Conference Report: International Workshop Dispersions Analysis and Materials Testing, September 2016, Berlin, Germany

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Over 80 participants from 14 countries came together at this year's workshop hosted by the LUM GmbH in Berlin (26-27 September 2016). CEO Prof. Dr. Dietmar Lerche welcomed 24 speakers representing companies, universities and other research institutes, which all use one or more of the LUM scientific instruments. The technical and scientific issues under discussion referred to the fields of particle characterization, mechanical strength, stability and processing. Four nominees for the Young Scientist Award 2016 presented their scientific work in a separate session.

Particle characterization

Analytical centrifugation with measuring time- and position resolved light transmission delivers extinction weighted size distributions of the particles' Stokes diameters. A cooperation project of TU Dresden, LUM and Doshisha University in Kyoto, Japan (Prof. Yasushige Mori) aimed at developing a transformation method from extinction weighted to volume or number weighted size distributions, which does not refer to a model that describes the optical behaviour of particles (e.g. Mie theory). As **Dr. Frank Babick**, TU Dresden, pointed out, this transformation can successfully be made by applying multi-wavelength analysis of photo-centrifugation data. Promising results were obtained with mineral materials SiO_2, Al_2O_3, TiO_2 as well as with Au. However, there seem to be materials, with which this transformation method without knowing the refractive index is not applicable..
Julia Groß, Boehringer Ingelheim Pharma GmbH reported about a study to evaluate the STEP technology (LUMiSizer) for protein particle detection and protein aggregation studies, especially for the analysis of mAB solutions and highly concentrated liquid formulations (HCLFs). The main challenge for analysing these protein formulations is given by their low turbidity. It was shown that the LUMiSizer could successfully be applied, if the turbidity of the protein solution had previously been increased by mechanical or thermal stress on the proteins.
Dr. Svetoslav Jovtchev from Medical University of Sofia, Bulgaria, focussed on the influence of different polymers on the tendency of red blood cells to aggregate. Polymers like dextran, polyethylene glycols or starches are used in medical solutions like plasma expanders or organ preservation solutions. While zeta sedimentation technique (ZSR) has been used for years to determine the haematocrit value of polymer-RBC formulations, the recently applied LUMiFuge delivered various parameters of the sedimentation process. Thus the aggregation potential of different polymer molecules in different concentrations could be analysed.

Analytical centrifugation has also proved a suitable tool to measure size distributions of nanoparticle formulations. Thus this measurement principle is currently evaluated

in the frame of the EU project NanoDefine (cf. www.nanodefine.eu), which was presented by **Christian Ullmann** from TU Dresden. According to the definition given by the European Commission in 2011, nanomaterial is a material with more than 50 % of the particles in the number size distribution having their smallest dimension below 100 nm. Within NanoDefine the accuracy and reproducibility of measuring “real world materials” (not spherical, some of them are borderline materials with dimensions near 100 nm) with different analytical centrifuges were compared.
The research group of **Prof**. **Dr**. **Eli Sloutskin** of Bar-Ilan University, Israel, discovered the spontaneous emergence of density staircases that is regions of constant particle concentration during the settling of nanoparticle suspensions. The staircases turned out to be a thermal effect due a (very small) vertical temperature gradient in the cell. Settling under centrifugation was carried out with different core materials (e.g. Ag, Cu@Ag, Fe_2O_3), different ligands, different solvents, and different core diameters from 7 to 14 nm. The results showed that the observed phenomenon does not depend on the chemistry of particles or solvents. It can be amplified by larger gradients and suppressed by a filling height of sample below 10 mm. Interestingly; particle size distribution has also an influence upon this phenomenon.

Mechanical Strength

This session addressed the testing of materials and material compounds by using the adhesion analyser LUMiFrac. **Jörg-Manfred Stockmann**, Bundesanstalt für Materialforschung und -prüfung (BAM) compared the established tensile testing machine for hardness testing of materials with the centrifuge technology. The hardness of a material is determined as amount of deformation of a material sample after being dented by a solid body (as sphere (Brinell hardness) or four-sided pyramid (Vickers hardness)) with a fixed force. While only one material sample can be tested with one indenter and force at the same time in the conventional tensile testing machine, the centrifuge allows measuring up to 8 samples at the same time. For this purpose, the indenters are fit into mass bodies, and each mass body and the corresponding material sample are installed in a guiding sleeve to allow only radial forces to act on the mass body. For identical testing forces (determined by the rotational speed of the centrifuge) and identical indenters the deviations of the test results between conventional and centrifuge methods were only 1 % for Brinell and 4 % for Vickers. The hardness data from the centrifuge complied with existing standards.
LUMiFrac was invented for measuring the bonding strength of coatings or composite materials. As **Daniel Grunwald**, BAM, showed in his presentation, the bonding strength depends on the bonding area and the temperature. It was found for all considered adhesives that the bonding strength decreases with increasing bonding area. It was assumed that with larger bonding areas the probability of areas with defective adhesive layers and the effect of possible lateral forces increase. The influences of storing and measuring temperature on the test results, depending on the particular adhesives, were also shown.

Young Scientist Awards

Four young scientists from institutes in Germany, Switzerland, and Australia had been nominated. At the INM Leibniz Institute for New Materials in Saarbrücken, **Dr. Johann Lacava** investigated the ageing stability of hexane-in-water emulsions containing gold nanoparticles [1]. The nanoparticles build up clusters with a defined structure inside the emulsion droplets, but the emulsions undergo severe aging during storage. Surfactants are added to stabilize the emulsion and prevent the nanoparticles from segregating to the liquid-liquid interfaces [2]. The impact of different surfactants on the interfacial tensions within the emulsion and on the emulsion stability was examined by using the LUMiSizer.
Sam Skinner from University of Melbourne uses analytical centrifugation, gravity sedimentation and constant pressure filtration as lab-scale tests to quantify dewatering characteristics of wastewater sludges. For this the two material functions compressive strength $P_y(\Phi)$ and the hindered settling function, $R(\Phi)$ (also called rate of dewatering) of different sludge samples are measured. Skinner showed that the filter size prediction based on the measurements with the analytical centrifuge showed errors up to 20 %, due to the influence of wall effects in the comparably small measuring cuvette. Further analysis with the LUMiSizer in combination with the X-ray sedimentation analyser LUMiReader X-Ray helped to develop a modified analysis method which takes these effects into account [3|.
Michel Vong from Swiss Laboratories for Materials Science and Technology (Empa) reported on optimizing the fabrication process of polyurethane foams containing new solid, environment-friendly flame retardants (FR) based on bis-DOPO derivatives. The dispersion process for FR particles in polyol consists of two steps: dry-milling of solid FRs followed by milling the crushed FRs with the polyol. The proper temperature, concentration, chemical structure of DOPO derivatives as well as the molecular weight of the applied polyol were chosen by means of stability analysis in the analytical centrifuge.
The research by **Johannes Walter** from Nürnberg University mainly focuses on applying an analytical ultracentrifuge (AUC) for multidimensional nanoparticle characterization [4]. This instrument type differs from an analytical centrifuge (AC) in different aspects: the particles undergo much higher centrifugal accelerations under vacuum, and particle analysis uses the whole wavelength spectrum from NIR to visible light. The AC LUMiSizer applies four individual light wavelengths, and the maximum centrifugal acceleration is much lower than in the AUC. Walter demonstrated how the LUMiSizer capabilities with respect to particle characterization could be successfully increased by adopting knowledge and software for data analysis from recent AUC developments.
Due to the very good applications, the YSA prize 2016 was upgraded and awarded to two of the four nominees: Samuel Skinner and Johannes Walter.

Stability

Dispersion stability is an important issue in the industrial production of new materials, food products, pharmaceutical and cosmetic products, and for all these cases examples were presented**. Albert González,** Institute of Advanced Chemistry of Catalonia, Spain, tested aqueous polymer solutions containing high concentrations of inorganic filler particles. Sedimentation velocities were measured in a LUMisizer using NIR light, if possible. Some of the samples under consideration were too opaque, thus the combination of centrifugation and sedimentation analysis with LUMiReader X-ray was chosen. In some cases the discrepancy between measured sedimentation velocities and expected values according to Stokes' law led to the conclusion that viscoelastic behaviour occurred during centrifugation.
The presentation of **Dr. Kai Reinecke**, GNT Europa GmbH, Aachen, dealt with dispersions of colouring foods. For example, dispersions of colouring materials in sunflower oil are applied as fat glazes. Their stability depends on the particular colour. This is due to the fact that particles of different colours are extracted from different raw materials and have different sizes. In soft drinks, colouring ingredients may undergo creaming or sedimentation during storage. Here stability analysis is applied to optimize homogenisation processes, e.g. particle disintegration by ultrasound.
Dr. Claudius Weiler, Boehringer Ingelheim Vetmedica GmbH, reported on the characterization of pharmaceutical suspensions, which are produced for oral administration to animals. Besides characterizing the sedimentation behaviour by analytical centrifugation the particle size distribution was determined by laser diffraction. In addition, viscosity measurements and visual inspection via light microscopy were carried out. Some of the suspensions exhibited slower sedimentation velocities than expected according to Stokes' law, due to inter-particulate effects and rheological characteristics of the liquid phase.
The French company Agronutrition produces liquid fertilizers that are applied by spraying over leaves and stems of plants. **Vincent Pradines** explained that some products are dispersions of insoluble mineral particles in a liquid that consists of water and some additives like thickening and wetting agents. Prior to dispersion the particles are grinded to obtain sizes of 1-2 µm. Analytical centrifugation helps to determine the sedimentation kinetics. This turned out to be very sensitive to the chemical nature and concentration of the minerals and auxiliary substances, to possible impurities, and to the size and size distribution of the mineral particles.
Sarka Tumova from Brno University of Technology in Czech Republic compared analytical centrifugation to conventional techniques for the determining the temperature stability of cosmetic emulsions. As conventional measures storage at elevated temperature (45 °C) over a period of 3 months with intermediate visual inspection and the so-called Freeze Thaw test, that is alternating storage at -10 and +50 °C in three cycles with 24 h duration at each temperature, were carried out. 12 emulsion formulations from 3 different cosmetic companies were tested conventionally and in the LUMiSizer. Centrifugal tests were carried out at different

temperatures. The results obtained with conventional methods and analytical centrifugation were not exactly the same, but it was confirmed that analytical centrifugation is a useful tool for assessing temperature stability of emulsions.

Processing

Dispersion characterization is often useful and necessary to optimize production processes, among them homogenization processes are mentioned most frequently. **Brigitte Schade**, Particle Solutions BV, applied an analytical centrifuge for comparing two different high pressure homogenization processes. The considered formulation was a pharmaceutical 10 % oil-in-water emulsion for injection that should exhibit storage stability of at least one year. The particle size was limited to < 0.2 µm, for the emulsion had to pass a sterile filter. The homogenization of the pre-mixed formulation was carried out by means of a dynamic valve homogenizer and a newly developed static capillary geometry homogenization (PSI 20). The LUMiSizer served as a fast, accurate and reproducible emulsion characterizer and thus enabled the fine-tuning of the process.
The production of particles as raw materials for sintered ceramics is implemented via spray-drying of slurries with 80 wt.-% solids. **Dr. Patrick Höhne**, BAM, referred to the development of additives, which enable these highly concentrated slurries to be pumped and sprayed. The optimum spray-dried granules should have a minimum fraction of hollow particles that downgrade the density and hardness of the sinter body. The optimization of the granules was achieved by a controlled destabilization of the ceramic slurry.
Florian Häffele from Karlsruhe Institute of Technology measured sedimentation velocities in bacterial starter cultures that are used for the production of fermented food. The bacteria should deliver large amounts of exopolysaccharides (EPS), which influence the rheology and mouthfeel of the food product. Depending on the respective bacterium type and EPS type (capsuled or not) to be released, shearing the cells can increase or decrease the sedimentation velocity. Thus the optimum shear treatment for each culture can be found.
Martin Müller, European Centre of Dispersion Technologies (EZD), presented a talk on the characterization of particulate fillers in polymers. This type of composite material may occur as flame retardant adhesive as well as a strengthened thermoplastic automobile part. To maximize the effect of particulate fillers, they should be homogeneously dispersed in the polymer matrix. Here, epoxy resins and thermoplastic materials, both filled with $CaCO_3$ particles, were characterized by measuring space- and time-resolved X-ray extinction profiles with the LUMiReader X-Ray. This method enables the detection of variations of particles concentration along the sample length within 30 s. Dispersibility of particles and processing can be quantified based on attenuation fluctuations.
Sebastian Süß, University of Erlangen-Nürnberg, referred to a study that aimed at developing a standard procedure to determine the Hansen Solubility Parameters (HSP) of nanoparticles. The HSP quantitatively describes the affinity of particles as

combination of disperse, polar and H-bond forces. As HSP data of a large variety of solvents are available, the knowledge of particle HSP will help to choose appropriate solvents for optimized particle dispersions. With nanoparticles from carbon black (mean size 23 nm) and ZnO (mean size 5 nm), which were dispersed in different solvents with known HSP, the procedure of determining the particle HSP by analytical centrifugation was elaborated.

Sam Skinner, University of Melbourne, in his second talk again referred to the measurement of shear and compressive strength of suspensions. Now he focused on coagulated industrial suspensions. With model suspensions of $CaCO_3$, profiles of equilibrium solids concentrations over the sample height were measured for different centrifugal forces (LUMiSizer). The measured concentration profiles were compared to model predictions. A software tool was developed for equilibrium centrifugation data analysis to distinguish between shear and compressive strength and to account for the wall effects.

At Compiegne University of Technology, France, **Dr**. **Maksym Loginov** and his team use analytical centrifugation for the characterization of sludge filterability. In detail the pressure dependency of filterability of concentrated aggregated suspensions in terms of particle volume fraction and specific cake resistance was measured by applying different experimental protocols (centrifugation in one, two or more stages, different modes of varying rotational speeds) to concentrated suspensions. It was shown that samples need to be pre-consolidated at low rotational speed in order to obtain correct data on centrifugal consolidation afterwards.

The last talk of the event was given by **Dr**. **Sebastian Stahl,** Danisco Deutschland GmbH. He focussed on the influence of fermentation time in bioreactors on the sedimentation behaviour of the fermentation broth. The data obtained by analytical centrifugation revealed a decrease of sedimentation velocity with increasing fermentation time. Optimization of downstream processing and optimum harvesting point were achieved by this information

The next International Conference and Workshop Dispersion Analysis & Materials Testing will take place in Berlin, Germany, from 29-30 January 2018.

References

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