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Conference Report:

International Workshop Dispersions Analysis and Materials Testing 2018

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This year, the Workshop clearly focussed on particle characterization and stability analysis. With 16 lectures announced, of which two had to be cancelled, participants had good opportunities to discuss the interesting results from testing materials by means of analytical centrifugation and gravity sedimentation. A large variety of application fields was covered by the oral presentations, ranging from inorganic particles, bacteria cultures, dairy products, and fruit drinks to technical suspensions containing ceramic or organic particles as well as to emulsions for diverse industrial applications. Besides particle characterization and stability testing, the analytical instruments by LUM play a decisive role in the determination of filterability or in the optimization of production processes.

New at LUM

The main objective of the conference is to let customers from science and industry present and discuss their specific applications. Only in the beginning of the workshop, Prof. Lerche, managing director of LUM, took the opportunity to present recent developments within the company and their activities. In 2017 a new subsidiary, LUM Japan Co., Ltd., was incorporated in Tokyo.

The STEP-Technology®, which is implemented in the instruments LUMiFuge, LUMiSizer, LUMiReader as well as LUMiReader X-Ray, has proven to be well suited to characterize nanoparticles. This could be seen from the results of the EU project NanoDefine, which were described in detail in the presentation given by one of the nominees for the Young Scientist Award. During this project nano-particle data obtained by the LUMiSizer were compared with good results to the data from other measuring devices including a scanning electron microscope. SEM was regarded as reference method.

LUM is involved in diverse Technical Committees that develop and discuss standards for the characterization of particle systems and dispersions. For instance, a first draft of ISO/FDIS 18747 “Determination of particle density by sedimentation methods” (parts 1 and 2) has been published. Furthermore company members contributed ISO/TR1881:2018 on guidelines on stability testing of cosmetic products, which is now available.

Finally, the participants got the opportunity to see the new measuring system LUMiFlector, which was designed to determine the fat and protein content, and dry mass of milk and dairy products without pre-treatment or addition of chemicals within a measuring time of less than 20 seconds. The measuring device uses light from different wavelengths from UV to NIR to obtain data about refraction, scattering and fluorescence in one measuring step.

Particle and Surface Characterization

At the University of Leeds, Jessica Shiels works on the synthesis and characterization of two types of nuclear waste simulants, caesium phosphomolybdate (CPM, $Cs_3PMo_{12}O_{40}$ xH_2O) and zirconium molybdate (ZM, $[ZrMo_2O_7(OH)_2]$ $2H_2O$). She focuses on the sedimentation behaviour of these particles and the yield stress as well as on the permeability of resulting sediments. These research activities are part of extensive studies, which have already been done for several years with the aim to find a **p**ost **o**perational **c**lean **o**ut (POCO) strategy for the **h**ighly **a**ctive **l**iquor (HAL) that is produced from the fission products of reprocessing spent nuclear fuel. This waste is stored in so-called **H**ighly **A**ctive **S**torage **T**anks (HAST), and it is planned to vitrify and deposit it the future. Due to the extremely hazardous nature of the substances, there exists no possibility to monitor the particle behaviour within the HAL. Ms. Shiels measured the zeta potential of the simulant particles and analysed their sedimentation behaviour by analytical centrifugation in both acidic (2M HNO_3) and neutral environment (H_2O). As the nuclear waste is diluted in nitric acid before being stored in the tanks, the particle behaviour under these special acidic conditions is of special interest. It was shown that CPM shows similar sedimentation behaviour in both environments, and the compressibility and permeability of the sediment layer are similar as well. ZM revealed a much stronger dependency of pH. In acidic environment the particles tend to aggregate. Thus sedimentation velocity increases with larger aggregates, but the resulting sediment has a looser structure, which is easier to compress. However, up to now nobody can estimate, whether the particles within the HAL have the same form and size distribution and behave in the same manner as the simulants.

Particle stability and filtration behaviour of suspensions correlate strongly, because the porosity of a filter cake and the resistance for the filtrate may change, if particle breakage occurs during filtration. Benjamin Radel, from

Karlsruhe Institute of Technology (KIT), addressed the filterability of fragile protein crystals, which are recovered from fermentation broths by selective crystallization. As pharmaceutical proteins are very expensive, experiments that use only small volumes should help to find optimum conditions for a gentle solid/liquid separation. The influence of mechanical stress exerted on hen white lysozyme crystals (as model substance) during filtration was investigated by analytical centrifugation at different rotational speeds. The experiments were carried out in a specifically designed test cuvette with an integrated filter that allows the filtration of small volumes < 1 ml. The LUMiSizer delivered data about the sedimentation velocity and the filter cake height. The particle size distributions of the protein crystals were measured before and after filtration. Increasing the rotational speed in the analytical centrifuge, which corresponds to an increase of filtration pressure, led to a decrease of the coarse particles fraction and an increase of fines content. The investigations will be continued with differently shaped crystals.

In centrifugal sedimentation, different processes may lead to non-ideal sedimentation, e.g. if charged particles or non-Newtonian fluids are present or if hydrodynamic or thermodynamic interactions between particles and surrounding fluid occur due to higher particle concentrations. At the workshop 2015, Johannes Walter from Friedrich-Alexander University (FAU) in Nuremberg, first reported about the advantages of direct **b**oundary **l**ayer **m**odelling (BDM) of the data obtained with the analytical centrifuge [1]. With BDM, the accuracy and resolution of the measurement can be improved and systematic deviations from ideal sedimentation can be detected. This year, Maximilian Uttinger, from the same research group, presented an extended **B**rownian **D**ynamics (BD) based algorithm for simulating analytical (ultra)centrifugation experiments. This approach can be applied to describe interparticulate interactions by tracking the trajectory of individual particles. In doing so, both particle sedimentation due to the centrifugal force and the Brownian motion (diffusion) are taken into account. Concentration dependent sedimentation coefficients and diffusion coefficients are extracted from concentration series. When comparing the BDM approach to the simulation results from BD algorithm, a 100% match of sedimentation boundaries was found for ideal sedimentation. A detailed description of the BD approach is given in [2]. The simulation data give an indication of how to validate data from real centrifugation experiments.

Florian Häffele, Karlsruhe Institute of Technology (KIT), applied a disc centrifuge and the LUMiSizer to measure the influence of shearing pre-treatment on the particle size distribution and sedimentation behaviour of different **e**xo**p**oly**s**accharides (EPS) producing bacterial starter cultures. The aim of pre-shearing valuable microorganisms like lactic acid bacteria is to facilitate their separation from the fermentation broth. There exist two types of EPS producing bacteria: types with cell-bound (capsular) EPS and types that produce free EPS. Capsular EPS acts as a protective cover of the cells and aggravates sedimentation due to its parachute effect. Free EPS increases the viscosity of the broth. Pre-shearing with different energy inputs was carried out in a rotor-stator system and a pressure homogenizer. This pre-treatment was expected to either shear off capsular EPS from the cells or break longer cell chains. The first effect leads to a higher sedimentation velocity, while breaking cell chains reduces the sedimentation velocity. Consequently it could be shown that the effect of shearing pre-treatment on the sedimentation velocity depends on the type and amount of strain-specific EPS, but with all types sediment compression could be detected after shearing. The rotor-stator system and the pressure homogenizer were able to evoke the same effects, but the homogenizer did this job at a lower energy input. The research work was carried out within an AiF project, of which a summarizing report is available [3] (see also [4]).

Chika Takai, from Advanced Ceramics Research Center at Nagoya Institute of Technology, Japan, currently works as research fellow with Swiss Federal Laboratories for Materials Science and Technology (EMPA). She reported about her work on modifying the NIPS (**n**on-solvent **i**nduced **p**hase **s**eparation) process, which is applied to generate polymer networks, by adding silica nanoparticles. The aim of this process is to produce three dimensional particle networks in a polymer matrix that will finally be processed to conductive polymer films. The affinity between the polymer solution and the particles was expected to have a major impact on the outcome of the process. Thus the affinities between nanoparticles with various surface modifications (bare, with NH_2 or CF_3 groups) and cellulose acetate as polymer were quantified by using the Hansen solubility parameters (HSP). As pointed out by Prof. Lerche during the discussion following this talk, the “solubility parameter” is rather called “dispersibility parameter”, because the latter term better fits to the physical process, in which particle are to be dispersed in the polymer solution, but not dissolved. Starting from the Hansen spheres calculated for each particle modification by means of HSPiP software, particle dispersibilities in 26 organic solvents were examined from sedimentations profiles obtained by the LUMiSizer. The NH_2 modified particles and the polymer revealed best conformity with regard to the HSP spheres, and the microscope images of resulting networks showed equally distributed particles that were well bound to the polymeric structure.

Young Scientist Awards

This year three nominees from German universities and one candidate from China had been nominated and invited to present their research at the workshop.

Sophie Kühne, from TU Bergakademie Freiberg, works on the agglomeration behaviour of emulsion slurries before and after cake filtration. Emulsion slurries are three-phase systems consisting of an emulsion with dispersed solid particles. Typical examples are oily sands, used pickling acids, media from liquid/liquid extraction processes or wastewater. Questions to be answered by filtration experiments and by using the LUMiSizer referred to the tendency of agglomeration of the two dispersed phases before and after filtration and the structure and flow resistance of the filter cake as well as the quality of the filtrate. A system of hydrophilic micro glass spheres, isooctane, water as continuous phase, and a surfactant as emulsifier was applied as model emulsion slurry. The LUMiSizer analysis of the unfiltered dispersion showed clear separation of the three phases with the glass spheres as sediment and isooctane without any particles as creaming layer. Dead-end filtration experiments were carried out with different amounts of isooctane in different droplet sizes. No isooctane could be detected in the filtrate. However, re-dispersing the filter cake and subsequent centrifugation in the LUMiSizer resulted in incomplete separation with a creaming layer that contained a considerable amount of glass spheres. No clear mother liquid layer could be seen between creaming and sediment layer. This behaviour was explained by particle wetting in the course of the filtration process, which allowed for coalescence of the liquid phase as well as for agglomeration of particles and droplets.

Capsular or free EPS produced from lactic acid bacteria as mentioned in the talk of Florian Häffele, KIT, do not only influence the sedimentation behaviour of the cells, but are welcome substances for enhancing the texture of dairy products.

As the 2nd nominee Georg Surber, from Chair of Food Engineering at TU Dresden, pointed out, EPS do not need to be declared as food ingredients and are naturally available together with the bacteria that are applied in the fermentation process to produce curd, yoghurt or fresh cheese. However, different dairy products need different EPS effects: fermented stirred milk gel (yoghurt) should not segregate, while during fresh cheese or curd production, an early separation of whey from the product containing a preferably large content of proteins is aimed at.

On the enclosed picture from left to right:
Georg Surber, Sophie Kühne, Dietmar Lerche, Awarded Young Scientist 2018 Christian Ullmann, Wen Yong-zhu

Surber applied a LUMiSizer equipped with a near infrared light source to analyse the sedimentation behaviour of yoghurt-like stirred milk gels and curd-whey mixtures, which were produced in a lab-scale fermentation unit by adding different EPS producing starter cultures. The bacteria used in these experiments were selected according to their EPS production mechanism: one culture produces ropy and capsular EPS, another non-ropy and capsular EPS, the third produces only ropy EPS, and the fourth (as a reference) does not produce any EPS. The results obtained with milk gels were compared to gels containing modified starch as stabiliser. Besides the sedimentation parameters of gels and curd-whey-mixtures, the viscosity of separated whey and the molecular weight and polydispersity index of the EPS (the latter by size exclusion chromatography) were determined. It was shown that the sedimentation behaviour of both dairy products depends strongly on the applied EPS producing bacteria. For stirred milk gel (yoghurt), strains with capsular EPS are more suitable, because the gels are more stable against syneresis. On the other hand, ropy EPS lead to a decreased stability against forced sedimentation, which improves the curd-whey separation and increases the protein content of the fresh chease. This research was part of an AiF project [5], recent results are published in [6].

Christian Ullmann, from Institute of Process Engineering and Environmental Technology at TU Dresden, was a member of the NanoDefine researchers group. During this EU project different sample preparation and measuring technologies were evaluated with respect to their capability to clearly characterize particles according to the definition of nanomaterials, which was given by the European Commission: A material is considered to be a nanomaterial, if more than 50% of the particles in the number-based particle size distributions have one or more external dimensions in the size range of 1–100 nm. In all, 18 materials were analysed by using 15 measurement techniques within the project [7]. Mr. Ullmann reported on the comparison of four types of analytical centrifuges (LUMiSizer 610 with illumination at 470 nm and LUMiSizer 651 with illumination at 865 nm (NIR), a disc

centrifuge and an **a**nalytical **u**ltra-**c**entrifuge (AUC)) for characterizing a tri-modal polystyrene suspension (46, 100, and 350 nm) as model particle system and two grades of $BaSO_4$ powders (one in the nano-range and one that also included larger particles, as real-world materials). For determining the intermediate precision of the different measurements, samples were individually prepared and measured in triplicates on different days. Tests with the tri-modal polystyrene particle showed consistent results for all centrifugation results regarding the accuracy of the number-weighed modal diameters. Measurements of the nano-grade $BaSO_4$ with the cuvette centrifuges (LUMiSizer and AUC) provided divergent number-based and volume-based intermedian diameters $x_{50,0}$ and $x_{50,3}$ with intermediate precisions depending on the wavelength in the LUMiSizer. As pointed out during the discussion, measuring with NIR was only carried out for the sake of completeness, because this wavelength is rather suitable for large particles beyond the nanometre range. A comparison of relative standard deviations calculated from the data obtained with all centrifuge types showed that, with the exception of NIR illumination, the relative standard deviations of analytical centrifugation results (including sample preparation) for $x_{50,0}$ lied below 13 % and thus were in good agreement with the demands for classifying nanomaterials according to the EC definition. The results of the centrifuge measurements are published in [8], and a Methods Manual was published in the frame of the project, that gives an instruction which analysing method is available and recommended for which kind of material [9].

Wen Yong-zhu, from Master Kong Co. Ltd. Beverage IRD Center, gave an insight in his development work for the production of fruit and vegetable beverages. Furthermore, Master Kong is active in the development of drinks on the basis of milk and whey powders. With fruit drinks, de-stabilization by oil-slick flotation (migration of a dispersed solid phase to the top of the liquid continuous phase) should be minimized. Analytical centrifugation by means of the LUMiSizer was chosen as a fast method to predict this behaviour and subsequently find recipes as well as production routes by which the products remain stable. Fruit juice beverages consist of a large number of different flavours, of which single components could be identified as destabilizing factors. Destabilizing ingredients could be identified by comparing the transmission profiles with infrared fingerprints of different flavours. Furthermore, first results were presented to predict shelf life of these products based on LUMiSizer data.

Christian Ullmann was awarded the LUM Young Scientist Award 2018 for his research work within the frame of the EU project NanoDefine.

Stability analyses

Again, several talks given by users of LUM's analytical instruments coming from very different industry branches gave insight into the application of analytical centrifuges for stability testing and optimization of recipes and production processes for dispersions.

Kurita Europe GmbH produces chemicals for water treatment including corrosion inhibitors. Julia Jasper reported on the development of new chemicals for the application in steam generators and closed cooling or heating systems. With new additive compositions, the company intends to turn away from substances that may present a health risk or are harmful to the environment. The actual products consist of fatty amines, water-soluble amines and emulsifiers. Before applying the LUMiSizer, their stability was tested by storing 250 ml samples in bottles over a period of minimum six weeks and visually inspecting them afterwards. In doing so, turbidity, coloration, streak formations, and phase separations were detected. Additional evaluation of microscope images turned out not to be sufficiently representative and reproducible, due to the small sample sizes and the subjective choice by the user. Quicker and more reproducible results about storage stability were obtained by analytical centrifugation. Furthermore, this method was applied to evaluate different homogenization processes. High performance dispersing turned out to produce more stable products than conventional stirring. An excellent correlation between the results obtained with the LUMiSizer and long term storage tests was found.

CP Kelco is a global supplier of hydrocolloids and biopolymers that are sold to the food industry for jellifying, thickening or stabilizing liquid foods. Claus Rolin, from the company's Danish subsidiary in Lille Skensved, gave a talk on the characterization of hydrocolloid-stabilized protein suspensions. In detail, the effects of different concentrations of pectin on acidified skimmed milk were analysed by analytical centrifugation. Pectin, which is produced from lemon shells, adsorbs to the protein particles and prevents them from agglomeration. Thus a minimum concentration of negatively charged pectin is necessary to cover the positive charged casein micelles, on the other hand further increase of pectin concentration does not lead to considerably further improvement and is uneconomic. So far, pectin dosage had been evaluated by centrifugation of the stabilized drinks, weighting the emerging sediments and comparing this sediment weight to a pre-defined reference value, which should not be exceeded. As new and faster way to evaluate pectin dosing, the LUMiSizer was applied with its almost entire range of rotational speeds. The multi-sample approach and high gravity of measurement allowed for trying lots of different pectin concentrations lying close to each other. Now the sedimentation velocities obtained by front tracking and the instability indices are plotted versus the pectin concentration instead of the sediment weight. These measurements were accompanied by viscosity measurements that revealed a shear thinning effect, if pectin concentrations were too low.

At Fraunhofer Institute for Ceramic Technologies and Systems (IKTS) in Dresden Anja Meyer works in the field of thermal spraying of suspensions containing ceramic particles in the size range of 10 nm–100 µm. Thermal spraying is applied to make surfaces harder, more resistant against abrasion or corrosion, or to change electric conductivity or surface friction (for sliding processes). Contrary to dry powder spraying, suspension spraying allows for using smaller particles and creating thinner, smoother surfaces. The optimum spraying suspension should be inexpensive, free of hazardous substances, have a low viscosity at the spraying shear rates and a low sedimentation tendency. As particle materials, Al_2O_3 (stabilized via pH adjustment) and Cr_2O_3/TiO_2 (stabilized by a dispersing agent that was not named) were tested. The suspensions were characterized by viscosity measurements and accelerated sedimentation, the latter carried out in the LUMiSizer. The Al_2O_3 suspension revealed a flow behaviour that clearly depends on the pH value. While a shear independent viscosity (Newtonian behaviour) was detected at pH 4, this suspension showed shear thinning behaviour at pH 7 (near the iso-electric point). The Cr_2O_3/TiO_2 suspension showed Newtonian behaviour. Non-Newtonian behaviour demands centrifugal analysis at several rotational speeds, as the sedimentation velocity does not linearly increase with increasing centrifugal acceleration. In all, the combination of rheological and sedimentation measurements was stated to be well suited for characterizing spraying suspensions.

Syngenta is a globally leading corporation that is active in the production of seeds and agrochemicals like herbicides, fungicides, and insecticides. For applying these chemicals in the field, appropriate formulations, either as powders or as liquid, must be found. As Robin Wesley, from Jealotts Hill International Research Station in UK, explained, typical ready-to-use suspensions contain about 25% active ingredients, the other 75% are water, dispersing agents, anti-freezing agents and, if demanded, bio enhancing agents. Due to the high content of suspended substances, the LUMiReader X-Ray was applied for stability testing. The measurements turned out to be very challenging, because the signal-noise ratio was too high to interpret the raw transmission data directly. The solution to this problem was averaging over a series of measuring cycles, of which a suitable SOP had to be found for one formulation first. In a second step, measurements could be carried out by varying parameters of interest, e.g. the concentration of a polymer that influences the rheology of the system. In the presented application, the polymer acted as flocculant, and increasing the polymer concentration led to increasing sedimentation. However, the farmer, who applies the final product, wants to have an easy to dilute concentrate without particle sediments that can hardly be dispersed. This could be validated through the measurements with the LUMiReader X-Ray.

Lazar Benyahia, from Le Mans University in France, reported on the stabilization of water-in-water emulsions by adding solid nanoparticles. Normally, two aqueous solutions of two hydro-soluble, but incompatible polymers like polyethylene oxide (PEO) and dextran, the polymers used in the presented study, will segregate soon during storage. As there is only a slight difference between the surface tensions of both phases, adding surfactants as stabilisers will not help. For stabilization, the so-called Pickering effect (Named after its discoverer S.U. Pickering) is made use of: nanoparticles added to such a mixture adsorb onto the interface between the two phases and thus inhibit or slow down the phase separation. In this case, the LUMiSizer was applied to study the effect of different types of solid nanoparticles on the stability of the above-mentioned water-in-water emulsion. Nanorods in form of **c**ellulose **n**ano-**c**rystals (CNC) [10] together with salt (NaCl) in different concentrations were added to the mixture of polymer solutions. In addition, the structures of different emulsions were obtained using confocal scanning laser microscopy. The main focus of this research was on the physics of stabilisation/destabilisation of water-in-water emulsions. However, there are possible industrial applications, for example in form of fat-free, but creamy food or the use of nano-carriers without organic solvents.

Application course: Characterization of diffusion driven phenomena by STEP-Technology

Destabilization of dispersions may occur due to mechanical forces (sedimentation) as well as due to diffusion driven phenomena (Ostwald ripening and/or coalescence), and often both mechanisms take place at the same time. While sedimentation can be accelerated by increasing the effective mechanical force, that is to say by changing from a gravity-driven system to a centrifugal system and by increasing rotational speed, diffusion driven phenomena are temperature-dependent and need certain dwell times.

How to distinguish between these both types of destabilization mechanisms and clearly identify coalescence and Ostwald ripening on the basis of transmission profiles obtained in an analytical centrifuge was explained in the application course given in the frame of the conference. In short, if only sedimentation occurs, transition profiles should not change, if measuring times are shortened by simultaneously increasing centrifugal accelerations. If any diffusion driven process takes place, this should be detected by variation of measuring time and rotational speed. In addition, measuring at different temperatures also provides a deeper insight at diffusion driven processes.

The next, the 9th International Conference on Dispersion Analysis and Materials Testing will be held from 22-23 May 2019, in the year of the 25th foundation anniversary of LUM.

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