MONITORING NANO-PARTICLES IN THE PRESENCE OF LARGE PARTICLES USING ACOUSTICS

Monitoring the presence of nano-particles in liquid dispersions with a broad particle size distribution presents a challenge because larger particles could mask nano-particles in many size measuring techniques. Sensitivity of the particular technique to nano-particles in broad polydisperse systems is practically unknown. This study examines acoustic attenuation spectroscopy, a known and proven tool for particle characterization in concentrated systems. The complementary technique of electroacoustics based on ultrasound for characterizing zeta potential is used to monitor the aggregation stability of dispersions selected for this study. These dispersions are prepared using eight different ZnO powders – a material widely used in sun-screens.

Introduction

Nano-ecology and nano-toxicology are rapidly growing scientific disciplines dedicated to studying the impact of nanotechnology on the environment and human health. The growing number of consumer products that contain engineered nano-particles creates a sense of urgency for these studies. One of the problems that must be addressed is selection of the best methods for monitoring nano-particles in particular products. Many of these products are liquids containing various particles which might be on both the nano-scale (accepted to be less than 100 nanometers) and much larger sizes. Acoustic attenuation spectroscopy is investigated in this study to determine the sensitivity to particles below 100 nm.

Figure 1: The DT-1201

Experimental

For this study eight different powders were purchased from different manufacturers:

- Zinc oxide, reagent ACS and Zinc oxide, 99.5+% manufactured by Acros Organics
- Z50-500 and Z52-500 USP powder packaged by Fisher Scientific
- S80249 by Fisher Scientific
- Zinc oxide ACS reagent grade by MO Biomedicals, LLC
- Zinc oxide Polystormor™ by Mallinckrodt Chemicals
- Zinc oxide Nanopowder by American Elements

Samples were prepared at 5 wt % of ZnO in water. Particles were stabilized against aggregation electrostatically by enhancing their electric surface charge with sodium hexametaphosphate. Optimum dose of surfactant was determined by measuring the zeta potential of each suspension

All measurements in this study were performed using the DT-1201 system manufactured by Dispersion Technology (Figure 1). This instrument is designed for characterizing concentrated dispersions and emulsions with the volume fraction above 1% with no dilution. The configuration for this study included sensors to monitor particle size, zeta potential, temperature, pH and conductivity.

Results and Discussion

A particle size distribution was measured for individual samples and for one mixture of two different samples at different ratios.

Individual samples

Multiple measurements of particle size distribution (PSD) were performed for every sample. Table 1 presents the arithmetic average of the median particle size and the cumulative percentage of particles with diameter less than 100nm. These powders have very different sizes in the range from 220 nm to 660 nm. Precision of this measurement is defined as ratio of the "absolute average deviations" to the "average content". The precision of samples other than the last listed in the table is below 2% - values characteristic of this instrument.

POWDER Name, Manufacturer	Median size, microns	Cum % of nano-particles <100 nm
Zinc oxide, 99.5+% by Acros Organics	0.273±0.01	11.0±1.4
Zinc oxide, reagent ACS by Acros Organics	0.430±0.02	7.0±0.5
Z50-500 USP powder packaged by Fisher Scientific	0.561±0.017	2.7±0.39
Z52-500 USP powder packaged by Fisher Scientific	0.660±0.037	1.9±0.4
S80249 by Fisher Scientific	0.398 ± 0.001	6.1±0.2
Zinc oxide ACS reagent grade by MO Biomedicals, LLC	0.349±0.017	8.2±2.1
Zinc oxide Polystormor by Mallinckrodt Chemicals	0.223±0.009	19.6±1.8
Zinc oxide Nanopowder by American Elements	0.631±0.1	4.7±2.5

Table 1: Average median particle size and percent smaller than 100 nm

The measured particle size distributions are shown in Figure 2. All distributions are broad (understood to be wider than one decade) with sizes on nano-scale, sub-micron and micron scales.

The powder with the largest size is Z52-500. This powder has the least amount of nano-particles, about 2%, as seen in Table 1. The powder with the most content of nano-particles is from Mallinckrodt, containing ~20% nanoparticles. These two powders were used for making the mixture consistency test described below.

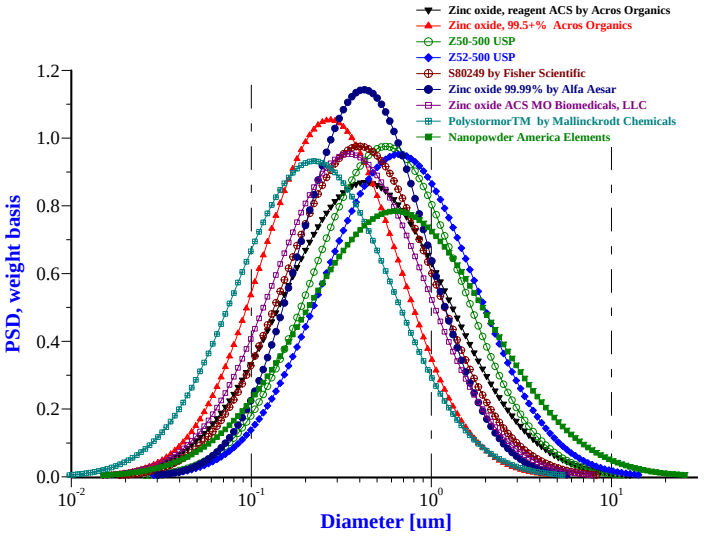

Figure 2: Differential particle size distributions calculated from acoustic attenuation spectra assuming lognormal distribution shape.

Mixture Test

A mixing test was performed as a final verification of the method and instrument. The base powder for the mixing test is Z52-500. The initial sample weight is 100 g, sufficient for filling the DT-1201 sample chamber. The Mallinckrodt sample was added to the Z52-500 in the increments of 2 g and then 4 g. The final mixture contained 26 g of Mallinckrodt sample and 100 g of Z52-500 sample. There are two ways to estimate the nano-particles content in this set of mixtures with different content of Mallinckrodt in Z52-500. The Mallinckrodt sample contains 20% of the nano-particles and the content of the Mallinckrodt sample in the each mixture is known. This is sufficient for calculating the nano-particles content in each mixture. This number is the X-axis value in Figure 3. For the other data set the attenuation of the each

mixture is measured and the particle size distribution is calculated. This is the same procedure as for the individual samples. This number is shown on the Y-axis value in Figure 3.

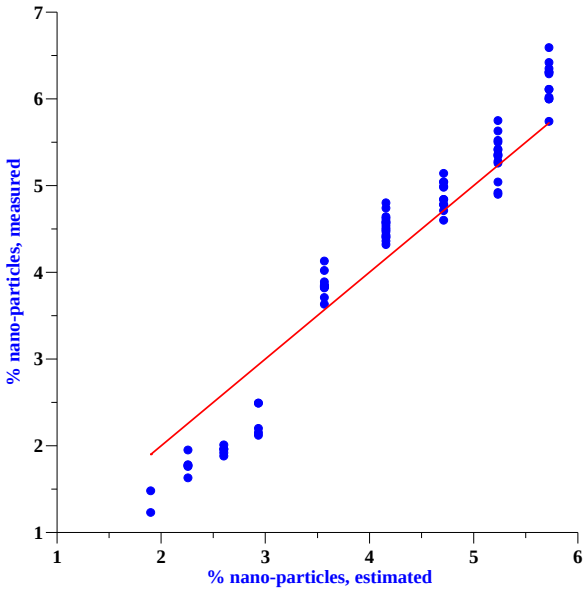

Figure 3: Percentage of nano particles in Z52-500 sample after incremental additions of the Mallinckrodt Chemicals sample. The X-axis is a percentage calculated from the known amount of the added Mallinckrodt sample, assuming that it contains 20% on nano-particles, according to Table 1. The Y-axis is a percentage calculated from the attenuation spectra, which is measured for the mixture.

If everything is consistent, both methods should yield the same nano-particles content in each particular mixture. Graphically this would mean that this ideal situation would be represented by the median line in Figure 2. Actual measurements are represented with circles in Figure 5. Acoustic spectroscopy yields nano-particles contents in these mixtures that agree well in trend with the expected values. Observed deviation is on the scale of 1%. This is significantly less than the ~ 2% precision level determined for the individual samples. This mixing test confirms the consistency of the described characterization procedure.

Conclusions

Acoustic particle size characterization provides the ability to monitor nano-particles content in dispersions with broad particle size distributions with precision of at least 2%. Measurement can be achieved in concentrated dispersions, thus improving the representative nature of the sample compared to those methods that require dilution. This conclusion is confirmed by multiple measurements of individual samples of eight different ZnO dispersions and their mixtures.

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