Physical Stability of Nanoparticle Dispersion

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ABSTRACT

Nanoparticles applications in the industry are getting more and more important and concern many different fields (drug delivery, carbon nanotubes, display technologies, etc.). In the last decades a vast amount of scientific research has been developed to improve the understanding of these complex dispersions. Using new analytical techniques, it is now possible to control and tailor properties of suspensions and to get a better understanding of time behaviour. Following this idea, stability measurements, which were commonly done by simple visual observations, can now be performed automatically via an optical device.

This instrument is based on Multiple Light Scattering and is associated to a vertical scanning of the sample. It enables to identify and quantify instability phenomena before they are visible to the operator (up to 200 times earlier). Physical parameters and kinetics can be computed in order to facilitate and improve sample comparison. Examples of carbon nano tube (CNT) dispersibility measurements are presented using this technique and enable to fine tune the dispersion in terms of solvent, surfactant content etc.

Keywords: nanoparticle stability, suspension stability, nanoparticle migration, carbon nanotube, Fuel cell.

1 INTRODUCTION

Semi-conductors, flat panel displays, multilayer capacitors, and most electronic devices which surround everyone of us in our everyday life are fabricated via a process where a suspension is involved. Even if these dispersions are not end-products but are used in a process, their stability is crucial for the good quality of these very high tech systems. Sedimentation and flocculation phenomena need to be tracked and quantified in order to minimize their intensity, hence getting reproducible and high quality processes.

In this paper, we propose a unique tool, the Turbiscan®, to help the formulator in his day-to-day job of identifying and monitoring instabilities. Various behaviours are described as they are shown with the Turbiscan®.

2 EXPERIMENTALE PROCEDURE

The heart of the optical scanning analyser is a detection head, which moves up and down along a flat-bottomed cylindrical glass cell (Figure 1) [1,2]. The detection head is composed of a pulsed near infrared light source (λ = 880 nm) and two synchronous detectors. The transmission detector (at 180°) receives the light, which goes through the sample, while the backscattering detector (at 45°) receives the light scattered backward by the sample. The detection head scans the entire height of the sample, acquiring transmission and backscattering data every 40 µm. The Turbiscan® can be thermo-regulated from 4 to 60°C and linked to a fully automated ageing station for long-term stability analyses.

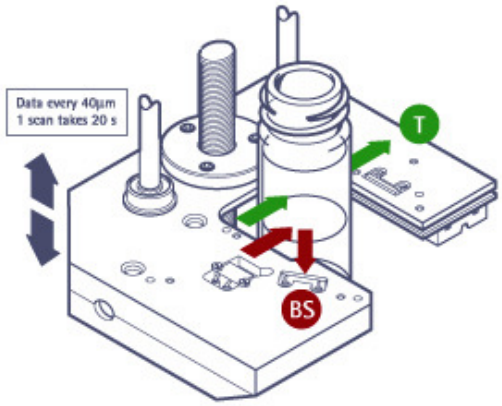

Figure 1. Principle of Turbiscan® measurement.

The Turbiscan® makes scans at various pre-programmed times and overlays the profiles on one graph in order to show the destabilisation. Graphs are usually displayed in reference mode, whereby the first profile is subtracted to all other profiles, in order to enhance variations. The obtained profiles versus ageing time enable to identify nascent destabilisation processes like coalescence, flocculation, creaming, sedimentation (figure 2).

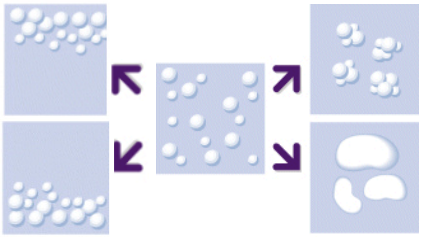

Figure 2. Main destabilisation phenomenon

3 RESULTS AND DISCUSSION

3.1. Stability of Platinium Nanoparticles for Fuel Cell Applications

Fuel cells have been extensively studied during these last decades as they appear as environmentally friendly power sources. They convert the chemicals hydrogen and oxygen into water and electricity, via a reaction between fuel (on the anode side) and an oxidant (on the cathode side) in the presence of an electrolyte. The reactants flow into the cell, and the reaction products flow out of it, while the electrolyte remains within it. Fuel cells can operate virtually continuously as long as the necessary flows are maintained.

Platinum is typically used as a catalyst to facilitate the chemical reaction in polymer exchange membrane fuel cells (PEMFC). It consists of a dispersion of nanoparticles.

In this work we present three formulations of platinum nanoparticles : formulation 1 consists of 50 nm Pt nanoparticles in water ; formulation 2 contains 50 nm Pt particles dispersed in IPA ; and finally formulation 3 corresponds to 100 nm Pt/Ru (1:1 wt%) nanoparticles dispersed in IPA. All these products are black colored samples, which have been studied in the Turbiscan LAb at ambient temperature for 5 hours.

Formulation 1 displays no variation of transmission or backscattering over the 5 hours of analysis (Figure 2), hence proves to be highly stable.

Figure 2. Transmission (top) and backscattering (bottom) for formulation 1 at 25°C

Formulation 2, on the other hand, is undergoing large sedimentation (Figure 3), with an important increase of the transmission signal towards the top of the sample. It is important to note that when transmission signal is greater than 0.2%, backscattering signal should be overlooked as it is affected by secondary reflections on the glass. Therefore, in this example backscattering should only be considered in the bottom part (from 0 to 6.5mm).

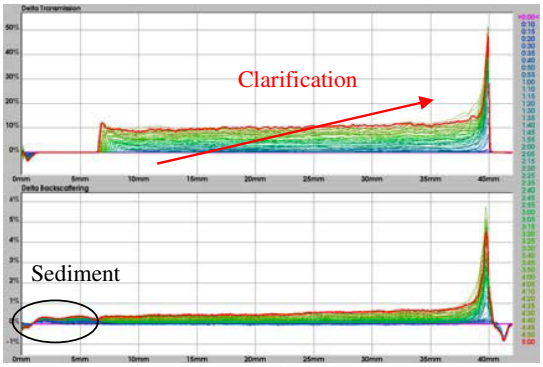

Figure 3. Delta transmission (top) and delta backscattering (bottom) for formulation 2 at 25°C.

The polarity of the solvent is therefore playing a major role in this case, in the stabilisation of the nanoparticles.

The last formulation consists of a mixture of platinum (Pt) and ruthenium (Ru) nanoparticles dispersed in IPA. Figure 10 shows that no transmission is displayed over the duration of analysis, hence no major clarification. The variation of backscattering shows an increase of the backscattering at the bottom of the vial, as the particle concentration increases due to sedimentation. At the top, a slight decrease of backscattering is seen as clarification takes place. The middle part is more peculiar, as it displays a progressive increase of the backscattering towards the bottom of the sample. This could be due to the coupling of aggregation and clarification of one of nanoparticles type, when the other type simply settles. As the nanoparticles

aggregate, backscattering increases and this is emphasized by sedimentation.

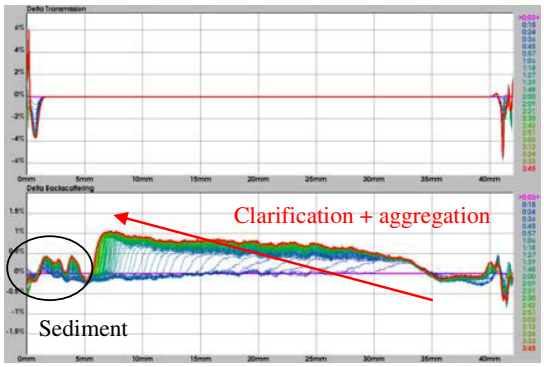

Figure 10. Delta transmission (top) and delta backscattering (bottom) for formulation 3 at 25°C.

The two populations of platinum and ruthenium nanoparticles would therefore exhibit a different behaviour. It is likely that platinum is showing only sedimentation, when looking at data from the two other formulations. Therefore the middle part would be due to the aggregation and sedimentation of ruthenium nanoparticles.

3.2. Stability of Multi-Walled Carbon Nanotubes (MWCNT)

Carbon nanotubes have attracted a vast amount of attention because of their exceptional electrical, thermal and mechanical properties. Many research groups are currently working on their incorporation in various materials to enhance their physical properties. However, one of the major issue they are facing is the difficulty to disperse them. Surface modifications and addition of surfactants or polymers are commonly used to face this problem [3,4,5,6].

Kim et al.[3] have used the Turbiscan to monitor the effect of various surfactants on MWCNT dispersibility: NaDDBS, CTAB and Triton X-100. The concentration of each surfactant was 0.3wt% for 0.02wt% of MWCNT dispersed in water. The MWCNT were characterised by SEM and TEM giving sizes of 1.3±0.7 µm in length and 20±3nm in diameter (n=50).

Figure 4 the mean value of transmission is computed over the total height and shows that without any surfactant (squares), the variation of transmission is large, indicating an aggregation of the particles. When surfactant is used, this aggregation is not observed and the MWCNT remains well dispersed.

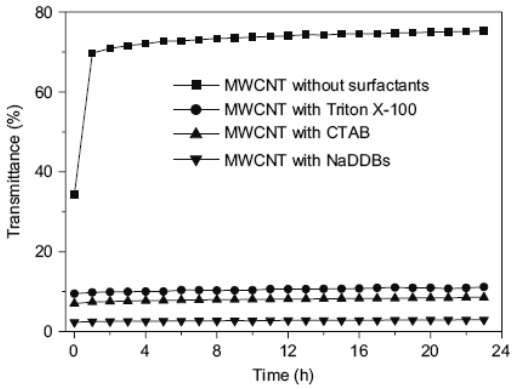

Figure 4. Mean value of transmission for MWCNT stabilised by different surfactant systems.

3.3. Stability of Ceria Slurry for Chemical Mechanical Polishing (CMP)

Chemical-mechanical polishing (CMP), is a technique used in semiconductor fabrication for planarizing a wafer or other substrates. The process uses an abrasive and corrosive chemical slurry in conjunction with a polishing pad and retaining ring. The abrasive accelerates this weakening process and the polishing pad helps to wipe the reacted materials from the surface. This removes material and tends to even out any irregular topography, making the wafer flat or planar at the Angstrom level.

Cerium(IV) oxide, also known as ceria, is an oxide of the rare earth metal cerium. It is known to have a high polishing efficiency for oxide film, but also it has an unfavourable reputation for problems linked to its quick sedimentation and agglomeration of particles, which can alter significantly the CMP process, leaving unwanted defects. Therefore it is necessary to tailor the ceria slurry in order to reach the right stability requirements for CMP applications.

Polymeric dispersants are typically used to stabilise ceria particles, via steric stabilisation. Hence, the molecular weight of the dispersant plays a key role in the stability efficiency.

We present here stability analyses of three suspensions of ceria using the Turbiscan LAB at 35°C for 12 hours. Formulation A contains high, formulation B intermediate and formulation C low molecular weight of dispersant.

All three formulations display a similar behaviour (Figure 5) with a decrease of the backscattering signal at the top as the particles deplete from this region due to a sedimentation process. Simultaneously backscattering increases at the bottom of the vial, where the particles settle. Transmission increases at the top when clarification is large enough for light to cross the suspension.

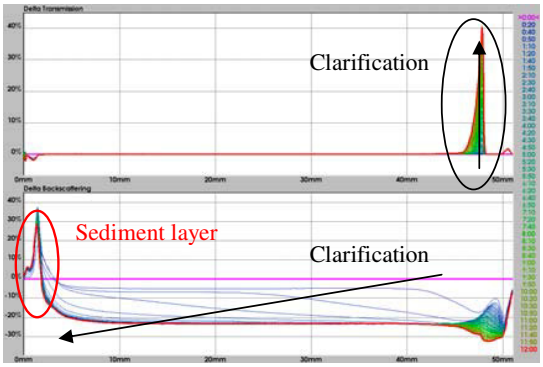

figure 5. Delta transmission(top) and delta backscattering (bottom) for Ceria suspension A at 35°C

In order to compare the extent of sedimentation in the three formulations; it is possible to compute the speed of clarification (table 1) from the slope of the thickness of the clarified layer (Figure 6).

Table 1. Thickness of the clarified layer after 8 hours of analysis and clarification velocity of the three ceria suspensions

Sample	Thickness layer after 8 hours (mm)	Clarification velocity (mm/h)
A	0.29	0.17
B	29.20	2.34
C	46.00	13.87

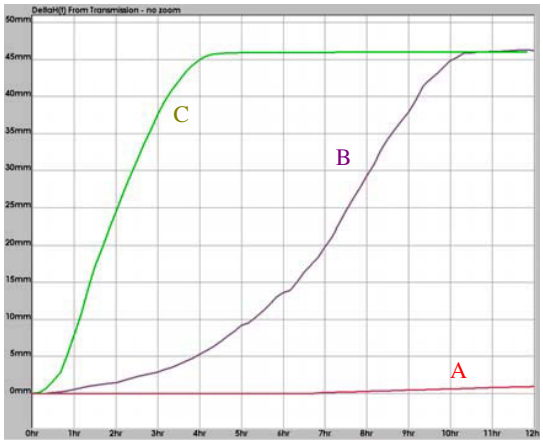

figure 6. Thickness of clarified layer for the three ceria suspensions.

These results enable to show that at 35°C, it is possible to classify the stability against sedimentation of the ceria suspensions in a few hours. Formulation A displays the best stability and formulations C the worst. This highlights the effect of the molecular weight of polymer dispersant, where long polymer chains give rise to better steric repulsion, hence better stability.

4 CONCLUSION

Therefore, we have shown that the Turbiscan® is a complete technique that can be used during all the development of a product from the formulation in the lab through the stability study to the production and the control of the quality of the products. It enables to measure stability of various types of pharmaceutical dispersions and to identify what sort of instability is taking place, even when several phenomena occur simultaneously or when nothing is visible to the eye. All the destabilisation can be analysed and followed separately using the different parameters available in the software. The overall stability study can be shortened from 10 to 50 times, allowing quicker developments.

Moreover, the analyses can be accelerated and automated through the temperature increase and the use of the ageing station

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