Press Release

Conference Report: International Workshop on Dispersion Analysis and Materials Testing 2014

Again, the LUM GmbH, specialized in the development and production of analytical devices for dispersion analysis and particle characterization, hosted their traditional annual International Workshop in Berlin, and this year the event coincided with the 20 th anniversary of the company. In the course of the years this workshop has steadily grown in the number of participants and internationality. So researchers from Germany, Switzerland, Belgium, France, Great Britain, Russia, Israel, Japan and Australia joined the meeting to present and discuss their research results concerning the production and optimization of nanoparticle suspensions, foams and emulsions as well as separation characteristics of solid-liquid systems. For the first time, a special award for young scientists, who work with analytic systems of LUM GmbH, had been launched before, and the audience was presented a series of very remarkable and ambitious research projects by the nominated candidates.

Characterization of particle surfaces and particle interactions

For many years, Prof. Nirschl and co-workers from the Institute for Mechanical Process Engineering at Karlsruhe Institute of Technology (KIT) have been researching in the field of particle-particle interaction as well as interactions between particles and rigid walls. Prof. Nirschl gave an overview over the different types of interactions, which, among other things, are essential parameters for the success of filtration processes and the possibilities to clean filter media from filter cakes. In recent time special emphasis was laid on the centrifugal separation of super-magnetic particles, which are functionalized with ion exchanger molecules, from liquids. The superposition of the centrifugal field and a gradient magnetic field is achieved by a wire matrix installed inside the centrifuge chamber. The functionalized particle surface binds target molecules, and a strong magnetic field induced by the wire matrix together with the centrifugal field allows for a very selective separation at high throughput. Inter alia, the separation of target molecules from fermentation broths was mentioned as application. For analysing all adhesive forces acting on those particles the superposition of magnetic and centrifugal forces was realised in a LUMiFuge equipped with newly developed sample holders, where different magnets could be used for attracting magnetic particles on defined substrates. Force load applied simply by centrifugal field upon interacting particles allows to quantify interaction strength, and contrary to alternative analytical systems this measuring system allows determining a high number of particle interactions with a limited number of experiments. In doing so, the magnetic and van der Waals adhesion force can be distinguished, and the dependency of total adhesion forces on the strength of the magnetic field, the diameter of magnetic particles, and on other particle characteristics (e.g. surface roughness) can be differentiated. However, comparing the adhesive forces measured with and without applying a magnetic force revealed, that the particles are deformed by magnetization.

To evaluate the solubility of molecules within different solvents the Hansen solubility parameters (HSP) are regarded as quantitative measure. In detail they describe affinity as combination of the energies from dispersion forces, from dipolar intermolecular force, and from hydrogen bonds between molecules. In the three-dimensional parameter space the HSP form the centre of a sphere with a so-called interaction radius. If a molecule and a solvent have similar HSP, the molecules are easy to disperse within the liquid ("like seeks like"). Shin-ichi Takeda from Takeda Colloid Techno-Consulting in Japan described, how he extended the HSP concept on nano-particles which are to be dispersed in liquids, and how the HSP parameter sphere can be determined by a LUMiReader. The way is to measure the dispersibility of a nanoparticle in different solvents with known HSP (HSPs of solvents are available in a database under www.hansen.solubility.com). The relative sedimentation velocity of the particle under consideration (sedimentation velocity normalized by the quotient of solvent viscosity and density difference of particle and solvent) serves as measure for the HSP calculation.

Measurement of size distributions in nanoparticle suspensions

Optical centrifugation analysis is one of several methods to determine particle size distributions in colloidal suspensions. As colloids often contain particle agglomerates, large variations in the measurable size and shape of detected particles may occur in such formulations. Dr. Frank Babick, Technical University of Dresden, addressed the differences between the results that different measuring systems deliver from colloidal aggregates. He compared the particle size distributions obtained with two systems for dynamic light scattering and sedimentation technique (LUMiSizer) for pyrogenic powders and showed how the characteristic parameters measured with the respective systems (intensity of scattered light and hydrodynamic properties) depend on the fractal dimensions of the aggregates. Apart from the different particle properties measured with different systems, these systems use different methods to weigh different size fractions. On the basis of the relationships between agglomerate structure and measured properties together with some assumptions concerning the aggregate structure (monodisperse, spherical primary particles, DLCA-like aggregate structure) the measured particle size distributions were converted from optically weighted to number weighted distributions, which were more similar for both measurement techniques. This research is described in detail in [1], [2].

The RUSNANO Metrology Center at the Moscow Institute of Physics and Technology offers reference nanoparticles from Al2O3, TiO2, SiO2, and ZnO in form of colloids with certified number-based and intensity-weighted mean particle sizes. Such reference colloids can be applied for the calibration of particle measurement systems, for in vitro assessments of the impact of nanomaterials on living systems, and for round robin filter tests. Anna Lizunova described the measurement procedures that are carried out to determine sizes and size distributions. They use transmission electron microscopy, acoustic spectroscopy, optical centrifugation analysis with the LUMiSizer and dynamic light scattering. TEM results revealed that ZnO particles have a grained, subangular shape, while the other materials have almost spherical shapes, and that all colloids exhibit log-normal size distribution with the exception of SiO2, which showed a normal distribution. The TEM diameter for all colloids was about 30% lower than the values given by acoustic spectroscopy and analytical centrifugation. Dynamic light scattering delivers intensity weighted hydrodynamic mean diameters, which are about twice as high as the mean values obtained with acoustic spectroscopy and analytical centrifugation. With spherical particles and a normal size distribution, best agreement of data from different measurement systems was achieved. The highest discrepancy of measured values from different systems could be found with ZnO, due to the non-spherical shape of the particles.

Dr. Keren Fogel, Perrigo Israel Pharmaceutical Ltd., gave a talk about the application of LUMiSizer as bioequivalence tool in nasal spray development in the generic industry. Bioequivalence means that the generic product is comparable to an innovator product (Reference Listed Drug –RLD) in dosage form, strength, route of administration, quality and performance characteristics, and intended use. The U.S. Food and Drug Adminsitration (FDA) requires bioequivalence of the generic product to be between 80 % and 125 % of the RLD. In this particular case, the pharmaceutically active compound is present in form of solid particles in a liquid. As the Active Pharmaceutical Ingredient (API) is micronized, but agglomerated, the whole mixture is homogenized in a high-shear mixer. Comparison of particle size distributions of the API in the RLD and the primary formulation was done by spectroscopic particle analysis, and the optimization of the generic formulation by varying the homogenization time was controlled by applying the LUMiSizer. The optimum formulation was again analysed by using the spectroscopic method to verify similarity in the particle size distributions of RLD and generic product.

Bioavailability of lipophilic APIs that are poorly soluble in aqueous liquids can be increased by reducing the particle size of colloids, e.g. by wet media milling. Dr. Michael Juhnke, Novartis Pharma AG, Basel, reported on the development of colloidal drug suspensions, which can be delivered in dragees or tablets or by injection. In the preclinical and early clinical development stage, only very small amounts of API are available to carry out milling experiments and collect samples for measuring purposes, which are necessary to optimize the respective formulations. The results of milling trials in planetary mills are analysed by means of the LUMiSizer system. To date particle sizes of about 200 nm of his API can be realised. Apart from the particle size distribution, rheological properties, electrokinetics and physical stability of the formulations are tested.

At the Materials Research Centre of Brno University of Technology in Czech Republic, Prof. Miloslav Pekař and co-workers prepare hydrocolloids from lignite by high-speed dispersion and wet-milling. The idea is to use lignite as natural fertilizer and soil conditioner in the form of concentrated fluid dispersions or pastes, because these formulations are easier and cleaner to handle as dusty powdered lignite. In addition, preparing hydrocolloids leads to the release of parts of the inherent humic substances into the aqueous phase, making them accessible to the soil directly after the application. Besides water, different additives like KCl, citric acid or urea can be added to support the fertilizing effect. Here the results of different analysing procedures by means of the LUMiSizer, a rheometer, laser diffraction etc. were shown. Wet-milling reduces the size of original particles from about 10 µm to about 1.5 µm (D50 in a relatively wide distribution). The advantages of the direct sedimentation analysis in original concentration, quantified by Instability index, allowed the successful use of LUMiSizer. As expected the wide particle distribution was not displayed by the analytical centrifuge, because particles sedimented as swarm, when measuring in the original high concentration. A dilution of the samples would help. With increasing milling time, the stability of the hydrocolloids increases and so does the viscosity. Addition of urea in high concentrations has a similar effect that was explained by interactions between urea and lignite particles.

Stability of suspensions

Stable suspensions are essential prerequisites for many industrial processes. Dispersions of carbon black in n-alkanes are stabilized by adding block copolymers on the basis of poly- styrene. Dr. David. J. Growney from University of Sheffield, UK, used the LUMiSizer to assess the effect of different polymer compositions and their concentrations as dispersants in different solvents. It could be shown that e.g. the same dispersant exhibits a good stabilizing effect in n-alkanes as solvent, because here the dispersant attaches to the particle in form of micelles, while in toluene as solvent the stabilizing effect is poor, due to the fact that single copolymer chains are adsorbed to the particles. Besides the dispersion stabilisation the measurement of sedimentation velocities allows for calculating the new particle density (new particle built of carbon black and absorbed copolymer) and for subsequently determining the true particle size distribution in the stabilized dispersion. The degree of dispersion with polystyrene diblock copolymers is influenced by the polystyrene content, because with higher PS content larger micelles that aid dispersions are built. It was also shown that Star diblock copolymers act as flocculant at low concentrations, while at concentrations above 6 wt % they exhibit a stabilising effect.

Dr. Stephan Appel from company OSRAM gave insight into the production of fluorescent lamps and outlined the meaning of the sedimentation characteristics of coating suspensions for the products. In an early production step of low-pressure fluorescent lamps the inner surface of a tubular bulb made from glass is coated with a phosphate suspension. The phosphate particles have a quite wide particle size distribution, which is necessary to get all wavelengths from irradiation with UVS, resulting in white light being emitted from the lamp. The coating is dried and burnt afterwards, and for the functioning of the lamp a dense coating layer over the entire surface of the glass is needed. Internal fissures within the coating as well as a coating thickness gradient along the bulb length are unwanted. It was shown with the aid of transmission profiles obtained with the optical centrifuge, that fissures within the coating are the outcome of particle aggregation. On the other hand, a high residual turbidity after a certain time of sedimentation, e.g. a very high dispersion grade, leads to a higher risk of thickness gradient. The coating suspensions reveal viscoelastic behaviour, and the comparison of rheological data with the transmission profiles led to the conclusion that the optimum suspensions are those with nearly equal G' and G'' modules.

Wear-resistant gold coatings are the aim of research activities of Dr. Anja Meyer and co-workers from Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Dresden. They try to produce gold coatings with integrated nanocrystalline ceramic particles, which are added to the electrolytic bath for electrochemical precipitation. In doing so, nanoparticles with positive surface charge can be deposited on the substrate together with the gold ions, or uncharged nanoparticles may be incorporated into the gold layer, when they are randomly distributed near the cathode. As prerequisites the nanoparticles (Al_2O_3) must be well dispersed within the bath. The LUMiSizer was applied for the screening of dispersing agents in different suspension preparations. As for adding dispersion agents directly to the electrolyte bath the effect of the dispersion agents was omitted by the high electrolyte content, the preparation route was changed. The better route was to prepare a stable dispersion from particles and water with the aid of a dispersing agent, subsequently dehydrating this suspension and adding the electrolyte solution afterwards. Particle size distributions and sedimentation velocities for this route revealed a stable dispersion of fine particles, and first coating trials resulted in Au-layers with clearly detectable, incorporated nanoparticles. The research with respect to influencing parameters on achievable hardness, layer thickness, and other features of the coating is going on.

Dr. Isabel Giraud, University Paul Sabatier (Paris) gave two examples from very different application fields of testing the stability of aqueous dispersions. In aerospace new composite materials are made from temperature stable thermoplastics with embedded carbon fibres. As carbon fibres and thermoplastics show low compatibility, the production of defect-free materials turned out to be complicate, and there is no sizing available for these polymers. The solution of the problem was found in aqueous dispersions made from the respective polymer particles (Polyetherimide (PEI) and Polyetherketoneketone (PEKK), which are stabilized by surfactants. The optimum composition (polymer concentration, nature and concentration of surfactant) was found by analytical centrifugation and dynamic light spectroscopy (details cf. [3]). The second example was given from the field of cosmetics and referred to the preparation of dispersions of gelled sunscreen oil. By adding an organogelator to the oil, jellylike nanoparticles are formed that are dispersed in water afterwards by using a stabilizing agent. The stability of these dispersions was compared to the stability of a standard O/W emulsion made from the sunscreen oil. Gellifying the oil turned out to make more stable dispersions than the standard emulsifying procedure.

Emulsions and foams

Yogev Dahan from Perrigo Israel Pharmaceutical Ltd. described the production and stability analysis of emulsion foams, which are considered to satisfy a growing demand on the pharmaceuticals markets because of their convenient application possibilities contrary to ointments or liquid formulations. The question of stability arises, because the original aerosol is stored under elevated pressure in the can before being applied. The LUMiFuge results (transmission curves and results of separation front tracking) showed that the foam stability depends on the preparation of the oil in water emulsion. The ways of preparation differ from each other in the temperatures of the two phases during mixing and afterwards. Product stability for about two weeks at 25 °C means an equivalent separation time within the analytical centrifuge of 20 to 40 min. As in the competitive area of the pharmaceutical industry, development time is an essential factor, applying the LUMiFuge means a clear progress in this field.
Double W/O/W (water/oil/water) emulsions are applied in the production of fat-reduced creamy foods such as light mayonnaise, or if a sensitive substance must be embedded to prevent oxidation. Mathieu Balcaen and collegues from the Particle & Interface Technology Group of Ghent University, Belgium, work in this field and they tested analytical centrifugation for yield determination of such emulsions. A W/O/W emulsion is made by preparing an O/W emulsion, which is subsequently emulsified in water by using a stabilizing agent. The yield parameter to be analysed is the resulting percentage of aqueous phase remaining within the oil droplets after the second preparation step. As the analytical method that has been applied so far, a low resolution PFG (pulsed field gradient)-NMR-spectroscopy, is a costly and time-consuming method due to complicate data analysis, a LUMiFuge was applied. Here oil droplets with internal aqueous phase (referred to as cream) are separated from the surrounding water phase (serum). With front tracking the volume of the cream layer can be calculated, and by subtracting the oil volume from this value, the yield parameter is obtained. To prevent rebound of the creamy phase, measurements must be carried out at high rotational velocities. Several samples with different compositions were analysed with both systems for comparison. Good matching of the results obtained with PFG-NMR-spectroscopy and the LUMiFuge was observed. However, the LUMiFuge offers a much more simple and straightforward data analysis.

Characteristics of sediments

The colloidal interactions through sedimentation and the compressive yield stress data were in the focus of Prof. Simon Biggs from University of Leeds, UK. These features are of major interest when a colloidal dispersion settles out, especially with respect to filtration, pumping or and/or re-suspension issures. As practical applications the optimization of inks for printers, polymer depletion flocculation processes and experiments with colloidal dispersions that serve as models for highly active nuclear waste (cf. /4/) were mentioned. Reprocessing of spent nuclear fuel produces a highly active liquor (HAL) waste stream. These liquids are stored in tanks and continuously cooled. Over the time particles are known to precipitate, which cannot be removed from the enclosed system. One has to take care, that the particles remain dispersed in order to prevent incrustation of heat transfer areas.
At the Particulate Fluids Processing Centre of the University of Melbourne Dr. Shane Usher also examines colloidal interactions through sedimentation and measures compressive yield stress data, in detail with focus on the dewaterability of suspensions like mineral sludge and sewage sludge. Dewaterability is expressed by a phenomenological model using the parameters compressive yield stress Py and the hindered settling function, R. Both parameters depend on the volume fraction of solids, which is proportional to the viscosity and inversely proportional to the permeability of the sediment. As further characteristic a gel point that is the minimum volume concentration, at which gelation sets in, is determined. To cover a broad range of volume concentrations, sedimentation was examined with batch settling, pressure filtration and centrifugation. Centrifugation was realized with a LUMiFuge (cf. [5]) at intermediate concentrations of solids. It could be demonstrated that equilibrium centrifugation data can be used to predict the yield stress Py as function of the sediment porosity (realized with step-wise rising rotational velocity), when the concentration was below the gel point and

rotational speed is high enough to exhibit sediment compression. With step-wise lowering the rotational speed re-expansion was observed. With rebound yield stresses and the yield stress at maximum solids volume fraction within the sediment the elastic rebound factor was determined. This factor was between 2 and 4 for all materials tested so far. It was assumed that it is correlated to a natural physical constant as the Trouton ratio.

Sedimentation characteristics with focus on the filterability of solid-liquid systems are examined by a research group at Laboratory of Agro-Industrial Technologies at University of Compiègne in France. Maksym Loginov explained the measuring procedure with a small filter element mounted into the cuvette of the LUMiSizer. Twelve samples can be analysed simultaneously and allow a heigh through put. With this equipment the filtration kinetics for different juices and extracts, suspensions and sludges were determined. From experimental data the filter resistance, permeability and specific resistance of the filter cake can be calculated.

Biomechanical properties of bone samples

With the application of a LUMiFuge to determine the elastic moduli of bone samples a new application field for analytical centrifugation was probably opened up: the testing of solid bodies. Prof. Bäumler and his co-workers from university hospital Charité in Berlin are interested in the influence of different disinfection methods (sterilization by per-acetic acid or heat treatment) on the mechanical properties of bone material that is intended to be transplanted into the jaw. Similar to the determination of yield stress in sediments the deformation of a bone sample under the influence of different rotational velocities was measured in the LUMiFuge. The trabecular structures of bone samples were examined by Micro-Computer Tomography (μ-CT), and elastic moduli obtained by analytical centrifugation were compared to the results achieved with a conventional test bench for determining mechanical properties for biomaterials. The application of the LUMiFuge turned out to be successful. Furthermore analytical centrifugation has several advantages compared the test bench: It allows for the simultaneous characterization of at least 8 samples, the samples are exposed to lower mechanical deformation, therefore less structural damage occurs during the measurement, and the testing can be carried out in different environments including cell culture media.

New analytic system for measuring adhesive strength

The new Adhesion Analyser LUMiFrac is a novel testing device which uses centrifugal force as tensile testing force in a multisample arrangement within a drum rotor of a desktop centrifuge. The system was developed by LUM GmbH and the Federal Institute for Materials Research and Testing (BAM = Bundesanstalt für Materialprüfung) in Berlin. Stefan Hielscher from BAM described the new system and showed results of a comparative study on the adhesive strength of optical and ophthalmic coatings. For determining adhesive strength only single-sample tests have been available so far, and most of them delivered rather qualitative than quantitative evaluations of the stability of joints between coating and substrate. LUMiFrac allows for simultaneous determination of strength values (as N/mm²) for up to 8 samples under identical test conditions. Here the influence of adhesive parameters (e.g. substrate thickness, surface-pretreatment or adhesion-promoter) can directly be analysed.

Young Scientists Award

Four contributions of young scientists from Israel, Iran and the United Kingdom were presented to the audience.

Suzanna Azoubel from Hebrew University in Israel gave a talk on the formation of carbon nanotube dispersion and their characterization by analytical centrifugation. CNT dispersions are examined as possible cost-effective alternative for indium tin oxide as transparent conductive material, which is applied in touch screens. To produce a flexible film from CNT, they must be supplied as stable dispersion. CNT are hardly soluble in many liquids and show a strong tendency to aggregate. To overcome these obstacles, CNT dispersions were homogenized under high pressure. Inter alia the dispersibility of CNT was increased by functionalizing through carbonisation increases the dispersibility. The LUMiFuge was applied for the rapid quality controlling of the CNT dispersions.

Lalel Solhi from Iran Polymer and Petrochemical Insitute focussed on the stabilisation of Montmorillonite (Na-MMT) nanoclays in dilute dental adhesives against unwanted segregation. Aim of the investigations is the improvement of the physic-mechanical properties of dental adhesives by adding poly(acrylic acid) grafted nanoclay platelets. Separation Analyser LUMiReader was applied for the determination of the sedimentation behaviour of these newly prepared dental adhesives in comparison to formulations with pristine Na-MMT nanoclay structures. The adhesives containing the

modified nanoclay showed a significant increase in the sedimentation time of the particles through the dilute solution of the bonding system (details see [6]).
"Probing the Stability of Sterically Stabilized Polystyrene Particles by Centrifugal Sedimentation" qualified Huai Nyin Yow from the University of Leeds, UK, for the final round of YSA candidates. In her talk the attention was put on colloidal dispersion stability. The presentation was given by her supervisor Prof. Simon Biggs, due to her absence caused by illness. The capability of the LUMiSizer was documented for the characterization of rheological properties of suspensions with polymer decorated „smart“ particles.
The prize was awarded to M.Sc student Shir R. Liber from Bar-Ilan University in Israel for her contribution “Dense colloidal fluids form denser sediments”. In her research the LUMiFuge was applied to relate the density of colloidal fluids with the nature of their randomly packed solid sediments, Centrifuge experiments with different concentrations of poly(methyl methacrylate)(PMMA) colloidal spheres suspended in decahydronaphatalene revealed that the packing densities of the sediments vary monotonically with the volume fraction of the initial suspension. The experimental data were reproduced by computer simulations (details see [7]).
The next International Workshop on Dispersion Analysis and Materials Testing will take place on 22-23 January 2015 in Berlin. On this occasion the Young Scientist Award 2015 will be launched.

References

[1] Babick F, Schießl K, Stintz M: Characterization of Pyrogenic Poweders with Conventional Particle Sizing Technique: I. Prediction of Measured Size Distributions, Part. Part. Syst. Charact. 29 (2012) 104 -115
[2] Babick F, Vorbau M, Stintz M: Characterization of Pyrogenic Poweders with Conventional Particle Sizing Technique: II. Experimental Data; Part. Part. Syst. Charact. 29 (2012) 116 -127
[3] Giraud I, Bergerat JM, Dantras E, Perez E, Lacabanne C: Novel stable aqueous dispersions of high-performance thermoplastic polymer nanoparticles and the uses of same as film-forming agents, in: CNRS, AIRBUS Operation, France, US2011300381, 2011
[4] Paul N, Biggs S, Edmondson M, Hunter TN, Hammond RB: Characterizing highly active nuclear waste simulants; Chemical Engineering Research and Design 91, Issue 4 (2013) 742-751
[5] Usher SP, Studer LJ, Wall RC, Scales PJ: Characterisation of dewateribility from equilibrium and transient centrifugation test data, Chemical Engineering Science 98 (2013) 277-291
[6] Solhi L, Atai M, Nodehi A, Imani M, Ghaemi A, Khosravi K: Poly(acrylic acid) grafted monmorillonite as novel fillers for dental adhesives: Synthesis, characterization and properties of the adhesive, Dental Materials 28 (2012) 369 -377
[7] Liber SR, Brohovich S, Butenko AV, Schofield AB, Sloutskin E: Dense colloidal fluids form denser amorphous sediments PNAS vol. 110, April 2013, 5769-5773

Author of this report: Dr.-Ing. Hildegard Lyko, Freelance specialised journalist, MLyko@t-online.de

Press contact
LUM GmbH
Justus-von-Liebig-Str. 3
12489 Berlin, Germany
Tel. +49-30-6780 6030
Fax +49-30-6780 6058
support@lum-gmbh.de
www.lum-gmbh.com