Industrial Polymerization Monitoring

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Summary: Monitoring and control of polymerization reactions is essential for high process safety, high product quality and competitive production costs. Ideally the entire process chain is regarded, starting with raw material analysis and the polymerization reaction up to the measurement of polymer- and application-properties. Process data like temperatures and pressures can be used to monitor reaction trajectories in a cost effective way, e.g. using calorimetric evaluations. Additional sensors can provide chemical or morphological information but must be robust and inexpensive for commercial applications (e.g. NIR- or Raman spectroscopy). Data from these different sources can be used for multivariate data analysis, delivering additional insights that might not be obtained by direct measurement.

Keywords: online spectroscopy; polymerization monitoring; soft-sensors

Introduction

Many polymers are products by process, meaning that variations in the production process might strongly influence product properties. The polymerization process can vary due to chemical or technical changes. Chemical variations often have their source in changing raw material quality. Sources of technical variations can be routine maintenance, change of process setups or fouling of inner reactor surfaces, to name only a few. It is important to know to what extend specific variations can still be tolerated, and when to reject raw materials or start technical / control actions to ensure that the next polymer batch will attain the necessary product quality. Polymerization monitoring systems have thus to be tuned to maximize batch quality while keeping expenditures and efforts on a low level for commercial success. This is true for the entire production process, from raw material control and the polymerization up to follow up product processing and might also encompass pre-mixers, dissolvers, kneaders, degassers and other process components beyond the polymerization step in the reactor itself. Besides keeping quality high and production costs low, polymerization monitoring also plays an essential role in process safety, as many polymerization systems are highly exothermic. Temperature and pressure measurements can not only be used to ascertain that the ongoing reaction is following a safe trajectory by using calorimetric evaluation systems, they can also be used in combination with other sensory data for multivariate mathematical analysis systems (soft-sensors) that can yield further information on the process or product. The latter approach helps to circumvent some limitations (including costs of acquisition and maintenance) of available classical hardware sensor systems, especially when dealing with complex heterogeneous, multi-phase systems like polymer dispersions.

Living with the Variability of Incoming Materials

Variations in the composition and quality of raw materials can have a strong effect on polymerization processes. Ideally, this variability will be kept as small as possible.

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The logistic and commercial need to evade single-sourcing on the other hand, normally leads to the use of several different manufacturers of one and the same substance. The quality of the raw material does not only depend on the manufacturer, additionally influences might come from the handling of the material, with distributors potentially introducing contaminants or even mixing up deliveries.

Often used methods for raw material quality control in industry are non invasive techniques like near-infrared (NIR), Raman or x-ray fluorescence (XRF) spectroscopy. Small hand-held devices are now available that are simple to use and have an unambiguous result presentation.[1,2] They thus can be applied in routine work by shift personnel e.g. directly at the site of delivery. The result visualization can be in form of a green (ok) or red (not ok) indicator at the device and further visualization is often done using easily comprehensible principal component analysis (PCA) plots, as seen in Figure 1. PCA reduces the number of (possibly correlated) variables into a smaller number of informative variables.[3,4] In this NIR example, a spectrum with 400 data points is reduced to 3 variables (principal components) and the sample can thus be visualized as a point in the 3D plot.

NIR and Raman spectroscopy are mostly used for the measurement of organic compounds. The control of some materials might pose difficulties, as substances must not only be either IR- or Raman-active, obtained spectra must also contain enough information of the desired analyte, which might not be the case when dealing with complex matrices or low concentrations. If the latter is the case, most of the time conventional analytics like chromatographic methods are still needed. Other properties of incoming materials like molecular weight distributions can also not yet be measured in a simple and fast way. When dealing with inorganic substances, the use of hand-held XRF spectrometers might be an ideal solution.

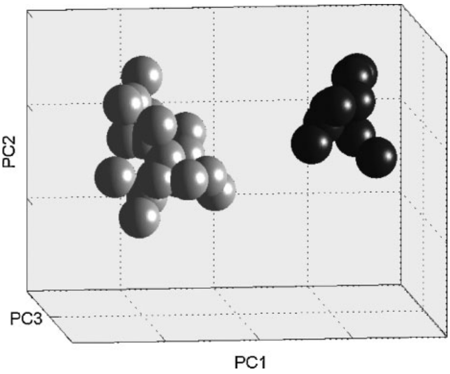

Figure 1.
Principal component analysis plot of several lots of an incoming raw material measured with NIR. Black spheres denote lots with diverging spectra and were thus not automatically released for use in production.

All these methods are used to evade classical, often time consuming and labor intensive chemical analysis of incoming materials. While NIR spectra, with bands due to overtones and combinations of vibrations normally have to be processed by multivariate methods,[5] Raman spectra might yield direct information on substance concentrations using specific bands, making its use much simpler as no models have to be created and maintained.[6] But this kind of multivariate approach is often nevertheless used to be able not only to measure concentrations,[7] but also to detect deviations from historical raw material batches known to be in-spec. When these kinds of models are created, it must be ascertained that the model is robust enough to stay valid over prolonged timeframes to minimize the costs of maintaining it.

Reaction Monitoring

Several different parameters of a reaction process can be measured to gain insight on the process. Some of these parameters are

- concentration of components (polymer, monomers, solvents, dispersing agents, pH)
- thermal information (temperature, heat quantities and flows, thermal conductivity)
- mass density (density, reaction mixture volume, pressure)

- optical characteristics (haze, refractive index, absorption)
- mechanical properties (viscosity, modules of elasticity and shear)
- (di)electric properties (conductivity)

There are still no affordable and robust industrial sensors available for the measurement of many of these parameters in (high pressure) polymerization processes. Parameters that normally are continuously monitored are reactor temperatures, pressures, agitator power intake and speed as well as feed rates, as they are needed to control the process and to ensure its safety. The analysis of this kind of data can yield further information on the process, the product or even application properties of the produced polymer. As polymerizations are strong exothermic reactions, the resulting heat-flows can be used to gain information on monomer conversion. This is done by means of heat balance calorimetry that quantifies the amount of energy removed from the reaction system by measuring the difference of the temperatures of the ingoing and outgoing cooling agent.[8,9] Other contributions to the heating and cooling of the reactor have to be considered for an accurate evaluation, like.temperature of feeds, energy contribution of the agitator etc.[10]

While the calorimetric approach yields information on reaction conversion it cannot differentiate between the conversions of specific monomer species in a system other than homopolymerization. This kind of chemical information can be obtained by chromatographic or optical spectroscopic methods. Latter ones have the advantage that no sample extraction and often no sample preparation are needed. As water has strong absorption in the IR region, Raman spectroscopy is often used when dealing with aqueous systems (e.g. dispersions). Further, standard glass fibers can be used in Raman and NIR spectroscopy making it possible to move the spectrometer further away from the reaction system and thus out of a zone with potential explosive atmosphere, further reducing equipment costs. Other advantages of Raman spectroscopy are the use of specific bands to obtain information on chemical substances and the proportionality of signal strength and concentrations.

For example, as monomer is converted into polymer the signal of the monomer's $C=C$ double bond vanishes (Figure 2). Other wavelengthes can yield information depending on the monomer system. Comparison of a vinyl acetate polymerization system (Figure 2, A) with a styrene / butyl acrylate system (Figure 2, B) shows that further information on the conversion of

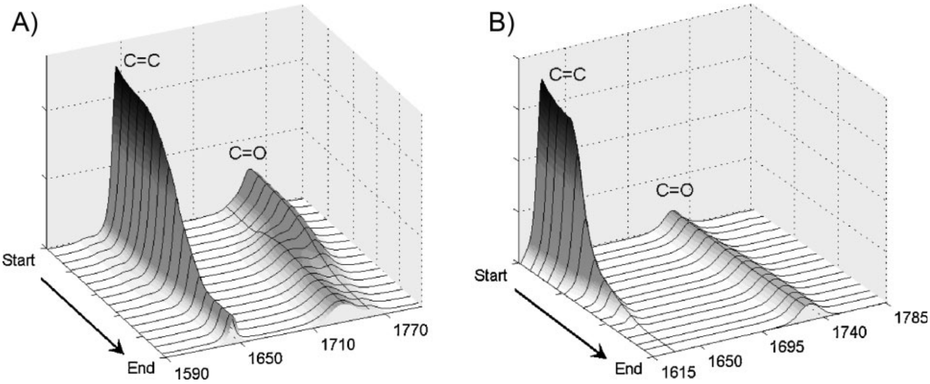

Figure 2.
Raman spectroscopic monitoring of polymerization systems from start to end of the reaction. A: vinyl acetate system. B: styrene / butyl acrylate system. Monomer consumption can be followed using the $C=C$ double bond signal and, in the vinyl acetate system, the $C=O$ signal for monomer to polymer conversion.

monomer to polymer can be extracted from the carbonyl stretch signal in the vinyl acetate system: the peak shifts from 1758 cm^{-1} in the monomer to 1738 cm^{-1} in the polymer. This shift is so pronounced that it can also be used for conversion monitoring by using two separate peak integrals with individual baseline correction.

It is also possible to obtain further information about polymer properties and application properties of the polymer through analysis of the reaction profiles in time.[11]

Combination of data from other sources and multivariate analysis (creating so called soft-sensors) can also provide additional process and product quality information and provide a warning if a batch shows deviations from other batches known to have produced in-spec material. These kinds of soft-sensors can provide outputs right at the end or during the batch run, thus also helping to evade down-stream bottle necks like delays due to time consuming quality control and to shorten cycle times, both important topics in industrial settings. Once models are created using available process data (which might include spectroscopic information) it must be made certain that the output quality of the soft-sensor stays on an adequate level. In industrial settings, were a process can change due to maintenance work, changes in recipes, reactor fouling etc. the fit of the model to the current data has to be monitored. The information on the quality of the fit can either help plant personnel detect and counteract unwanted process changes in a timely manner or give an indication that the model has to be updated with new data from the current process setup. Either way, the performance of soft-sensors should always be monitored and maintenance actions triggered by increased deviations (Figure 3).

Measurement Challenges

Measurement of colloidal properties can be important when dealing with emulsion and suspension polymerization systems, which are often used in industry. In these systems, monomer droplets and micelles are transformed into polymer particles with a defined particle size distribution (PSD) during the reaction. Possible measurement systems for particle sizing are based on spectroscopy, light scattering and separation, although monitoring systems that rely on sample extraction often are not feasible due to clogging of the extraction lines.

A cost effective way to gain particle size information can be the use of inexpensive online NIR spectroscopy.[12] Figure 4 shows how average particle sizes of vinyl acetate / ethylene dispersions measured using NIR spectroscopy correlate with classical laser diffraction reference measurements. The

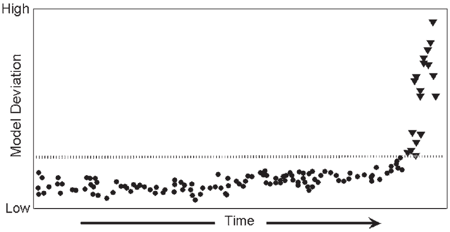

Figure 3.
Deviations of batch-data (each data point one batch) from the data-set used to create a soft-sensor. Once the deviation rises above a critical threshold process or model maintenance is triggered.

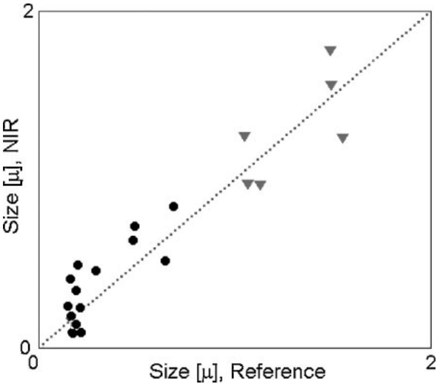

Figure 4.
Detection of deviations (triangles) from the wanted (circles) average particle size of a vinyl acetate / ethylene dispersion using NIR spectroscopy and comparison with classical laser diffraction reference measurements.

prediction can be done using a PLS model calibrated using samples with known particle sizes and is dependant on the correlation of the target value with the existing data set.[13] Although the accuracy using NIR measurements was limited in this case, it is high enough to detect batches with too large average particle size.

The installation of additional sensors in (high-pressure) polymerization systems can still be a challenge. For example, even robust, affordable online pH measurements at pressures of $p = 85$ bar and temperatures of $T = 85\,^\circ C$ over prolonged times are not possible yet. Further, as inner reactor surfaces are often cleaned using high pressure jets of cleaning solutions to remove polymer films, all installed sensors must either withstand far higher pressures or be protected from direct hits.

The determination of the amount of residual monomer, volatile organic compounds (VOCs) or residual peroxides after the reaction step, the steam stripping step and in the final product normally is achieved by conventional chromatographic methods on obtained samples. Robust, cost effective online solutions are not available either. Further characterization of the polymer concerning its gel-content, degree of crosslinking, degree of branching or oligomer content is only possible with time consuming laboratory analytics.

It should also be kept in mind, that the reaction mixture in big industrial reactors might not always be the same at different locations depending on the position of feeds and baffles (e.g. feeding from top or bottom). Approaches for the use of reactor tomography to gain information on hydrodynamics, mixing quality and the presence of potentially dangerous local temperature hot spots have been shown,[14,15] albeit mostly in smaller scales and difficult when dealing with industrial high pressure reactor systems that often cannot be enhanced with complex sensors or sensor systems due to safety considerations.

A different challenge lies in the detection of biocontamination. Online or fast at-line detection for a quick quality release would be very helpful, especially if the method could be applied by (specially trained) plant personnel on site.

Easy detection of corrosion in complex systems would optimize plant maintenance and reduce costs.

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