Inline Raman Spectroscopy of an Emulsion Copolymerization in an Industrial Pilot Plant Using Indirect Hard Modeling

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Raman spectroscopy is used to determine the concentrations of monomers and polymers in the second stage of a two-stage emulsion polymerization process. The indirect hard modeling (IHM) approach is applied to monitor inline the reaction in semi-batch operation in lab scale and pilot scale. This method requires the spectra of all pure components. While the pure spectra of water and monomers are easily measured as pure components, the spectra of two different copolymers are constructed from reaction spectral data containing mixtures. Good predictive capabilities of the developed model are demonstrated.

Keywords: Emulsion polymerization, Indirect hard modeling, Model transfer, Raman spectroscopy

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1 Introduction

Emulsion polymers are widely applied materials for adhesives, paints and other applications. Their wide range of properties may be extended by structured particles containing different polymers, which form separate polymeric phases within the particle if the phases are incompatible [1]. Such structured particles can combine the advantages of both polymers while reducing their disadvantages [2]. The formation of a particle morphology occurs in the second stage of the polymerization, when the second stage polymer is polymerized upon the first stage polymer seed particles. All emulsion polymers are products-by-process [3] and therefore monitoring the nonlinear process is of crucial importance to meet safety requirements as well as secondly the desired product quality. Emulsion polymers are produced mainly in semi-batch mode, often in monomer-starved regimes, requiring tight process control. Advanced process control relies on accurate estimation of the current state of the process, in order to compute optimal inputs to steer the process efficiently and counteract disturbances. Online monitoring of emulsion polymerization processes is still a challenging task despite past and recent efforts to solve the challenges. In [4], an overview of different measurement techniques is given for monitoring polymerization systems. Raman spectroscopy is a suitable method for monitoring emulsion polymerization processes since the abundant water is scattered only weakly.

Van den Brink and coworkers [5] use Raman spectroscopy to determine conversions of styrene and butyl acrylate online using partial least squares (PLS). McCaffery and Durant [6] monitor styrene online in a mini-emulsion process using the peak of the phenyl ring as internal standard. Hergeth and coworkers [7] give an insight into the industrial practice of polymerization process monitoring techniques, among others Raman spectroscopy. PLS is used to determine the individual monomer concentration in a copolymerization system [8]. In [9], the polymerization of styrene using bulk, emulsion and mini-emulsion polymerization is followed using Raman spectroscopy by computing the ratio between the area of the Raman peaks of the C=C double bond band and the aromatic band. Dropsit and coworkers [10] monitor the conversion of a styrene emulsion polymerization by analyzing the aromatic ring breathing at 1000 cm⁻¹ as the contribution of styrene monomer and styrene polymer. These works use either peak integration methods, i.e., analyzing single peaks or PLS regression. In [11], both Raman and spatially resolved near infrared spectroscopy are used to monitor the polymer content in a copolymerization system operated in semi-batch. PLS regression is used to analyze the spectra, but no individual monomer contents are predicted.

A physically motivated method to interpret the Raman spectra is the indirect hard modeling (IHM) technique [12].
The method may also be used with first derivative spectra [13]. The general idea is to fit pure species with hard models to the measured spectrum and derive the concentrations from the weights of each component species. It has been applied to polymerization systems in [14] for batch copolymerization, in [15] a normalization of spectra based on using pure homopolymer spectra for the corresponding monomer is used in conjunction with IHM to monitor a semi-batch copolymerization. In [16], IHM is applied to monitor the homopolymerization of a microgel and in [17] a copolymerization of microgel is considered.

While most works consider only batch systems, in this work, a semi-batch operation is considered both in lab and pilot scale in starved conditions and high solid contents. The semi-batch operation for polymerization systems is more difficult than batch operation since no internal standards can be used. While monitoring the concentrations can allow to detect a faulty batch, the final goal is to use this information for process control to adjust the operation and produce in-spec material. Optimized semi-batch operation for desired particle morphology [18], [19] requires tight control as the particle morphology depends strongly on the conversion and reactor temperature. In [20], a closed-loop advanced process control for particle morphology is described using online Raman measurements for concentration predictions.

2 Experimental

The goal of the synthesis is to produce polymer particles with a distinct non-equilibrium morphology, i.e., the shape of the polymer particles, formed due to the incompatibility of the seed polymer phase and the second stage polymer phase. The chosen recipe is reported in [21] as case 1. Only the second-stage polymerization is considered in this work. In the first stage, the seed particles are polymerized using four monomers methyl methacrylate (MMA)/butyl acrylate (BA)/acrylic acid (AA)/acrylamide (AAm) in ratio of 88/10/1/1 mass based. The solid content after the production of the first stage polymer is about 38 %. For the second stage, styrene (S)/BA/AA/AAm are fed in the weight ratio 88/10/1/1, reaching a final solid content of about 47 %. The seed makes up approx. 60 % of the total mass of the batch. Sodium persulfate, tert-butyl hydroperoxide and acetone bisulfate are used as initiators while sodium lauryl sulfate and Emulan-OG are used as emulsifiers. The reaction temperature is maintained at 80 °C and the feeding period takes 90 min.

2.1 Materials

All chemicals used are from BASF. All water is deionized before being used in the reaction.

2.2 High Performance Liquid Chromatography

High performance liquid chromatography (HPLC) is used as reference measurement technique for the weight fractions. It is calibrated using a range of 10 to 12 calibration standards. The samples of typically 5 to 10 mL are taken from the reactor. Inhibitor is added to stop the reaction and the samples are stored at 4 °C.

2.3 Reactors for Lab and Pilot Scale

Two different setups were considered, a lab-scale reactor and a pilot-scale reactor. The lab reactor has a volume of 3 L, the pilot-scale reactor is 2300 L. Both reactors have inlets for the pre-emulsified monomer mixture and the initiator feed. They are equipped with cooling jackets and the reactor temperature is controlled. Both reactors are flushed with nitrogen.

2.4 Inline Raman Spectroscopy

The Raman spectra were collected inline using a RXN2 Raman Analyzer, Kaiser Optical Systems, Ann Arbor, MI, USA, at 785 nm with 400 mW excitation power. A short focus wethead NIR process probe under ATEX guidelines was used and 290 mW power was measured at the probe at lab scale. The software HoloPro 3.2 (Kaiser Optical Systems) was used for recording the spectra. Cosmic ray filtering was activated. The acquisition time was set to 50 s. Two different devices were used for lab scale and for pilot scale. In the lab scale, a single accumulation is performed, leading to new spectra obtained every 104 s. In the pilot scale, two acquisitions were made, leading to 204 s in-between two recorded spectra.

3 Spectral Modeling

As the indirect hard modeling approach reconstructs the measured spectra by known species, it is necessary to have all main species available as hard models. The software PEAXACT (version 4.5., S-PACT GmbH, Aachen, Germany) is used for the modeling, calibration and prediction of concentrations. Pseudo-Voigt functions, which are the linear superposition of Gaussian and Lorentzian functions, are used to mathematically describe the peaks of the hard models. The measured raw spectra are pretreated before the fitting process. The Raman spectral range is taken from 590 to 1800 cm⁻¹, with exclusions from 710 to 800 cm⁻¹ and 1550 to 1560 cm⁻¹ as they represent peaks of the device. All spectra are normalized using the standard normal variate (SNV) method.

For the considered second-stage polymerization, water and copolymer-1 (P1) are already present in the mixture.
Upon this copolymer seed of P1, a copolymerization of BA and S, with AA and AAm as functional monomers is started. Therefore, at least five components are needed as species, viz., water, copolymer-1, copolymer-2, BA and S. The concentrations of the functional monomers (AA and AAm) are very low, with less than 0.08 wt % and 0.05 wt %, respectively. Hence, they are neglected in the spectroscopic models.

For the calibration, hard models for all five components are needed. However, the two copolymers are only available in mixtures with water. Consequently, the approach of complementary hard modeling [22] is used and is described in following. After the feeding period of the first monomer mixture forming polymer P1, the remaining traces of free monomer are given time to polymerize. During this postpolymerization period, the measured spectra are almost unchanged. Since only water and polymer P1 are relevant in this mixture, the spectrum of pure P1 can be obtained from the spectral difference of the measured spectrum and the available water spectrum. The same method was applied to generate a component spectrum of P2. However, in this case, both water and copolymer P1 are present in the mixture during the postpolymerization. The hard models of the monomers are constructed from Raman measurements of the pure monomers, BA and S. At the considered wave lengths, water is a weak Raman scatterer. The hard models of PMMA-BA (P1), PS-BA (P2), water (W), BA, S consist of 20, 18, 2, 9, and 13 pseudo-Voigt peak functions, respectively.

The fit of the developed model for a measured, but pretreated spectrum is shown in Fig.1. The gray areas show the excluded regions of wavenumbers. For the root mean spectral residuals vary between 0.04 and 0.08. The weights of each of the components are linearly regressed against the HPLC measured weight fractions.

4 Results and Discussion

The results of the calibration and validation experiments are presented in this section.

4.1 Calibration

The model building samples are obtained from polymerization runs in the lab reactor. 27 samples are available for training with measurements for all considered species taken from 3 different runs in the lab reactor. The samples taken from the reactor are analyzed using HPLC. The regression is cross validated by leaving out 10 % of the data. In Tab. 1, the root mean square errors of cross validation are given for all five components. This absolute deviation is larger for components with higher mass fractions. However, the relative error is smaller than for the monomers, which have usually less than 1 % weight fraction. Due to the spectral similarity of the polymer spectra and the monomer spectra, the low weight fractions of the monomers along the high weight fractions of polymers pose a challenge to IHM.

| Substance | RMSECV [wt %] |
|-----------|---------------|
| BA        | 0.17          |
| S         | 0.15          |
| P1        | 0.59          |
| P2        | 1.17          |
| W         | 1.52          |

4.2 Validation

With the developed IHM model, the concentrations are predicted for polymerization reactions online and are validated. The model is used both in the lab-scale and the pilot-scale reactor.

4.2.1 Validation: Lab-Scale Reactor

An experiment was performed, running the calibrated IHM model online. The most relevant information is the weight fraction of styrene, which is depicted in Fig.2. During the first 90 min, the monomers and initiator are fed. Thereafter, the post-
polymerization phase begins and only initiator is fed. The predictions of the IHM model are close to the HPLC-analyzed samples. However, an offset for the styrene weight fraction is observed during the postpolymerization phase. This offset of the styrene predictions is due to a fitting error. The overall spectral fit improves by erroneously increasing the weight fraction of styrene. Reducing the deviation to the measured spectrum at 1000 cm\(^{-1}\) outweighs the error introduced at the wavenumber of the double bond at around 1630 cm\(^{-1}\). The root mean square error of predictions for the five components are given in Tab. 2.

### 4.2.2 Validation: Pilot Plant Reactor

For the control task, described in [20], only the mass fraction of styrene was considered. For the pilot plant operation, only HPLC measurements of styrene are available. The experiments were run in a 2300-L pilot plant reactor. The settings of the Raman spectrometer differ from the lab settings, see Sect. 2.4.

In principle, the same reactions take place as in the lab-scale reactor. However, a larger amount of product is lost if the batch is off-spec and in turn affects the profitability. Additionally with increasing volume, the surface to volume ratio decreases making the control of the exothermic reaction more challenging.

In total, four experiments were conducted. Three experiments were run with the optimized recipe as described in [20] and one was run with the standard recipe. In Fig. 3, the evolution of styrene is shown for the optimized recipe. The predictive capability of the IHM for styrene is demonstrated for this example. For all four pilot plant experiments, the RMSEP for styrene is 0.16 wt %, which supports the good predictive capabilities. A parity plot for the experiment is shown in Fig. 4, where deviations are small for the region of interpolation and a larger error is observed for an extrapolated styrene weight fraction.

### 4.3 Discussion

The previously shown results of the IHM predicted concentrations show that this spectral data can be well interpreted by IHM. In this work, only the IHM method is applied to the dataset in detail. Other often used methods to analyze spectra data include peak integration and partial least squares. Peak integration relies on unique peaks for

| Substance | RMSEP [wt %] |
|-----------|--------------|
| BA        | 0.10         |
| S         | 0.15         |
| P1        | 0.83         |
| P2        | 1.03         |
| W         | 3.02         |

Table 2. Root mean square error of prediction (RMSEP) for validation experiment in lab reactor.
every component to be predicted. This poses challenges for copolymerization if all monomers need to be individually identified. For the experiments conducted, the ratio of the two monomers is always the same. Therefore, a simple monitoring of the \( \text{C}=\text{C} \) double bond peak around 1630 cm\(^{-1} \) can also yield good results for the prediction of the monomers, which share approximately the same concentration ratio over the course of the reaction. PLS is widely used to analyze spectral data as shown in the literature review, but his contribution focuses on the application of the IHM method. A comparison of PLS and IHM is presented in [12]. Only styrene is measured for the pilot plant experiments and a very good fit is shown in Fig. 4. However, there is an outlier for a very high styrene mass fraction. IHM fits the component spectra to the measured spectrum by minimizing the root mean square spectral residuals. For the outlier this spectral residual is larger than usual explaining the discrepancy between the model prediction and the HPLC sample. For the other validation samples with styrene weight fractions above 0.8 wt %, the styrene weight fraction is mostly underestimated compared to the HPLC measurements. Comparing the IHM spectral fit with the measured spectra shows the model peak is beneath measured peak for the \( \text{C}=\text{C} \) double bond, explaining this deviation partly. This underestimation is made as the overall fitting error increases for a better fit of the double bond peak. Another possible explanation is that the Raman device used for calibration and the device used for validation in pilot plant differ in their spectral signal.

5 Conclusion

We have shown a successful application of the indirect hard modeling (IHM) approach for monitoring an emulsion polymerization process operated in semi-batch monomer-starved regime. The transfer from the model developed from lab measurements and lab reactors to a pilot plant was successful. While the solid content of the polymerization was high with around 50 %, the weight fraction of the monomers was below 1 % for both styrene and butyl acrylate, posing a challenge to IHM. The functional monomers acrylic acid and acrylamide were below detectability for the model. While simple methods like peak integration give first insights into the remaining unreacted monomer, IHM gives the concentration about all modeled species. This is especially beneficial if complex models are required to run the process which need good estimates of the current state of the reactor. However, not only online concentration measurements are of interest, but also quantities that are related to polymer properties. Particle size distribution, molecular weight distribution or particle morphology are examples for such polymer properties. They are still not measurable fast and robustly in order to be used for direct quality control, posing an important challenge for future measurement techniques.

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### Abbreviations

- AA: acrylic acid
- AAm: acryl amide
- BA: butyl acrylate
- HPLC: high performance liquid chromatography
- IHM: indirect hard modeling
- P1: MMA-BA copolymer
- P2: S-BA copolymer
- PLS: partial least squares
- S: styrene
- W: water

![Figure 4. Parity plot for calibration and validation of styrene using all available experiments.](image-url)
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Research Article: A two-stage emulsion copolymerization process is monitored via Raman spectroscopy, both in a lab-scale reactor and in an industrial pilot plant reactor. The Raman signals are analyzed using the indirect hard modeling approach. Good predictive capabilities of the developed model are presented.