

Implementing NIR for Polymer Production Process Monitoring

Dr. Hari Narayanan, Senior Product Manager – Spectroscopy, Metrohm USA Inc

Introduction

Polymers are a very important class of organic materials, widely used in many fields due to their unique properties such as tensile strength and viscoelastic behavior under deformation. With more stringent demands on the quality of polymer products and pressure to reduce cost in production and processing, the need for fast, accurate and reliable monitoring methods is greater than ever.

Analytical methods, which require time-consuming and intensive sample preparation, are difficult to implement effectively in a process or quality control environment, and waste precious time and materials. Efficient process control demands a measurement technique which is rapid, requires little or no sample preparation and minimal technical expertise. It should be reliable, rugged and easily automated.

Near-infrared (NIR) spectroscopy meets those needs by being both rapid and precise. NIR analyzers provide rapid results, often in less than a minute. Sample preparation is minimal or eliminated via use of a probe, and is enhanced by the scan speed and high signal-to-noise performance typical of these systems. Speed can be further boosted by utilizing the ability of NIR to monitor multiple components simultaneously, or by placing the analyzer on-line or in-line. The latter also eliminates the need for routine sampling of the process, which can be time-consuming and involve safety risks. Furthermore NIR analyzers provide high precision results, due to the high stability of the analyzers and to the elimination of variability arising from sampling and sample preparation. As these benefits become more widely known, interest in the use of NIR spectroscopy as a tool for process monitoring in polymer fields has grown.

NIR for Polymer Polymerization Processes

Monitoring polymerization reactions is important from research through to production. At the fundamental level it provides information on kinetics and mechanisms necessary for the development of new materials,

while at the bench or pilot plant level it can be used to optimize reaction conditions. Finally, when used in a complete feedback-control-loop at the industrial reactor level, significant improvement in product quality can be expected, as well as savings of non-renewable resources, energy, reactor and personnel time. Creating an effective NIR implementation strategy depends on the type of polymerization process, the properties of interest, and measurement conditions.

Polymerization Processes

NIR spectroscopy can be used for bulk, solution, emulsion and suspension polymerization monitoring, providing information on copolymer composition and distribution, monomer conversion, molecular weight averages, average particle sizes and more.

Bulk polymerization

In bulk polymerization, the reaction is carried out in the absence of a solvent, diluent or other materials. It is adaptable to copolymerization with other compatible comonomers and results in very high product purity. Bulk polymerization can be used when the polymer does not form cross-linked gels or wall deposits, which would contaminate continuous polymerization equipment. Heat removal is critical to avoid formation of explosive compounds.

Solution polymerization

In contrast to bulk polymerization, solution polymerization is carried out in the presence of an inert solvent and initiator. Solution processes have advantages in the low viscosity and homogeneous properties of the reaction medium. The main disadvantages are lower reaction rate, productivity, and molecular weight average of the final product as compared to bulk polymerization.

Suspension polymerization

Suspension polymerization processes are widely used for production of polymer beads. In a typical suspension process, an organic phase constituted of an initiator

(or catalyst), comonomers and the final polymers are suspended in an aqueous phase which contains additives and residual monomer, and the reaction occurs in this heterogeneous mixture. The main advantage of suspension processes is that the polymer material is much easier to purify. It is important, however, to maintain control of the average particle size and particle size distributions of the final polymer particles, as compounding, processing and bulk-handling properties are affected by these variables.

Emulsion polymerization

Emulsion polymerization is a widely used industrial process for the production of synthetic polymer colloids or latexes of several different types. These are used in a wide variety of applications as synthetic rubber, coatings, paints, adhesives and binders. A typical emulsion polymerization recipe includes water, monomers, surfactant, water soluble initiator and additives, and leads to a heterogeneous reaction mixture composed of submicron solid polymer particles dispersed in an aqueous medium. Particle size of the polymer depends on droplet size and rate of agitation, making constant agitation a necessity in emulsion polymerization.

Sampling and off-line measurement is most commonly used to monitor emulsion polymerization, as online probes can easily become fouled or coated. Emulsion polymerization systems are quite complex, involving different phases (aqueous phase, monomer droplets and polymer particles) and several compounds (aqueous, monomer, polymer, initiator, stabilizer and buffers). Additionally, they yield spectra that are particularly difficult to interpret, making NIR monitoring more challenging compared to other polymerization methods.

NIR analysis strategies

Today's NIR instrumentation can be installed in the laboratory, at-line or directly into a process stream, dryer, extruder, or reactor. Overall, the most appropriate NIR measurement mode and location of the NIR analyzer is dictated by the optical properties of the sample, the method's selectivity and sensitivity for the required analytes, the duration of the process run, and monitoring and control requirements. Fiber optic probes are an enabling technology for NIR process monitoring,

allowing measurements to be made directly in a wide range of sample types and environments, even when the measurement system is remotely located.

In-line analysis

In this analysis strategy, a process NIR analyzer is interfaced directly to the process using fiber optics. A probe constructed of stainless steel or other material is inserted directly into a port installed in the process stream or vessel. This analyzer configuration is dedicated to performing a particular analysis on a specific sample type, and can provide results in <10 s. The direct interface requires minimal supporting hardware, and provides unattended, optimized, near real-time analysis on specific media. The downside of this strategy is that maintenance cannot be performed unless the process is shut down. In addition, for transmission analysis, the narrow optical path lengths combined with the fluid dynamics of process streams can occasionally make this analysis strategy difficult to implement. In-line analysis is best suited to closed-loop monitoring and control strategies for scale-up and manufacturing operations.

Typical application: Polyester batch reaction, analyzed using an interreflectance immersion probe

On-line analysis

In this analysis strategy, an NIR analyzer is interfaced to the process using a sample loop and performs a particular analysis on a specific sample type, yielding results in <10 s. NIR spectral measurements are performed on a continuous flow of sample as it passes through a flow-cell, conveniently accessed via side-streams. Side-streams are used for sample conditioning such as heating, filtering, or degassing. They help in performing maintenance, and allow calibration and test samples to be analyzed, all while the process is operating. Like in-line monitoring, on-line monitoring provides optimized, unattended, near real-time analysis on specific media, and works well in closed-loop monitoring and control strategies for scale-up and manufacturing operations.

Typical application: Polyurethane production process, analyzed using an interreflectance immersion fiber optic bundle probe

At-line analysis

In this analysis strategy, an NIR analyzer is located close to a process stream, but does not interface directly. It is a good solution for performing a particular analysis on a specific sample type where in-line or on-line monitoring is not possible, as in emulsion polymerization. At-line analysis strategies require manual sampling, delaying results by several minutes or more. Additionally, the analyzer must meet appropriate classifications, such as IP55-NEMA12. At-line analysis finds application in process monitoring and control strategies, and in manufacturing operations.

Typical application: Polyacrylamide emulsion, measuring residual monomer content via reflectance measurement

Instrumentation for Polymerization Reaction Monitoring

Process NIR analyzers provide near real-time chemical process information while operating in harsh manufacturing conditions, thus the process sample interface is dictated by the sample type and process conditions. Contact transmission and reflectance probes are used for analyzing clear to opaque liquids and solids. Non-contact reflectance measurements are performed on materials transported in hoppers, and on transport and conveyor lines.

Once NIR light has interacted with the sample, a number of technologies exist for its measurement, parsing the spectrum by frequency for qualitative or quantitative analysis. One class of instruments looks at bands of frequencies, providing spectral coverage over a narrow spectral region (50–100 nm). These include broadband, discrete filter photometer, and light-emitting diode (LED) based instruments. Another class provides more continuous and full-spectrum coverage by dispersing the spectrum or scanning across it. These include diffraction grating, interferometer, diode-array and acousto-optic tunable filter (AOTF) based instruments. Selection of the appropriate technology is usually based upon the sensitivity and selectivity needed to observe the required analytes, as well as reliability, ease-of use, and implementation needs. Ability of the instrument to operate in harsh production environments and vibration resistance must also be considered.

Method Calibration

NIR spectroscopy does not directly provide quantitative analysis of chemical mixtures. To use NIR spectra for quantitative analysis it is first necessary to find a relationship between the measured data and the concentrations. The most common model to express this relationship is a regression analysis containing first-order or higher-order polynomials, known as calibration curves. They correlate the concentration of the analyte to the response of the spectrometer.

Developing an accurate regression model is an iterative process. After the construction of a model it is necessary to assess the model quality through observation of model parameters and validation via independent data. An on-line analyzer will always be calibrated before it is installed in the process. This may be accomplished off-line using process grab samples and/or synthetic samples. It may also occur by installing the analyzer in a lab-scale reactor, or in a semi-works or pilot plant. It is sometimes possible to transfer a method developed with an off-line analyzer or an on-line analyzer at a different plant to the new on-line analyzer. Occasionally, none of these options are possible, and the analyzer must be calibrated on-line.

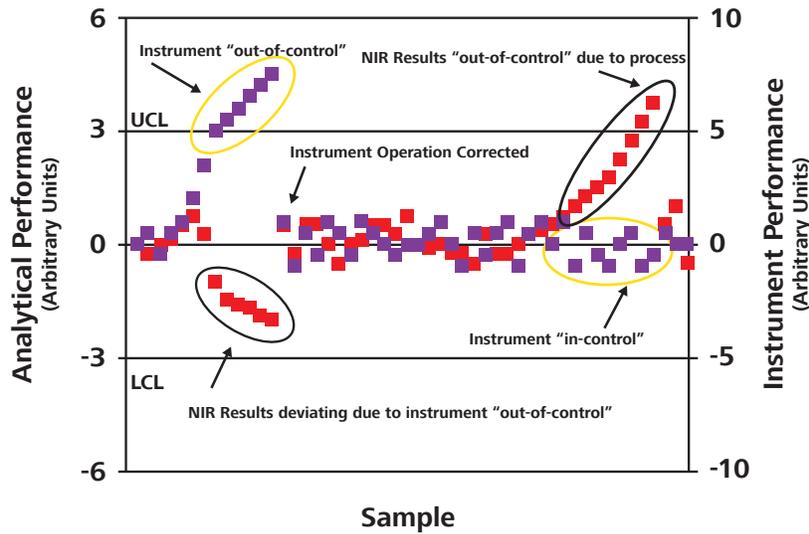
Method Standardization

NIR analyzers use a combination of internal performance standards to maintain instrument stability and response and NIST-traceable external standards placed directly at the sample location to precisely match photometric and wavelength response for all analyzers. By precisely matching the performance for all instruments, a quantitative calibration model or a qualitative library developed on one NIR analyzer can be used to predict quantitative or qualitative results on subsequent analyzers (of similar configuration). It can also be applied to the same analyzer after service (lamp or component change) without requiring a bias or slope adjustment or any other data manipulation.

Method Maintenance

Over time, changes in raw materials, process improvements, or other “uncontrolled” factors can potentially cause the performance of an NIR method to be compromised. NIR instrumentation malfunction is also possible. Routine

Figure 1: Control chart for monitoring the NIR analyzer and method performance to identify "out-of-control" situations.



control tests should be performed regularly to monitor the process and the analyzer and maintain confidence in the accuracy of the NIR measurement, shown in Figure 1.

NIR for Polymer Extrusion Processes

Polymer extrusion forms the basic process for manufacture of a wide range of plastic products, ranging from microscale implants for biomedical applications to major vehicle components. Control of extrusion processes is of paramount importance to a large number of industries, and can also be accomplished via NIR spectroscopy.

A simple polymer extruder accepts polymer pellets from a hopper at a cooled feed zone of a rotating Archimedean screw. Additives such as fillers, colorants and UV inhibitors are often used and can be mixed into the resin prior to arriving at the hopper. The use of in-process spectroscopic monitoring allows molecular-specific information to

be extracted from the melt flow, as opposed to the physical information derived from more conventional in-line methods (this may include temperature, pressure and rheological measurements). NIR spectroscopy can be applied to monitoring the polymer composition, additive concentration and flow properties during the extrusion process. Depending on the type of sample to be analyzed, either a reflectance, transmission or an immersion probe can be used. Measurement of variations in talc, polypropylene, ethylene-octene copolymer and UV additives during the extrusion process using a diffuse reflectance probe is shown in Figure 2.

NIR for Polymer Curing Processes

The final properties of thermosetting resins depend to a large extent not only on the chemical nature of the monomers utilized, but also on the curing process. Light curing resin technology is a breakthrough that allows

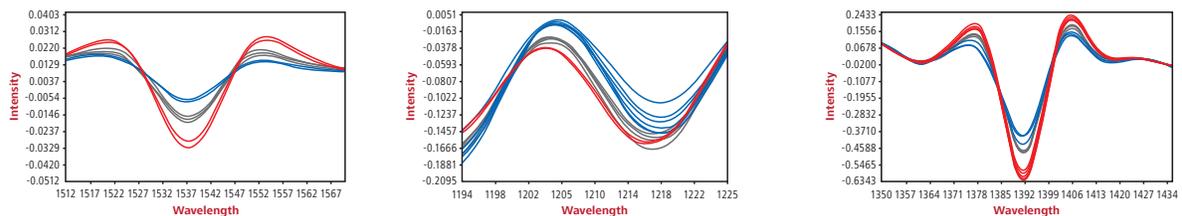
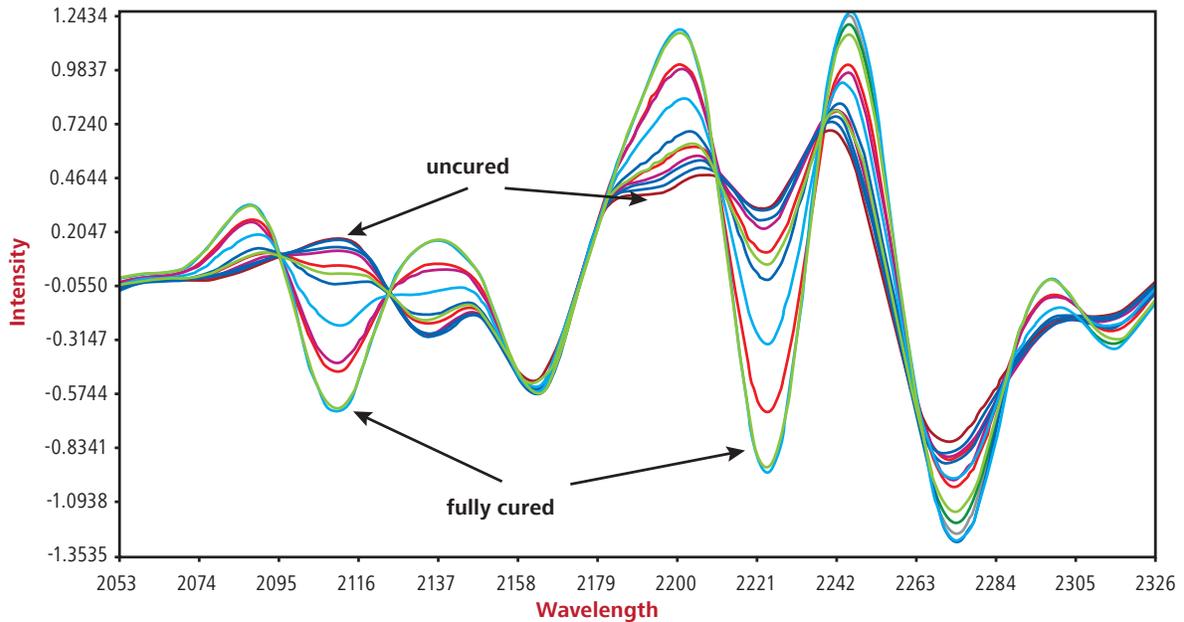


Figure 2: Spectral changes due to a) high and low UV Additive b) high and low EAO C) high and low talc

Figure 3: Curing process monitoring using a non-contact probe



polyester, vinyl ester, and urethane resin to be used in new applications and fabricated via new methods, opening up many new opportunities in both coatings and composites. These resins use ultraviolet light to activate polymerization, allowing them to be made one-part, solvent-free, and fast-curing.

These resins overcome many of the drawbacks of conventional adhesives, and demand for ultraviolet-curing resins is increasing year after year. Additional advantages that come with the technology include reduction in waste and environmental compliance issues. At present, light-cured resins are used for a wide range of applications, including plate-making materials, resists, paints, inks, and electrical and electronic materials. The curing process can be accurately monitored by NIR spectroscopy in real-time, providing opportunities to study curing kinetics, optimize curing conditions, and validate the extent of curing. Figure 3 shows the use of a non-contact probe to collect the NIR spectra of resin coated fiber during curing process monitoring.

Summary

NIR process spectroscopy allows us to obtain a more detailed understanding of polymeric materials and changes at the molecular level which occur during processing, at very low cost per analysis. No reagents or chemicals are needed, eliminating ongoing costs associated with purchase and disposal of consumables.

The monitoring of component composition during a process and observation of trends provides guidance as to whether a process is, in fact, under control. This can enable closed-loop control by use of specific measurements of material properties or process variables, improving batch-to-batch consistency and yield. Batch failure can be eliminated, resulting in substantial financial benefits and reduced waste of raw materials.

Given the tremendous economic and quality benefits derived from implementing NIR spectroscopic monitoring, along with its speed and ease of use, it is not surprising that NIR process monitoring is becoming the tool of choice in polymer manufacturing processes.

References

1. NIR Spectroscopy – A guide to near-infrared spectroscopic analysis of industrial manufacturing processes – Metrohm NIR Systems - NIR Monograph
2. Analysis of polymer using near-infrared spectroscopy – Metrohm NIR Systems – AB 414
3. Increase the accuracy of your NIR measurements with instrument calibration – Metrohm NIR Systems – AN 12
4. Increase the accuracy of your NIR measurements with reference standardization – Metrohm NIR Systems – AN 13
5. Near-infrared analysis of polyols: process monitoring in a hostile environment- Metrohm NIR Systems – AN 7
6. NIR for polymer research quality control and reaction monitoring – N.Heigel et al., Journal of Near Infrared Spectrosc. 15, 269-278 (2007)
7. Coupling of near infrared spectroscopy to automatic continuous online monitoring of polymerization reactions - F.H. Florenzano et al. / European Polymer Journal 41 (2005) 535–545
8. Applications of process spectroscopy to polymer melt processing - S.E. Barnes, M.G. Sibley, H.G.M. Edwards and P.D. Coates- IRC in Polymer Science & Technology, School of Engineering, Design and Technology, University of Bradford, Bradford,UK
9. Process Monitoring of Polymer Systems by using Near-Infrared Spectroscopy - Wei Li,School of Materials Science and Engineering, Shenyang Aerospace University People’s Republic of China
10. NIR monitoring of a hot-melt extrusion process – Spectroscopy Now. Volume 26, Issue 8, pp. s8-s17

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