

The Versatility of Fiber Optic Probes for Polymer Production Process Monitoring

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

Introduction

Ironically, the very properties for which polymers are synthesized – chemical resistance, elasticity and strength – can impede their chemical analysis. As a result, the quality control methods used to determine additive levels in polymers varies, influenced by the chemical and physical characteristics of the polymer. During the polymerization process, even small changes in the process parameters can lead to significant variability in the properties of polymer products. It is therefore essential to measure the polymer properties continuously and adjust the processing parameters via rapid feedback to assure product quality and consistency.

NIR spectroscopy is well suited to the task, providing real-time structural and kinetic data. It is rapid, requires little or no sample preparation and minimal technical expertise. Many of these benefits are due in no small part to its most popular method of interface – a fiber optic probe placed directly into the reactor system. This eliminates the need for sampling, and consequently, reduces time and experimental error associated with the sampling process.

Advantages of Fiber Optic Probes

The use of fiber optic probes in NIR spectrometer systems has opened up new perspectives for process monitoring in polymer manufacturing. An NIR probe connected to a spectrometer via optical fiber allows direct on-line and in-line monitoring without interfering in the production process. Fiber optic probes can be placed in very harmful working environments, while the spectrometer and analysis computer remain safe and secure in a process monitoring room. In fact, remote monitoring can be achieved at large distances without significant impact to signal-to-noise ratios.

A wide variety of NIR optical probes are now available, from transmission pair probes and immersion probes to reflectance probes suitable for contact and non-contact measurements. This diversity allows NIR spectroscopy to be applied to almost any kind of polymer – including melts,

solutions, emulsions and solid powders.

Finding the Right Match

Selecting the right probe, or sample interface, to use within an NIR system is crucial to successful process implementation for in-line or on-line process monitoring. For the system to perform optimally, the probe must be optically matched with the spectrophotometer and with the optical fiber that transmits the spectral data. Some of the challenges faced by NIR sampling interfaces for polymerization reaction monitoring include sustained high temperatures, sudden changes in temperature, pressure extremes, polymer flow issues and fouling of the probes.

In order to be successful the probe must be selected based on the application, the measurement technique and environment in which it is to be used. Probe materials cannot react with the materials in the process, yet they must withstand the anticipated temperature and pressure extremes. Careful consideration of the relative thermal expansion coefficients of the window material and the probe materials during probe design can minimize the risks caused by sudden large changes in temperature. The majority of polymer process monitoring applications can be met with commercially available probes. These are typically constructed of 316L stainless steel or hastelloy in combination with a sapphire window, and are designed for use at temperatures up to 300°C and 5,000 psi pressure.

Clear and scattering liquids are most often measured using micro interactance immersion probes or a micro transmission probe pair. These probes can also accommodate slurries with up to 15 – 20 % solid content. Above this level, a micro interactance reflectance probe is needed, which transitions well to measuring solids. Specialized probes are needed to measure some solids, and include variations such as a micro interactance reflectance probe with purge capabilities on its collection tip, or an optimized 45° micro reflectance probe. Non-contact probes accommodate other cases, as when samples are passing by on a conveyor belt.

Table 1: Summary of probe types and their application

Probe Type	Applications	Processes	Installation
Micro interactance reflectance probe	<ul style="list-style-type: none"> • Solids (powders, granules) • Slurries with > 15 % solids 	<ul style="list-style-type: none"> • Bulk polymerization • Hot melt extrusion 	<ul style="list-style-type: none"> • Direct into process line • Compression fitting or welded flange
Micro interactance immersion probe	<ul style="list-style-type: none"> • Clear to scattering liquids • Slurries with < 15% solids 	<ul style="list-style-type: none"> • Solution phase • Temperature- & pressure-controlled extrusion 	<ul style="list-style-type: none"> • Direct into process line • Compression fitting or welded flange
Micro transmission probe pair	<ul style="list-style-type: none"> • Clear to scattering liquids • Slurries with < 15% solids 	<ul style="list-style-type: none"> • Solution phase • Temperature- & pressure-controlled extrusion 	<ul style="list-style-type: none"> • Direct into process line or reactor • Into a side-stream loop • Compression fitting or welded flange
Micro interactance reflectance probe with purge on collection tip	<ul style="list-style-type: none"> • Solids (powders, granules) • Environments where sample amount is variable (e.g., fluid bed dryer) 	<ul style="list-style-type: none"> • Drying of granules and powders 	<ul style="list-style-type: none"> • Direct into the fluid bed dryer, reactor, or process line • Compression fitting or welded flange
Optimized micro reflectance probe (45°)	<ul style="list-style-type: none"> • Solids (powders, granules) 	<ul style="list-style-type: none"> • Direct contact with granules and powders 	<ul style="list-style-type: none"> • Direct into process line • Compression fitting or welded flange
Non-contact probe	<ul style="list-style-type: none"> • Samples moving on a conveyor belt • Other non-contact measurements 	<ul style="list-style-type: none"> • Curing 	<ul style="list-style-type: none"> • Place so that sample passes 100-250 mm from window

Types of NIR Probes

Micro Interactance Reflectance Probe

This probe is placed in direct contact with the sample to be analyzed. It is designed to measure the diffuse reflectance of a sample, not the specular reflectance. The diffuse reflectance comes from the penetration of the NIR energy into the sample, while the specular reflectance is energy from the surface. It is well suited to solid samples, such as powders, granules, or slurries containing at least 15% to 20% solids, and is often used to monitor bulk polymerization and hot melt extrusion processes. It can be installed directly into the process via compression fitting (e.g., Swagelok™) or welded flange.

Micro Interactance Immersion Probe

This probe is used to analyze liquid samples in transmittance mode. The probe consists of a body and an adjustable high-energy mirror tip where the sample flows through the gap between the two. Adjusting the mirror tip position defines the pathlength for analysis, where the pathlength is equal to two times the gap. It is recommended for

clear to scattering liquids and slurries with less than 15% solids, and can be found in solution phase processes and temperature- and pressure-controlled extrusion processes. It can be installed directly into the process line or reactor, or into a side-stream loop via compression fitting (e.g., Swagelok™) or welded flange. The probe should be installed so that sample flows easily through the gap between the probe body and high-energy mirror tip.

Micro Transmission Probe Pair with Lenses and Spacers

A micro transmission probe pair is used to analyze liquid samples in true transmission mode. The probe pair consists of two lensed transmission probes along with threaded spacers. The transmission probes are placed 180° opposite one another with the spacer connecting the probes, and the threaded spacers are used to reproducibly set the pathlength between the transmission probes. This method works well for clear to scattering liquids and slurries with less than 15% solids, as in solution phase processes and temperature- & pressure-controlled extrusion processes.

This probe can be installed directly into the process line or reactor, or into a side-stream loop via compression fitting (e.g., Swagelok™) or welded flange. The probe should be installed so that sample flows easily through the gap between the two probes.

Micro Interactance Reflectance Probe with Purge on Collection Tip

This specialized reflectance probe is used to analyze solid samples (i.e., powders or granules) in an environment where the sample amount is variable (for example, in a fluid bed dryer). It has a collection tip or “spoon” on the end which collects sample at a user-defined time. The time delay allows for enough sample to be collected to yield a reproducible spectrum. After the spectrum is collected, a purge is activated, and the sample is blown off of the spoon, allowing for fresh sample to be collected and subsequently analyzed. This probe is often used to monitor the drying process for granules and powders.

It can be installed directly in the fluid bed dryer, reactor, or process line. Connection to the process is typically made via compression fitting (e.g., Swagelok™) or welded flange.

Optimized 45° Micro Reflectance Probe

This optimized probe is designed for better sample contact for granules and powder samples. The 45° angle of the probe tip allows the sample to sweep along the face of the probe in a consistent manner, yielding reproducible spectra. It can be installed directly into the process for direct contact with the sample via compression fitting (e.g., Swagelok™) or welded flange. Care should be taken to ensure that sample flows properly across the face of the probe.

Non-Contact Probe

This probe type is ideal for measurement of samples moving on a conveyor belt, as well as all other non-contact measurement needs. As a result, it is often used for monitoring curing processes. For best results, it should be installed so that the sample passes at a distance of 4-10 inches (approximately 100-250 mm) from the probe window.

Probe Maintenance

Probe fouling is common in polymer systems, and often begins to manifest as a gradual increase in the baseline absorbance over time. Care must be taken, however, to ascertain that the baseline increase is not optical degradation of the probes, or haziness in the process itself.

Challenges in probe fouling can be approached in several ways, depending on the process. If baseline shifts are small, they can be eliminated through baseline correction of the spectra, but it should be noted that probe fouling often causes changes in baseline tilt and curvature as well. These effects can sometimes be addressed within the calibration modeling when fouling levels are low.

Changes in probe location, orientation relative to the flow direction, or materials of construction can reduce the rate or severity of fouling. Removal and cleaning of the probes at a set frequency may also be possible.

Fiber Optic Interfacing

Generally, NIR light from the instrument is transferred to the process probe using fiber optic cables. As the light scattering properties of the process sample increases, the number of fibers used in the fiber optic bundle must be increased in order to maintain analytical performance.

Single fiber process NIR analyzers are typically employed to analyze clear liquids. Micro-bundle process NIR analyzers monitor slightly scattering liquid media, suspensions, and drying processes. Full-bundle process NIR analyzers are used for the most challenging of applications, such as monitoring the drying of hydrated media or analysis of low-level constituents.

The length of the fiber optic interface can be from 1 m (for a large fiber bundle) to 150 m (for a single fiber optic). The use of longer fiber optic lengths can enable a process analyzer to be located outside of electrically classified or safety classified areas, and can keep it isolated from harsh operating conditions like those with large temperature variations.

Table 2: Comparison of fiber optic interface, fiber bundle size and measurement mode.

Fiber Optic Interface	Fiber Size/ Count	Fiber Length(m)	Sample Type	Mode
Single Fiber	600 µm, 1 illumination/1 collection	1-150	Clear liquids, thin films, gases	Transmission
Small fiber bundles	200 µm, 40 illumination/40 collection	1-75	Turbid liquids and suspensions	Transmission
Small fiber bundles	200 µm, 40 illumination/40 collection	1-75	Powders and films	Reflectance
Large fiber bundles	200 µm, 210 illumination/210 collection	1-15	Pastes, slurries, pellets, fibers	Reflectance

Up to nine separate process streams or sampling points can be monitored using a multiplexed process NIR analyzer. Multiplexing decreases both the cost per measurement point and the overall implementation cost for a process NIR analyzer. However, a risk assessment should be completed to ensure the economic benefits clearly support the increased liability per measurement point.

Summary

Development of robust in-line high-temperature and high-pressure probes and fiber optics, as well as analytical instrumentation, has paved the way for the use of spectroscopic techniques to monitor polymer production processes in industrial environments. NIR spectroscopy has now become an important tool that can be used to simultaneously optimize process control and product quality, delivering better product to the market at lower cost. The versatility and flexibility of NIR probes not only eliminates the cost and complexity of reagents and chemicals formerly needed for analysis, but also accelerates the feedback loop by providing near real-time data for a wide variety of polymer manufacturing applications.

References

1. Implementing NIR for Polymer Production Process Monitoring – Metrohm
2. NIR Spectroscopy – A guide to near-infrared spectroscopic analysis of industrial manufacturing processes – Metrohm NIR Systems - NIR Monograph
3. Analysis of polymer using near-infrared spectroscopy – Metrohm NIR Systems – AB 414
4. Increase the accuracy of your NIR measurements with instrument calibration – Metrohm NIR Systems – AN 12
5. Increase the accuracy of your NIR measurements with reference standardization – Metrohm NIR Systems – AN 13
6. Near-infrared analysis of polyols: process monitoring in a hostile environment- Metrohm NIR Systems – AN 7
7. NIR for polymer research quality control and reaction monitoring – N.Heigel et al., Journal of near infrared spectrosc. 15, 269-278 (2007)
8. 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
9. 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
10. NIR monitoring of a hot-melt extrusion process – Spectroscopy now. Volume 26, Issue 8, pp. s8-s17