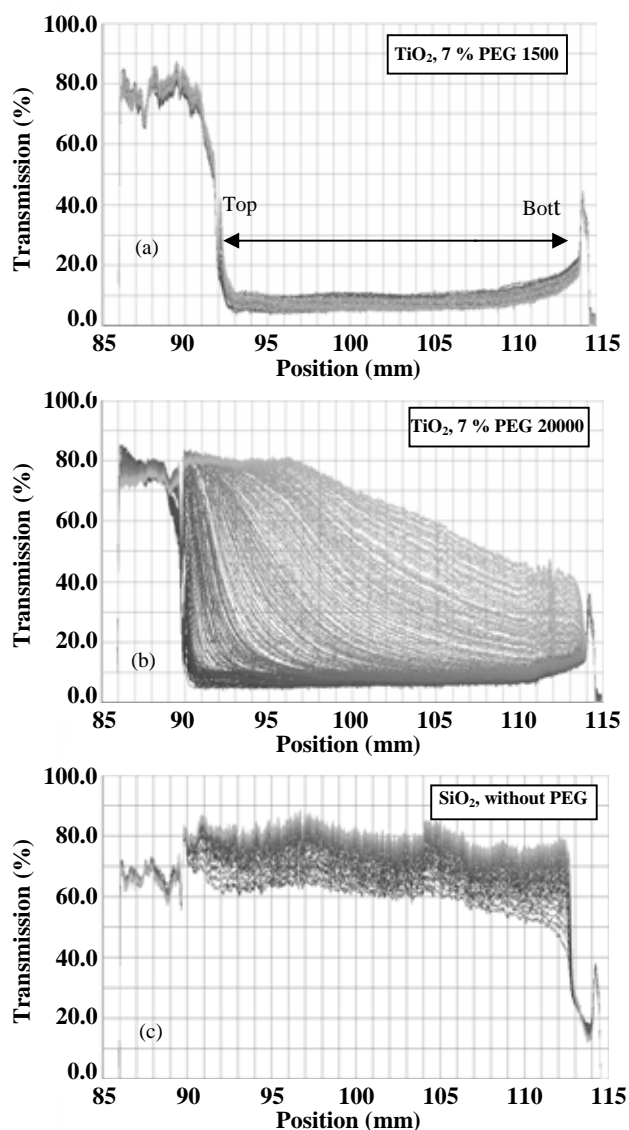


Fig. 7: Stability analysis results of redispersion of titania (containing 7 % PEG 1500 and 20000) and silica without PEG using a centrifugal light transmission apparatus under the same operating conditions.

better than the silica without PEG. This is an interesting result as in the silica nanoparticle assembly more interparticle hydroxide solid bonds are made during freeze-drying as compared to the titania assemblies in which PEG plays mainly the role of interparticle binders, not hydroxide bonds. This suggests that in the titania nanoparticle assembly the redispersion might be controlled by the characteristics of PEG such as its molecular weight and concentration.

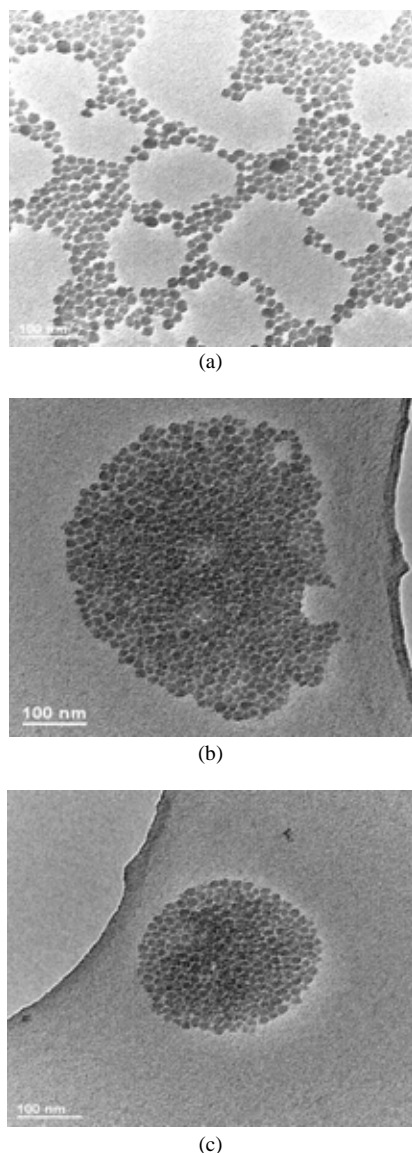
The stability of nanoparticle assemblies in colloidal form depends on the degree of disintegration of the nanoparticle assembly to the primary particles. The partial dispersion of an assembly in the aqueous system may lead to the integrated clusters where the large clusters are usually unstable and are settled down easily within the solution. Fig. 8 shows TEM images of the colloidal silica nanoparticles under different conditions; i) a well dispersed and stable initial solution (Fig. 8a) and ii) the partially dispersed nanoparticle assemblies (Figs. 8b, 8c) showing the integrated clusters.

To investigate the effect of molecular weight and concentration of PEG on the redispersion of  $\text{TiO}_2$  nanoparticle assemblies, the size distribution of redispersed assemblies in an aqueous liquid were characterised. Fig. 9 represents the size distribution of the redispersed solutions using two different molecular weights and concentrations of PEG.

As it is seen in Figs. 9a increasing the concentration of PEG 1500 in the initial solution of  $\text{TiO}_2$  (i.e. the solution before freeze drying) from 3 % to 7 % shifts the size distribution of the redispersed nanoparticles to the smaller sizes. However, for PEG 20000 no noticeable effect of concentration of PEG is seen on the size distribution of the particles (Fig. 9b). The average size of  $\text{TiO}_2$  nanoparticles is about 50 nm. Therefore, for PEG 1500 moving the peak of distribution curves to about this size with increasing the concentration (i.e. 3 % to 7 %) represents a more disintegration of the clusters into the primary nanoparticles as compared to the PEG 20000. However, a bimodal distribution of 7 % PEG affirms that the redispersion process has not completely led to the disintegrated primary nanoparticles.

Comparing the size distribution of two molecular weights of 1500 and 20000 in Figs. 9a and 9b reveals a better redispersion of  $\text{TiO}_2$  assemblies containing 7 % PEG 1500 as compared to 7 % PEG 20000. This latter





**Fig. 8: TEM images of colloidal silica solutions a) initial stabilised system b) and c) partially dispersed showing integrated clusters.**

result was compatible with stability analysis (Figs. 7a and 7b) in which a better stability was seen for  $\text{TiO}_2$  with PEG 1500 as compared to PEG 20000.

The achievements in this study are comparable in some aspects with the work of *Scott et al.* [7]. *Scott* and *co-workers* characterised the redispersion of a thin layer of  $\text{TiO}_2$  powders containing PEG binder in the demineralised water by solely measuring the mass reduction of powders in bed. They investigated the effect of molecular weight and mass fraction of PEG in the powder pack on the redispersion of particles. They

reported that the dispersion of the bed of  $\text{TiO}_2$  particles containing PEG was dramatically improved by increasing the mass fraction of PEG in the packed bed to above a certain value. This was more noticeable for the low molecular weights (i.e. 400-1000) as increasing the molecular weight of PEG had an adverse effect on the dispersion using a similar initial mass fraction of PEG. *Scott et al.* [7] confined their study to the dispersion of a thin layer of titania bed in a stagnate aqueous solution and their investigation did not include the stability analysis of the colloidal solution. In our study, the redispersion was carried out by gently mixing of the nanoparticle assemblies in the demineralised water using constant solid concentration, pH (i.e. 1.5 wt % solid concentration and pH=11) and mixing rate (300 rpm). The redispersion method and the consequent analysis used in this work were different as compared to the work of *Scott* and *co-workers*. However, the resultant effects were compatible in which increasing the concentration and/or decreasing the molecular weight of PEG improved the redispersion.

The experimental work carried out here demonstrated that the presence of PEG in the nanoparticle assemblies had a powerful effect on the aqueous redispersion of  $\text{TiO}_2$  assemblies. In this case, the stable colloidal solutions might be prepared without applying high mechanical energy (i.e. sonication or milling), just by governing the physicochemical effects of the dissolved interparticle PEG during redispersion. Application of PEG in the  $\text{TiO}_2$  nanoparticle assembly may lead to a significant osmotic pore pressure in the structure during the redispersion depending on the molecular weight and concentration of PEG [7]. In fact the osmotic pressure represents the stresses established in the structure of nanoparticle assembly as a result of chemical potential difference between the PEG solution in the pore structure of assembly and pure water outside the assembly. This is achieved initially by diffusion of pure water into the structure of assembly.

In this context, the theory of *Flory* [17] and *Huggins* [18] can be used combined with the general thermodynamic relationships to describe the behaviour of PEG polymer in the solution. Equation (1) defines the relationship of *Flory-Huggins* in which osmotic pressure ( $p$ ) is a function of concentration of polymer in the solution ( $c$ ) and its molecular weight (MW).

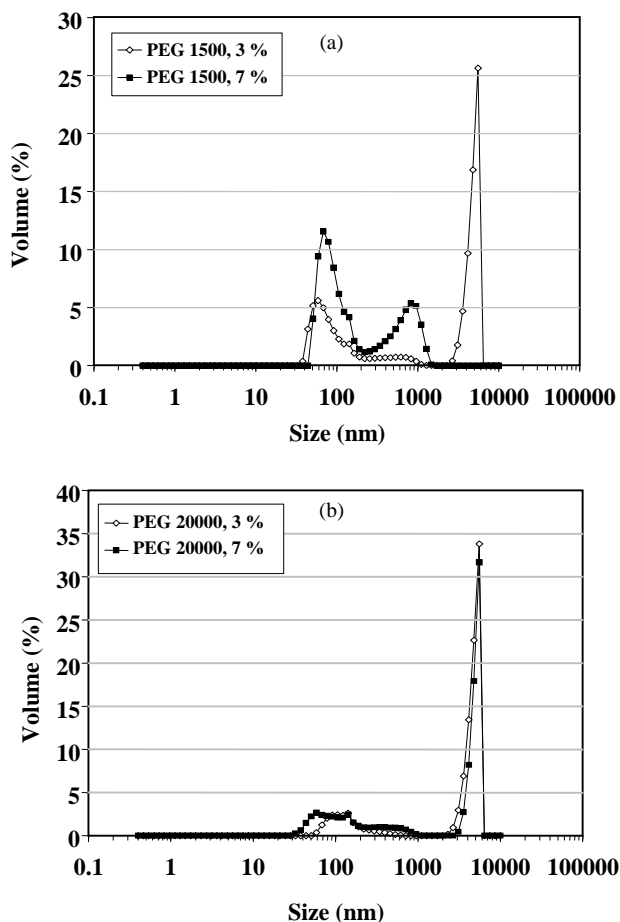


Fig. 9: Size distribution of redispersed  $\text{TiO}_2$  nanoparticle assemblies containing different molecular weights and concentrations of PEG a) Mw 1500, b) Mw 20000.

$$p = \frac{RT}{MW}c + \frac{RTv_p^2}{v_s}(0.5 - \chi)c^2 \quad (1)$$

In Equation (1),  $v_p$  and  $v_s$  are partial specific volume and molar volume of the polymer, respectively. In the relationship, the parameter of  $\chi$  represents the polymer-solvent interaction, which depends on the molecular weight and concentration of the polymer [18]. As it is seen, the main parameters affecting the osmotic pressure are concentration and molecular weight in which the osmotic pressure varies directly with the concentration of polymer and inversely with its molecular weight.

In this work, the large osmotic pressure of PEG solution led to the higher interparticle stresses than the interparticle bond strength of  $\text{TiO}_2$  nanoparticle assembly causing disintegration of the assembly. For silica and in the absence of polymeric binder the osmotic pore

pressure is much less than the titania containing PEG 1500 while the bonds look to be stronger than the titania assembly (i.e. due to the hydroxide solid bridges). On the other hand the  $\text{TiO}_2$  assemblies made of PEG 20000 are not disintegrated efficiently to the primary nanoparticles during redispersion producing large clusters which are not stable in the colloidal form.

## CONCLUSIONS

The combined method of electro-spraying and freeze-drying was employed to produce the nanoparticle assemblies of latex, silica and titania using their colloidal solutions as input materials. The nanoparticle assemblies were then redispersed in an aqueous solution to investigate the effect of material properties on the size distribution and stability of redispersed nanoparticles. Employing electro-spray and freeze-drying, it was possible to produce mono-sized and spherical nanoparticle assemblies using the appropriate voltage, temperature and pressure. The redispersion investigation showed that by optimising the concentration and the molecular weight of PEG, the nanoparticle assemblies could be made having adequate strength and good redispersion properties.

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