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General overview of inline/online NanoPAT solutions in different industrial processes

1. Introduction

The demand for nanoscale materials and nanoparticles in industry has been increasing rapidly in recent years. Novel process analytical technologies (PATs) have the potential to increase the production rate of nanomaterials, control their product quality, enhance product safety, and save valuable energy, material, and time resources.

The NanoPAT project is focused on advancing three complementary real-time particle characterization PATs - Photon Density Wave spectroscopy (PDW), OptoFluidic Force induction (OF2i), and Turbidity spectrometry (TUS) - from the "lab-status" (TRL 4) to a technology demonstration level at pilot scale in an industrial environment (TRL 6). This will provide, for the first time, real-time analysis for manufacturing processes of particles in the nanometer scale with sub-minute temporal resolution.

To achieve this aim, five industrially relevant cases have been selected: Polymer dispersion, silica, hydroxyapatite, zeolite, and ceramic case studies (see Figure 1). Over the past 18 months, our research and technology organizations have evaluated and optimized the three PATs for these specific case studies. Currently, the processes are being scaled-up to be implemented at the pilot plants of our industrial partners, Covestro, Evonik, FLUIDINOVA, Arkema, and Cnano. The following report provides an overview of the NanoPAT solutions in the five industrial processes.

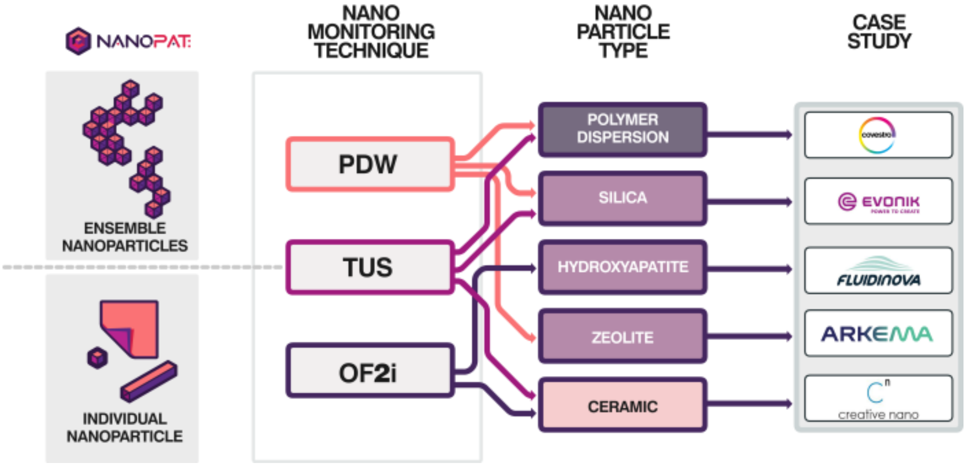

Figure 1: NanoPAT innovation and validation cases.

2. Case study I: Polymeric Dispersions

2.1 General description of process and application fields

Global demand for emulsion polymers has reached 13.3 million metric tons (dry basis) in 2018[1] (without considering styrene-butadiene rubber (SBR) and Polyvinyl chloride (PVC) emulsions which sum another 11.5 million tons) and is growing at a 4.6% annual rate. The Coatings Resins business of Covestro employs more than 2000 people, generating an annual turnover of nearly one billion EUR, to a large degree derived from the sales of nano-scaled polymer particles. Advances in NanoPAT will support increased production of water-based paints, coatings and adhesives, which are displacing solvent borne formulations because of the more stringent environmental regulations in relation to the emission of volatile organic compounds. Acrylics are the largest and fastest growing emulsion polymer type, comprising 40% of the global market in 2018. Industrial water-based coating resins are mainly obtained via batch processes, using a dozen batch reactors located worldwide. This batch process is frequently a water-based emulsion polymerization.

In particular, the ability to control the quality and reliability of products is extremely enhanced by the real-time nano-characterisation technologies of NanoPAT, since all industrial partners within the NanoPAT consortium currently rely on post process and/or sampling-based nanoparticle size analysers. Without the NanoPAT technologies, the present manufacturing reality will not be enabled for direct process and quality control of the nanoparticles during manufacturing: The current state-of-the-art characterisation of nanoparticle size as key material performance indicator simply exhibits too large lag times.

In short, new developed technologies of NanoPAT will provide to Covestro a useful tool for fast and accurate monitoring of the PSD (Particle Size Distribution) and other particle properties such a concentration. In the production environment, the new technology will mainly contribute to production efficiency. The batch processes are running between 6 and 24 hours. As the reaction progress is not monitored over time, each batch process includes additional reaction time (to secure finalization of the polymerization reaction). By monitoring the reaction progress, approximately 5-10% of the reaction time can be saved (and thus a 5-10% capacity/efficiency increase for their case in Waalwijk), which includes cost savings in terms of heating costs, manufacturing etc. and will easily sum up to approx. 2-5 M € per year.

2.2 TUS as NanoPAT solution to monitor polymeric dispersions synthesis processes

Turbidity spectroscopy (TUS) is an analytical technique that makes use of the transmitted light spectrum to obtain information of the analysed medium. The size of the particles dispersed in the liquid medium can be retrieved by the application of several models such as the ones used in Wavelength Exponent or Specific Turbidity methods.

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[1] Nanotechnology Market by Type (Nanodevices and Nanosensors) and Application (Electronics, Energy, Chemical Manufacturing, Aerospace & Defense, Healthcare, and Others): Global Opportunity Analysis and Industry Forecast, 2018–2025 DT-NMBP-08-2019, Page 22 of 70

TUS has been successfully applied to monitor semi-batch emulsion polymerization reactions of polyacrylates with a particle growth up to 400 nm, given that the samples withdrawn from the reactor are diluted down to single scattering conditions. An automatic dilution system is under development to provide real-time, online monitoring conditions.

2.3 PDW as NanoPAT solution to monitor polymeric dispersions synthesis processes

Photon Density Wave (PDW) Spectroscopy is a calibration- and dilution-free process analytical technology used to measure the absorption and reduced scattering coefficients of highly turbid liquid materials. The size of the dispersed particles can be retrieved from the reduced scattering coefficient by Mie theory and theories for dependent light scattering.

PDW has been successfully applied to inline monitor semi-batch emulsion polymerization reactions with a particle growth up to 350 nm and 40 % solids content.

2.4 Statement of industrial partner Covestro about suitability of NanoPAT solutions for their processes

The NanoPAT solutions PDWS and TUS are exciting novel techniques and have the potential to improve our production processes which will save energy and resources. We look forward to implement them in our pilot plants.

3. Case study II: Nanostructured synthetic amorphous silica (SAS) particles

3.1 General description of process and application fields

Precipitated silica is synthesized in a waterborne process with high solid content, where fundamental understanding of genesis of particles is key. Still, a reliable and robust online, preferably inline control system of particles and particle distribution is missing. The main goal of applying real-time process monitoring within this case study would be to gain higher process stability which leads to further improved product quality and more efficient manufacturing. Thus, Evonik represents one large scale industrial production process in which a novel inline particle analysis method carries large potential.

3.2 TUS as NanoPAT solution to monitor silica synthesis processes

A brief description of TUS was given in Section 2.2. The synthesis of nanostructured synthetic amorphous silica (SAS) particles has been successfully replicated at lab-scale (1 L and 6 L) by the University of Potsdam. First experiments indicated that TUS and PDW might complement each other very well in the silica case study since TUS measurements yielded the best results under low scattering conditions (before gelation point) and PDW measurements at high scattering conditions (after gelation point).

3.3 PDW as NanoPAT solution to monitor silica synthesis processes

A brief description of PDW Spectroscopy was given in Section 2.3. An inline monitoring of the synthesis process after the gelation point was successfully achieved with PDW Spectroscopy. The technology was capable of identifying different reactions stages such as gelation point, ongoing precipitation, and neutralization.

3.4 Statement of industrial partner Evonik about suitability of NanoPAT solutions for their processes

TUS: Unfortunately, due to problems (corrosion) of the TUS sensor, the suitability has not been tested so far at the University of Potsdam. Solutions are currently implemented to improve the sensor suitability for our reaction conditions.

PDW: The suitability after the gelation point of the reaction has been proven; further increase of sensor sensitivity in order to detect the reaction at an earlier stage is ongoing.

Meanwhile, the preparations for laboratory testing (>150 litre reactor) of both probe settings have been finalised at Evonik.

4. Case study III: Hydroxyapatite Nanoparticles

4.1 General description of process and application fields

Hydroxyapatite (HAp) is one of the most popular types of calcium phosphates in industry and it is widely used in several applications, from medical devices to cosmetic products. In particular, HAp is used in clinical applications such as restorative dental and orthopedic implants due to its close resemblance to the natural bones and teeth, its excellent bioaffinity and its enhancement in osseointegration. Moreover, it is also used as an ingredient for cosmetic products like toothpastes and mouthwashes since it effectively reduces dental hypersensitivity and ensures enamel remineralization. The HAp performance is increased when used in its nano-form: nano-hydroxyapatite (nHAp). FLUIDINOVA developed a proprietary technology - the *NETmix* reactor - that allows the continuous production of high quality nHAp using wet chemical precipitation methods. With this process, it is possible to obtain highly pure, rod-shaped nHAp particles with lengths below 100 nm. The physicochemical properties and morphology of these particles have been extensively monitored and characterized using offline analytical characterization technologies (e.g., microscopy techniques such as SEM, TEM) that take, at least, two weeks to provide results. Therefore, monitoring the particle size and morphology is currently a time-consuming task. Real-time analytical technologies such as the ones presented in the NanoPAT project have the potential to significantly reduce the time demand of such characterisation tasks.

4.2 OF2i as NanoPAT solution to monitor hydroxyapatite synthesis processes

The OptoFluidic Force Induction (OF2i) works as a highly sensitive, continuous single particle characterization method based on the combination of actively induced optical and fluidic forces. The minimal photonic forces are sufficient to deflect and (de)accelerate small particles from their fluidic induced motion. An ultramicroscope setup determines the actively altered particle trajectories, tracking algorithms and the underlying physical models translate the characteristic motion into characterization data such as particle sizes, number-based size distributions, D-Values and particle numbers (concentration) at a single particle base, updated each second. With the automated dilution unit, OF2i can be integrated in industrial processes as an on-line process analytical technology with live visualisation. Counting up to 4.000 particles per second, OF2i delivers statistically representative data of the overall particle population.

OF2i has been applied to monitor the dynamics of nHAp maturation after synthesis with a small-scale NETmix reactor provided by FLUIDINOVA (operated at the facilities of the Medial University of Graz). During 7hrs of maturation, a small amount of sample was continuously extracted and measured on-line, showing a clear trend in raising particle counts (concentration) and change of size distribution over time.

4.3 Statement of industrial partner FLUIDINOVA about suitability of NanoPAT solutions for their processes

During continuous nHAp production, changes on process parameters (e.g., reactants concentration, temperature, pH) can modify the material morphology and size, so real-time detection/characterization methods like OF2i would enable to improve product quality and allow faster development of new products and processes. In the last years, the Medical University of Graz and BRAVE Analytics have been working with a laboratory rig test setup, which is a lab-scale representation of FLUIDINOVA's *NETmix* reactor and therefore simulates the HAp reaction at a laboratory scale. With this setup, these partners have been able to perform particle size measurements using the OF2i sensor in our synthesis and consequently optimize their equipment to ensure a good performance in our industrial plant. The results obtained until now are very promising so it is expected that OF2i technology could contribute positively to further developments in the HAp industrial process.

5. Case study IV: Zeolite Nanoparticles

5.1 General description of process and application fields

Zeolites are crystalline aluminosilicates composed of SiO_4 and AlO_4 tetrahedral structures, assembled to form 3D porous materials. Zeolite crystals are non-spherical particles, produced with a large variety of mean sizes and size distributions (from submicronic to micronic size) depending on the targeted applications. Zeolites are synthesized by hydrothermal methods, in which a source of aluminum and a source of silicium in solutions are mixed to prepare a "synthesis gel", which is rather concentrated and viscous to achieve high yields. Those gels are submitted to an induction period (aging), while nuclei formation occurs, before being heated to relatively high temperatures for crystal growth.

The targeted crystallinity and crystal size of the zeolite is obtained if the process conditions are well controlled. The continuous tracking of the particle size and particle size distribution during the crystallization will help to properly tune the process conditions, in order to produce crystals of desired size and crystallinity. Conventionally, the quality of the zeolite is evaluated by offline techniques (SEM, XRD) after the completion of the synthesis process. Furthermore, real-time measurements will be much quicker and more efficient than the usual techniques, which require time-consuming sample preparation and analysis (few hours to days).

5.2 PDWS as NanoPAT solution to monitor zeolite synthesis processes

The monitoring of zeolite syntheses in real time is rather challenging due to the very alkaline medium (high pH value) and the relatively high temperatures and viscosities. Obtaining information on relevant quality attributes such as particle size and crystallinity in a timely manner is even more complicated. The commercially available focused beam reflection measurement FBRM as an inline technique is not feasible in this case, due to the zeolite particles being an order of magnitude too small and the sapphire window not being resistant to the reaction medium.

PDW spectroscopy as a fiber-optical process analytical technology which characterizes the optical properties of suspensions was chosen to monitor zeolite syntheses at ZHAW due to a much better fit in terms of the particle size and the potential to withstand the harsh process conditions.

Preliminary studies performed at the Zurich University of Applied Sciences have shown that with PDWS the onset and end of the zeolite crystallization can be detected inline. In the context of the NanoPAT project, commercial zeolite syntheses of two different zeolite types have been reproduced in lab-scale at the Zurich University of Applied Sciences, supported by Arkema. Monitoring several syntheses by means of PDWS, the standard process probe did not withstand the harsh process conditions on the long run, making the development of a more resistant process probe necessary. After screening different optical materials, a first prototype has been manufactured and also already been successfully tested.

5.3 Statement of industrial partner Arkema about suitability of NanoPAT solutions for their processes

The work at Zurich University of Applied Sciences over the previous years on monitoring the synthesis of zeolites has shown a potential in the PDW technology to monitor the progress of the crystallization process. ZHAW has recently demonstrated that the probes developed by themselves are compatible with a wide range of synthesis conditions. We support the ongoing work on the probe optimization and looking forward to transferring the technology to our pilot plants.

6. Case study V: Ceramic Nanoparticles

6.1 General description of process and application fields

Electroplating, also known as electrodeposition, is an electrochemical process which produces a metal coating on a solid substrate by applying electric current through a water-based solution (plating bath) to reduce dissolved metal cations to their metallic state. It is a versatile and low-cost process which can produce metal coatings with outstanding properties (e.g. wear and corrosion resistance, low friction coefficient) and an aesthetically pleasing appearance. To this end, hard chromium (HC) coatings have been widely used in industry for over 50 years by virtue of their excellent mechanical strength and chemical resistance which in turn can significantly prolong the lifetime of the coated substrates. However, HC electroplating uses hexavalent chromium Cr(VI) as the chromium source in the plating bath which is classified as a toxic and a carcinogenic compound and its use requires authorization by the European Commission. This has led to the exploration of alternative metal coatings to replace HC.

In that perspective, a promising alternative is Ni and Ni-P based nanocomposite coatings, i.e. nickel metal coatings whose properties are enhanced via the incorporation of ceramic nanoparticles such as SiC, TiO_2, Al_2O_3 into the Ni-matrix. For example, SiC nanoparticles can be added in a low phosphorous Brenner type plating bath to produce Ni-P/SiC nanocomposite coatings. The incorporation of the ceramic SiC NPs as reinforcing means in the Ni-P matrix can increase the hardness and the wear resistance of the respective Ni-P/SiC nanocomposite coatings to match or even surpass HC.

Importantly, a significant challenge that must be addressed during the formulation of the plating baths is the intrinsic tendency of the ceramic NPs to agglomerate and form larger particle aggregates. This leads to a broader particle size distribution and an inhomogeneous dispersion of the ceramic NPs in the bath which is "transferred" in the produced nanocomposite coatings during the co-electrodeposition process. As a result, the quality of the final coatings is decreased due to the non-uniform incorporation of the ceramic particles into the metal matrix.

Ultrasonication is the most common method to break down the larger particle aggregates and maintain a homogeneous dispersion of ceramic NPs in the plating bath. However, ultrasonication must be turned off during the actual electrodeposition process because it tends to remove the ceramic NPs from the metal coating, leading to lower quality final coatings. Therefore, it is crucial for Creative Nano's bath operators to monitor in real-time the nature, the particle size and the concentration of the ceramic NPs in the plating bath in order to take corrective actions such as applying ultrasonication and mechanical agitation or adjusting electroplating parameters to maintain a constant and homogeneous loading of the ceramic NPs in the nanocomposite coatings.

6.2 OF2i as NanoPAT solution to monitor ceramic coating processes

A brief description of OF2i was given in Section 4.2.

At the facilities of the Medical University Graz, a small-scale coating reactor with ceramic nano particles was established. A small amount of sample was continuously extracted and measured on-line with OF2i.

The effect of ultrasonication could clearly be shown: a decrease in particle size (splitting of particle agglomerations) with a simultaneous increase of particle counts (concentration) was observed, and the related time constants could be determined. For a homogeneous coating quality, very specific particle size distributions are required. Thus, OF2i can deliver process feedback information when activation of ultrasonication is required to assure proper coating quality.

Further, the effect of the different synthesis ingredients onto particle stability were investigated, showing a significant increase of particle agglomerations when adding certain chemicals.

Exerting optical and fluidic forces onto particles, splitting of large particle flocculates/agglomerates could be observed live with OF2i for a certain synthesis formulation, providing information about binding forces of particle flocculates/agglomerates.

6.3 TUS as NanoPAT solution to monitor ceramic synthesis processes

A brief description of TUS was given in Section 2.2. At the facilities of the Medical University Graz, TUS measurements have been performed with a small-scale coating reactor with ceramic nano particles simultaneously with OF2i measurements. Further experiments towards calibration routines have been investigated together with IRIS. First results indicated that the samples must be diluted to single scattering conditions to obtain exact size distributions. An automatic dilution system is under development and measurements will be performed from IRIS at the industrial environments of Cnano.

6.4 Statement of industrial partner Cnano about suitability of NanoPAT solutions for their processes

Currently, Cnano monitors the dispersion of the ceramic NPs by collecting samples from the plating baths at regular intervals and measuring the particle size by DLS after dilution. This is a time-consuming, off-line process, leading to delays and higher costs. Therefore, both NanoPAT solutions related to Cnano's production of nanocomposite coatings via electroplating, namely Of2i and TUS, are highly suitable for the real-time monitoring of the ceramic NPs dispersion in the plating baths. This will enable the operator to immediately interfere and rapidly take corrective measures to refine the dispersion of the ceramic NPs and therefore maintain a high and consistent quality final coatings without interrupting the electroplating process. Moreover, waste occurring from excess scrap, degrading or reworking of the process will be significantly reduced due to the higher and faster process control. Cnano has already developed a strong collaboration with both technology providers by carrying out in house measurements, exchanging data and arranging visits to its premises to optimize both technologies and will continue to do so.

7. PAT platform for monitoring technologies integration

The success of any monitoring technology also depends on external influences that may impact the accuracy of the measurements of the PAT devices such as the placement of the probing / sampling unit within a synthesis reactor. The location of the PAT device must be such that they measure correctly in meaningful locations. Using advanced modelling techniques such as Computational Fluid Dynamics, the NanoPAT team identifies the most efficient locations for the PAT devices in the pilot scale reactors individually for each case study. This work is currently still in progress.

Furthermore, an online platform to communicate the results to the end-users is being developed. NanoPAT proposes the application of the PatBox platform for the PAT devices so that the end-users will have online information of the nanomaterial production process to be shared to other parties within the respective organizations.

8. Summary and Conclusions

Three NanoPAT technologies (PDW, OF2i and TUS) have been successfully applied in five industrially relevant case studies (polymer dispersion, silica, hydroxyapatite, zeolite and ceramic). After the lab-scale optimisation of the PATs to each case study, the scaling up process has now been started. The industrial partners (Covestro, Evonik, FLUIDINOVA, Arkemam and Cnano) are ready to implement the PATs at pilot-scale to evaluate their suitability in industrial environments, aiming to advance the technologies to TRL 6 and exploring exploitation strategies for the new technologies to enhance their production processes.

List of abbreviations

FBRM	Focus Beam Reflectance Measurement
HC	Hard Chromium
MUG	Medical University of Graz
NP	Nano Particle
HAp	Hydroxyapatite
nHAp	nano-Hydroxyapatite
OF2i	OptoFluidic Force Induction
PAT	Process Analytical Technology
PDW(S)	Photon Density Wave (Spectroscopy)
UP	University of Potsdam
SAS	Synthetic Amorphous Silica
SEM	Scanning Electron Microscopy
TEM	Transmission electron microscopy
TRL	Technology Readiness Level
TUS	Turbidity Spectroscopy
XRD	X-Ray Diffraction
ZHAW	Zurich University of Applied Sciences