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Table of Contents

List of Abbreviations

BA	- Butyl Acrylate
DLS	- Dynamic Light Scattering
FAU	- Faujasite (specific type of zeolites)
FBRM	- Focus Beam Reflectance Measurement
LTA	- Linde Type A (specific type of zeolites)
MAA	- MethAcrylic Acid
MMA	- Methyl MethAcrylate
M*X*	- Month *X* of the project (M1 = June 2020)
PAT	- Process Analytical Technology
PDW	- Photon Density Wave
PDWA	- PDW Analytics GmbH
RTO	- Research and Technology Organisation (here: UP, UPV and ZHAW)
SEM	- Scanning Electron Microscopy
TRL	- Technology Readiness Level
UP	- University of Potsdam (Universität Potsdam)
UPV	- University of the Basque Country (Uiversidad del Pais Vasco)
WP	- Work Package
ZHAW	- Zurich University of Applied Sciences (Zürcher Hochschule fur Angewandte Wissenschaften)

1. Introduction

This deliverable D2.3 – "*Summary of PDW applications for NPs monitoring*" is developed as part of the NanoPAT project, which is a European Union Horizon 2020 Research and Innovation Program, under the Grant Agreement number 862583. It has been produced by PDWA, as leader of work package (WP) 2 on "*Photon Density Wave (PDW) spectroscopy development*", based on the inputs and contributions from WP2 project partners UPV, ZHAW, UP, Covestro, Arkema, and Evonik (the individual partners are introduced here).

WP2 is connected to Objective 2 of the NanoPAT project which aims to develop an inline monitoring tool based on Photon Density Wave (PDW) Spectroscopy for the real time characterization of polymer dispersions, silica nanoparticles and zeolite nanoparticles (= case studies 1, 2 and 4, respectively). This tool shall subsequently be implemented in the production processes at the sites of the industrial partners (WP6).

To accomplish this aim, WP2 pursues three objectives:

- the lab-scale replication of the industrial synthesis process of each case study,
- the optimisation of PDW inline monitoring for each process, and
- the comparison with standard reference measurement techniques.

The following deliverable gives a brief introduction to PDW spectroscopy and summarises the experimental work performed by the research and technology organisations (RTOs) in WP2 (M4 to M26), including inline PDW data for the specific industrial cases selected. It is linked to Tasks 2.1 (Laboratory test rig setup), 2.2 (RTO pilot tests for each relevant nanoparticles production case study), and 2.3 (Data analysis against reference methods) of the NanoPAT project.

2. PDW Spectroscopy

PDW spectroscopy is a fibre-optical process analytical technology (PAT) for turbid materials that can be applied inline, i.e., directly inside the reaction vessel without previous sampling or the dilution of samples[i]. With a time-resolution of less than one minute, processes can be monitored virtually in real-time. It works contamination- and calibration-free, and it is suitable for very high concentrations (i.e., above 60 wt%[ii]), stirred, or flowing systems, and even in potentially explosive environments.

PDW spectroscopy provides an easy-to-use approach which has already been demonstrated for chemical[iii,iv], physical[v], and biotechnological[vi] processes in highly concentrated liquid materials. Accordingly, PDW spectroscopy reached Technology Readiness Level (TRL) 4. The aim of NanoPAT is to develop PDW spectroscopy further to demonstrate its industrial feasibility (TRL 6).

It allows for the independent, absolute quantification of the absorption and scattering properties of disperse materials, i.e., the absorption and reduced scattering coefficients, respectively. The absorption coefficient contains information about the chemical composition and/or the temperature of the material. The reduced scattering coefficient is related to the number and size of the dispersed particles. The size of the dispersed particles can be retrieved from the reduced scattering coefficient by Mie theory and theories for dependent light scattering[vii].

The reduced scattering coefficient μ_s' depends on the particle diameter d and the particle volume fraction ϕ [viii, ix].

$$\mu_s' = \frac{3\phi Q_s}{2d}(1-g) \quad (1)$$

Q_s is the scattering efficiency, and g is the anisotropy factor. Both can be obtained from Mie-theory and depend among others on the refractive indices of the medium n_m and the particles n_p, and particle diameter d. Equation 1 is valid for monodisperse, spherical particles in the absence of dependent light scattering. Expressions for polydisperse particles and dependent light scattering were described before.[x] Such expressions were used to calculate particle sizes from the μ_s' measured by PDW spectroscopy.

A prerequisite of PDW spectroscopy is that multiple light scattering occurs in the material. Thus, the material needs to have a minimum turbidity to fulfil this prerequisite and to achieve sufficient accuracy for the determination of the optical coefficients. The turbidity depends on several factors such as the refractive index, number, and size of nanoparticles in a dispersion. In case of materials that have low scattering properties, the performance of a PDW spectroscopy measurement can be improved by applying shorter laser wavelengths at which light scattering is more pronounced.

3. General progress within WP2

In the NanoPAT project, the following three industrial nanoparticle production processes were monitored with inline PDW spectroscopy as a real-time process analytical technology:
a) Silica particles
b) Zeolite nanoparticles
c) Polymeric nanoparticles

Table 1 provides an overview of the involved research & technology organisations and the respective industrial partners for the case studies:

Table 1. Case studies within WP2 (PDW spectroscopy development)

Subtask	**Case Study**	**RTO**	**Industrial Partner**
2.2.1	Silica particles	UP	Evonik
2.2.2	Zeolite nanoparticles	ZHAW	Arkema
2.2.3	Polymer nanoparticles	UPV/POLYMAT	Covestro

In all three case studies, PDWA and UP have installed the PDW spectrometers at the corresponding RTOs, including technical training and instrument handling. The RTOs conducted the adaptation of the reaction vessels to fit the PDW probes. For the technical induction and support with data analysis, several exchanges between UP and the RTOs have taken place (see Section 6).

The industrial partners have provided reference material samples that were analysed by the RTOs with PDW spectroscopy as well as with reference measurement techniques. Furthermore, the industrial partners provided synthesis recipes of the industrial processes to be monitored at lab-scale at the RTOs. These processes were successfully replicated in all three case studies[1], applying diverse process variations (e.g., different ratio of reactants, mixing times etc.), and monitored inline and offline by PDW spectroscopy. The PDW measurements were then correlated with the respective process data (e.g., temperature, pH, stirring), and compared to reference measurements techniques. Overall, the PDW measurements agreed well with the reference.

Currently, the PDW setups are being adapted for the implementation into pilot plant demonstrators (WP6), and upscaling specifications for each case study are being defined. Furthermore, ZHAW and PDWA are jointly working on the adaptation of the PDW probes to the extreme conditions during the Zeolite synthesis.

The following section will provide case-specific details for each of the three case studies.

[1] Zeolite X synthesis is still under optimisation, see Section 4.3

4. Work performed in the three case studies

4.1 Silica case study

Thanks to their extensive PDW experience, the researchers at the UP achieved very advanced PDW measurements and data analyses in the silica case study. Three synthesis recipes provided by Evonik have been successfully transferred to lab-scale, the transfer of a fourth one is currently in progress. The processes have been monitored by inline PDW spectroscopy, and the results were compared to reference technologies (SEM, DLS, FBRM).

With help of the PDW measurements, different stages of the reaction (gelation, precipitation, growth of existing particles, aggregation – see example below) could be identified. The particle sizes were calculated from the measured scattering properties (μ_s' values) assuming spherical, monodisperse, and dense particles. However, the silica particles were found in irregular shapes and as porous agglomerates of smaller sub-units, which compromised the calculation of the particle size. Nevertheless, the particles sizes obtained from PDW data agreed reasonably well with the reference methods for the first and second recipe.

One challenge found in this case study was the lack of sufficient scattering when the solids content is too low, or the particles are (still) too small (e.g. before gelation). A new laser diode (405 nm) with a lower wavelength was implemented, for which stronger light scattering can be expected. While this was a successful improvement for the first and second recipe, the scattering was still too low for the third and fourth recipe. This was partially due to the lower volume fractions occurring in the syntheses 3 and 4.

In summary, multiple lab-scale silica production processes were successfully monitored by inline PDW measurements. The technology can readily be transferred to the industrial partner (WP6). However, parallel to the first industrial trials, additional research needs to be done to further improve the PDW measurements in this case study:

- Further syntheses are planned to be conducted in a 6 L reaction vessel. This could serve as an intermediate step to transfer the results from lab scale to industrial scale.
- Four laser diodes will be implemented in the current PDW lab setup to account for the polydispersity of the particles.
- The particle sizes obtained from PDW spectroscopy could be improved by adapting the data analysis model to the properties of the synthesized particles (e.g., their porosity).
- Especially for syntheses with very low solids contents, the PDW data could be improved by using laser diodes with even shorter wavelengths than 405 nm.

<u>Example for inline PDW monitoring of a silica synthesis</u>

Figure 1 gives a representative example of a silica synthesis monitored by PDW spectroscopy. It shows the reduced scattering coefficients μ_s' at 405 nm and 778 nm measured by inline PDW spectroscopy as well as the relative torque (indicator for viscosity), the reaction temperature, and the pH value at the reaction temperature as function of time. In general, the process data were found to be close to the recipe's specifications, hence the downscaling of the process was concluded to be successful.

The steep increase of the relative torque, or the viscosity, after 40 min corresponds to the point of gelation. The subsequent increase of μ_s' can be attributed to ongoing particle growth or aggregation and agglomeration. Neutralization happens after around 80 min, indicated by the drop of the pH value and a second increase of the relative torque. This second increase of the viscosity hints on an aggregation process, which might happen when the surface charge of the particles changes due to the neutralization.

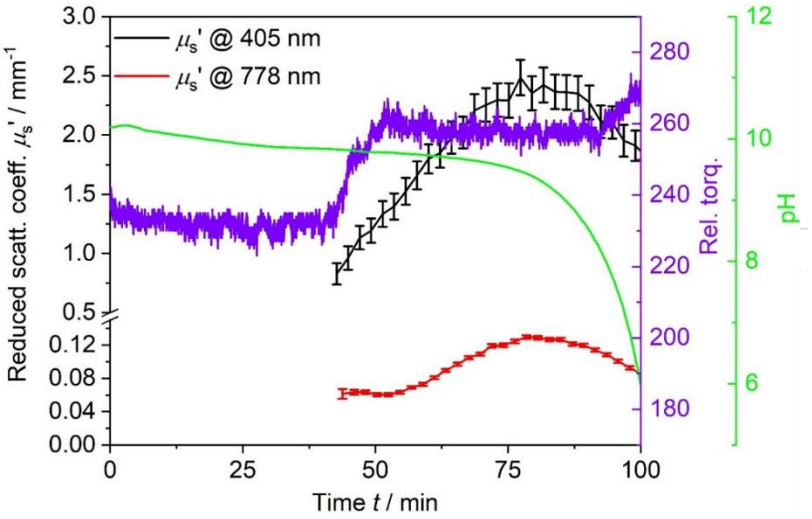

Figure 1: Reduced scattering coefficient $\mu_{s'}$ at 405 nm and 778 nm measured by inline PDW spectroscopy, relative torque, and pH at reaction temperature as function of time during a synthesis following a recipe provided by Evonik. The figure only includes PDW data after the gelation point (≈ 40 min), because before the gelation no meaningful results are obtained due to the low light scattering of the sample at early synthesis times.

4.2 Zeolite case study

ZHAW accomplished a robust and reproducible synthesis of Zeolite A (LTA) at lab-scale using two reaction variants. In the first variant, the reaction mixture is immediately heated (in the following referred to as “fast kinetics”). In the second procedure, the mixture is first stirred for ca. 2 hours (so-called aging step) before starting the heating process (“slow kinetics”).

Offline samples taken during the synthesis have been analysed with laser diffraction, scanning electron microscopy, and powder X-ray diffraction, and provide valuable references for process monitoring by means of inline PDW Spectroscopy. While offline samples are currently taken manually, an in-built sampling system is being implemented to avoid disturbances of the reaction (e.g. loss of pressure).

With the inline analytical results obtained with PDW spectroscopy using the process probe, the LTA synthetic procedures (slow and fast kinetics) can be distinguished, and the reduced scattering coefficients μ_s' show the characteristic course over time (see Figure 3).The lab-scale replication of the Zeolite X (FAU) synthesis at ZHAW is still being optimised before starting offline sampling and inline monitoring with PDW spectroscopy.

The harsh reaction conditions of the zeolite synthesis led to corrosion of the silica optical fibres of the PDW probe. Therefore, currently only short-term industrial pilot trials are feasible. First experiments towards the development of more robust PDW probes have already been initiated and will be continued in WP6 to exploit the full potential of the PDW technology in the industrial context of Arkema.

Example for inline PDW monitoring of a zeolite synthesis

Figure 3 provides a representative example of an LTA synthesis according to Arkema's slow kinetics procedure monitored by PDW spectroscopy. It shows characteristic curves of the reduced scattering coefficients μ_s' which increase during dosage of the silica phase, and show an asymptotic course during aging at 40 °C. The subsequent temperature increase leads to an immediate alteration of the reduced scattering coefficients μ_s' followed by another asymptotic equilibration of scattering during the crystallization phase.

The graphs demonstrate that real time monitoring of LTA syntheses using PDW spectroscopy offers a new insight in crystal growth even under the harsh conditions (pH 14, 100 °C, hydrothermal pressure, and high turbidity).

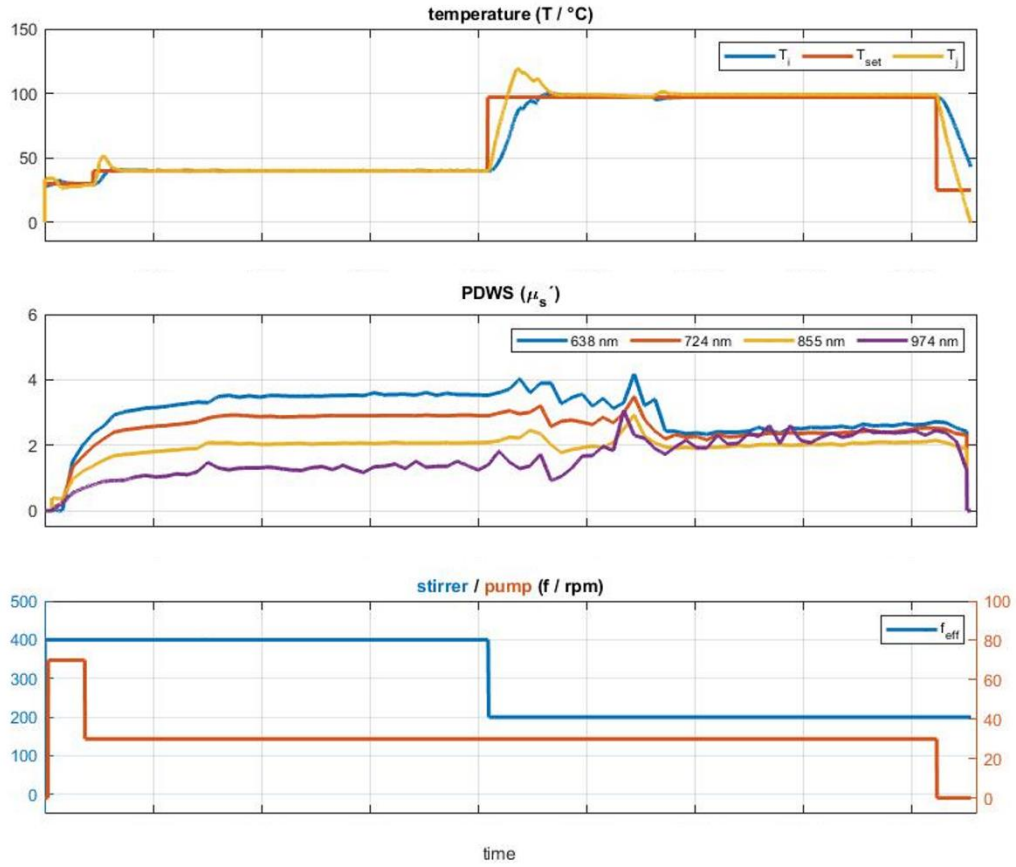

Figure 2. Zeolite A synthesis with different parameters over time: temperatures (top); reduced scattering coefficients μ_s' at 638, 724, 855, and 974 nm (middle), and stirring respectively pumping frequency (bottom). Concrete values on time axis removed for confidentiality.

4.3 Polymeric dispersions case study

The first PDW inline analysis of polyacrylate latex synthesis were successfully conducted during the stay of Usue Aspiazu (UPV/POLYMAT) at Potsdam University. In the end of July 2021, PDW equipment was implemented at POLYMAT, University of the Basque Country (San Sebastian). POLYMAT successfully accomplished the lab-scale replication of both industrial synthesis processes provided by Covestro (polyacrylates and polyurethanes). Both processes were also accompanied by inline by PDW spectroscopy, finding that particle growth and coagulation processes can be monitored with PDW.

Furthermore, the reproducibility of the synthesis and the PDW measurements was investigated. Figure 2 shows the evolution of the reduced scattering coefficient derived from the 636 nm laser signal for three repeated reactions with in-situ seed formation. The beginning and the end of the particle growth can be clearly identified using PDW spectroscopy. The reproducibility of the process is high, considering the variability that the seed formation process may have.

The model to obtain particle sizes from μ_s' (measured by PDW) agreed generally well with the DLS reference values and even slightly better when the changing solids contents over the course of the reaction were considered. Different methyl methacrylate/butyl acrylate/ methacrylic acid (MMA/BA/MAA) composition polyacrylates could be monitored by PDW and the retrieved particle sizes agreed with the DLS reference values. Furthermore, the PDW Spectrometer captured the particle aggregation processes, showing a huge increase of the reduced scattering when particle aggregation occurs.

The experiments to monitor polyurethane syntheses showed that the scattering properties of this polymeric dispersion are much weaker than those of polyacrylate dispersions (due to a different refractive index). Since PDW works ideally in highly scattering media, this introduces larger uncertainties into the PDW measurements, especially in the beginning of the dispersion process where particle concentrations are still low. Nevertheless, the obtained particle size trends were similar to the ones obtained offline by reference DLS analysis.

In summary, the first inline PDW measurements successfully monitored the synthesis processes in the polymeric dispersions case study and the technology is ready to be transferred to the industrial partner. However, there are still open points to improve the data quality of the PDW results which will be addressed in WP6:

- Explore the possibilities to upgrade the PDW software (e.g., input of the evolution of the solids content, refractive index and density during reaction)
- Adapt PDW technology to low scattering conditions (e.g., use shorter laser light wavelengths or adapt the intensity of the emitted light)
- Optimize PDW technology for very high scattering conditions (e.g., high solids contents and particle sizes)

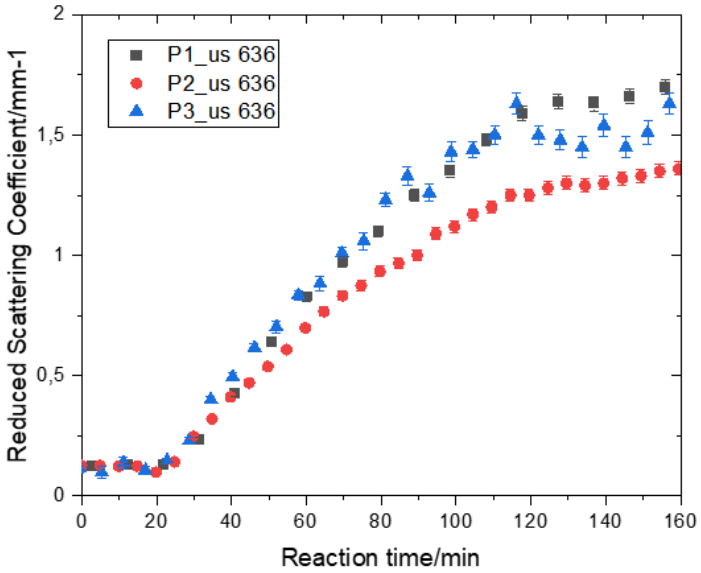

Figure 3. Reduced scattering coefficient evolution (636 nm laser signal) of three PA reactions with in-situ seed production, determined by PDW Spectroscopy.

5. Demonstrator construction for industrial pilot trials

To execute the industrial lab and pilot plant trials during WP6 for the Use Cases described here, a dedicated mobile PDW spectroscopy demonstrator is required which has been constructed within WP2. This instrument serves as a platform for further technology development from TRL 4 to TRL 6. Thus, this platform undergoes continuous further development with respect to general industrial requirements, e.g., instrumental safety features, and with respect to Use Case specific needs. Here, pilot conditions vary between the different industrial partners. This also includes specific modifications to the PDW process probes as essential part of the spectrometer.

It is assumed that the further development of the demonstrator will continue towards the end of the NanoPAT project, to reach prototype status in the industrial operational environment (TRL 6).

6. Networking within the NanoPAT consortium

The Horizon 2020 Funding Framework strives, besides for scientific excellence and innovation, also for a strong and successful researchers' network across Europe. Therefore, as much as the pandemic allowed for it, we encouraged networking and knowledge exchange between the partners of WP2 where possible: Usue Aspiazu (UPV/POLYMAT, Spain) and Despina Emmanouilidou (ZHAW, Switzerland) visited the University of Potsdam (UP, Germany) for PDW spectroscopy training (Fig. 4). In return, Stephanie Schlappa and Tobias Simon (UP) visited our partners at POLYMAT for technical and data analysis support. To give advice on the lab-scale replication of the particle production processes, Agnieszka Ochenduszko (Evonik, Germany) visited the University of Potsdam, and Heidy Ramirez (Arkema, France) is planning to do the same at ZHAW soon. Here, Covid-19 restrictions posed additional challenges for physical meetings for all partners. Therefore, numerous online meetings, including training sessions on the PDW technology, result discussions, and feasibility discussions with respect to the technical implementation envisioned for WP6 were executed.

Figure 4. "Mini NanoPAT meeting" at the University of Potsdam. From left to right: Anika Krause (PDWA), Usue Aspiazu (UPV/POLYMAT), Marvin Münzberg (UP), Sebastian Zimmermann (UP), Despina Emmanouilidou (ZHAW).

In preparation for WP6, the UP team (Potsdam, Germany) visited Covestro in Waalwijk (Netherlands) and Evonik in Wesseling (Germany) to discuss technical details for the implementation of PDW spectroscopy in their industrial pilot plants.

Figure 5. UP visits at Evonik (left) and Covestro (right) in preparation for WP6.

In June 2022, finally, the first in-person General Meeting took place in Potsdam, Germany (organised by the UP), allowing the consortium for the first time to meet face-to-face after two years of solely virtual meetings.

Figure 6. General Meeting in Potsdam (June 2022).

All these activities have been reported accordingly on the News section of the project website: https://www.nanopat.eu/news-media/

7. Summary

The work in WP2 of the NanoPAT project was a great success. All three case studies accomplished the given objectives, contributing to the successful completion of WP2. The PDW technology is ready to be transferred to the industrial partners (WP6) for all use cases. In the zeolite case study, a more robust process probe is being developed for the permanent transfer to industrial-scale measurements which might lead to new, unforeseen intellectual property within the NanoPAT project.

Despite the restrictions due to the Covid-19 pandemic, many exchanges within the NanoPAT consortium were realised, turning the group into a strongly collaborative and efficient network that will most likely stay connected beyond the duration of NanoPAT.

The next step will be the upscaling of the PDW technology to industrial conditions (WP6). For this purpose, a mobile demonstrator has successfully been constructed, and first preparational meetings have taken place. Therefore, we are optimally prepared to achieve prototype status in the industrial operational environment (TRL 6) for the PDW technology.

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