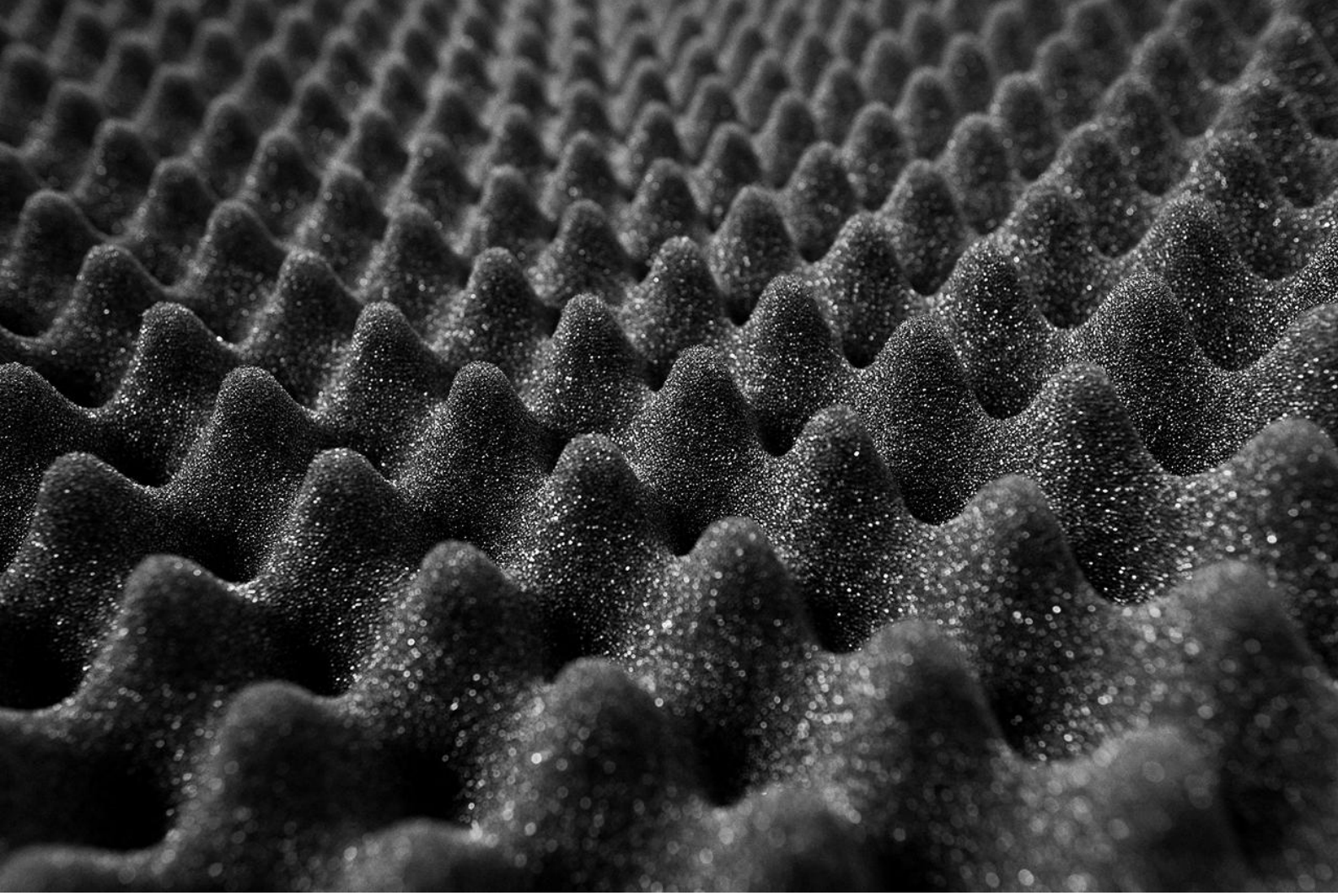


Application Note AN-PAN-1041

Inline monitoring of free isocyanate (%NCO) content in polyurethane

Polyurethanes (PU) are synthetic polymers used to create a wide range of products, from flexible or rigid foam structures to safety features in cars. The physical properties for PU products can vary widely. PU is formed by reacting liquid di/polyisocyanates and polyols with a catalyst and additives. Therefore, determining the free isocyanate content (%NCO) in the manufacturing process is a critical parameter to optimize production. Generally, spot samples are taken and analyzed in a laboratory by titration methods which are slow and generate waste. Inline monitoring of %NCO in real-time is a safer and more efficient way to monitor and improve PU production and reduce waste.

This Process Application Note presents a method to accurately monitor the percentage of NCO in the PU manufacturing process in «real-time» using near-infrared (NIR) spectroscopy. This can be done safely, reliably, and optimally with a 2060 *The* NIR-Ex Analyzer from Metrohm Process Analytics.

INTRODUCTION

Polyurethanes are a class of synthetic polymers used to create solid or foam structures – flexible or rigid – such as mattresses, shoe soles, safety helmets, insulation, packing material, surfboards, wind turbine blades, and several safety features in cars to name a few. The variety of densities, hardness, and durability found in PU products is vast due to the sheer number of recipes available. Polyurethanes are formed by reacting liquid di/polyisocyanates and polyols with a catalyst and various additives. The step additions of these chemicals occur in a reactor before the final mixture is spread on rollers or injected into molds to be further processed to customer specifications.

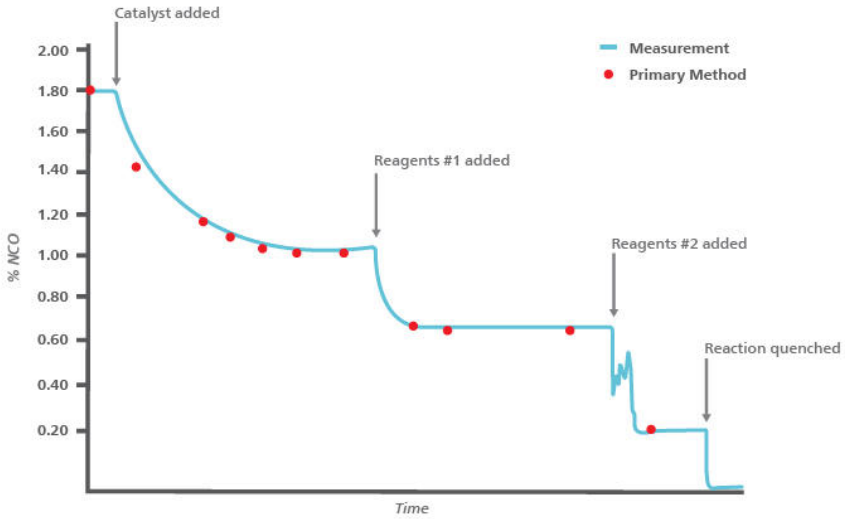
The reaction between polyisocyanates and polyols is quick and exothermic, beginning with the addition of a catalyst into the reactor. The process reaches an initial equilibrium, after which three stepwise chemical additions are made in the reactor to modify the PU properties (Figure 1a). The final reagent quenches isocyanate (NCO) functional groups from unreacted isocyanates. Therefore, knowing the precise NCO concentration is crucial here.

Determining the %NCO in the PU manufacturing process is a critical parameter to help determine the proper mixing ratio between the different reagents for optimized production of various PU characteristics. This is generally performed in the lab by titration methods after taking spot samples from the reactor at various points in the mixing process.

Laboratory titration is slow and uses chemicals that require proper disposal. Another issue is that during transportation to the laboratory, the sample properties change as it is exposed to ambient conditions not representative of the reactor. A safer way to optimize PU production, decrease waste, and save time and money is by monitoring %NCO inline in near real-time.

Reagent-free near-infrared spectroscopic analyzers enable comparison of spectral data gathered direct from the process to a primary method to create a simple, yet indispensable model for manufacturing process needs. The 2060 *The* NIR-Ex Analyzer (Figure 2) by Metrohm Process Analytics has IMPACT as the embedded software, which manages the transfer of results using well-known industry communication protocols to any plant control room.

a)



b)

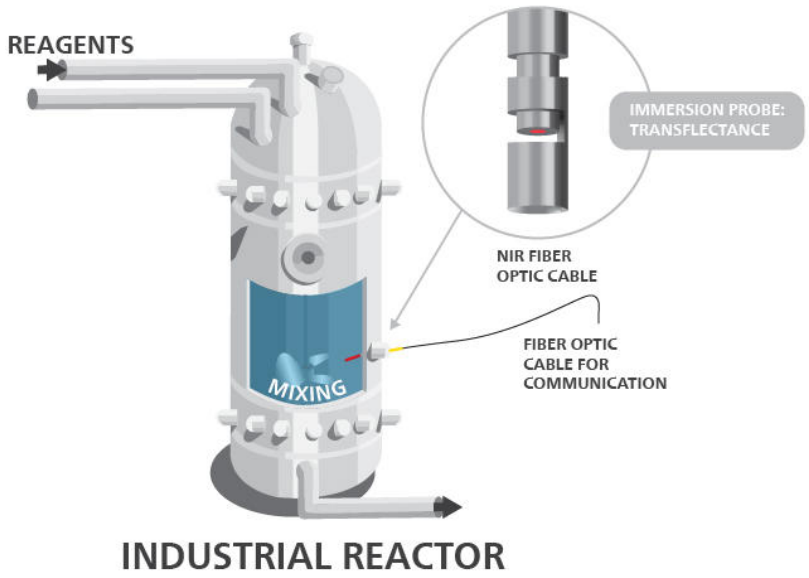


Figure 1. a) NIR model illustrating how different mixing steps in the PU production process can be shortened. Spot sampling (red dots) can miss certain events. b) Stylization of suggested placement for NIR probe in an industrial PU reactor.

Using NIRS technology, the process can be quickly monitored inline to determine the proper mixing ratio between the different reagents for optimized PU production. Figure 1 shows a trend chart of the %NCO versus time as determined by NIRS. An immersion probe specifically designed for these applications is used with a gap located in the probe tip (Figure 1b). Additionally, it is possible to gain more control over PU production using a 2060 *The* NIR-Ex Analyzer as it can monitor up to five process points with each NIR cabinet.

APPLICATION

Wavelength range used: 1950–2080 nm.
Inline analysis is possible using the properties of transflectance and the micro interactance immersion probe. The sample flows through the gap between the probe body and high-energy mirror tip and adjusting the mirror tip defines the pathlength (equal to two times the gap) for analysis.

Table 1. Parameters to monitor in an industrial PU reactor with inline NIR spectroscopy.

Parameters	Results
%NCO	0–30

REMARKS

A primary method (such as titration) must still exist as a reference method. An appropriate range of samples covering the process variability should be analyzed by both methods to build an accurate NIR model. Correlations are made to process specifications.

CONCLUSION

Polyurethanes are a versatile class of synthetic polymers used to create a wide range of products with varying properties and uses. Isocyanate groups are reactive components that play a crucial role in the formation of polyurethane. Monitoring the %NCO in PU production is crucial for ensuring proper mixing, curing, quality control, and tailoring the material's properties to meet the desired specifications.

A safe and efficient method to monitor %NCO in near real-time is reagent-free NIR spectroscopy. The Metrohm Process Analytics 2060 *The* NIR-Ex Analyzer offers inline analysis capabilities using transflectance and a micro interactance immersion probe. These probes are connected to optical fibers that allow the analyzer to be set up more than 100 meters away from the sampling point and still benefit from fast analyses. Additionally, this analyzer allows the connectivity of up to two NIR cabinets to one 2060 Human Interface, expanding the measurement points to ten sample streams (five for each cabinet). This gives users more savings per measurement point.

Figure 2. The 2060 The NIR-Ex Analyzer from Metrohm Process Analytics can measure %NCO in the PU production process in near real-time.

RELATED DOCUMENTS

AB-414 Polymer analyses using near-infrared spectroscopy

AN-PAN-1051 Inline process monitoring of the moisture content in propylene oxide

AN-PAN-1053 Monitoring of DOTP production via esterification with inline analysis

WP-036 Lean manufacturing of polyurethane, assisted by near-infrared (NIR) and Raman spectroscopy

BENEFITS FOR NIRS IN PROCESS

- **Optimize product quality** and increase profit with fast response times for process variations
- Greater and faster **return on investment**
- **No manual sampling needed**, thus less exposure of personnel to dangerous chemicals

Table 2. Dedicated solutions for your NIRS sampling needs.

Probe Type	Applications	Processes	Installation
Micro interactance reflectance probe	Solids (e.g., powders, granules)	Bulk polymerization	Direct into process line
	Slurries with >15 % solids	Hot melt extrusion	Compression fitting or welded flange
Micro interactance immersion probe	Clear to scattering liquids	Solution phase	Direct into process line
	Slurries with <15% solids	Temperature- and pressure-controlled extrusion	Compression fitting or welded flange
Micro transmission probe pair	Clear to scattering liquids	Solution phase	Direct into process line or reactor
	Slurries with <15% solids	Temperature- and pressure-controlled extrusion	Into a side-stream loop
			Compression fitting or welded flange
Micro interactance reflectance probe with purge on collection tip	Solids (e.g., powders, granules)	Drying of granules and powders	Direct into the fluid bed dryer, reactor, or process line
	Environments where sample amount varies		Compression fitting or welded flange

OTHER PROCESS NIRS APPLICATIONS RELATED TO THE POLYURETHANES SECTOR:

- Moisture determination in drying step
- Hydroxyl number determination
- Monitoring the curing of polyurethane elastomer
- Determining percent linear expansion in polyurethane resins
- Water content of polyols (%)
- Determination of acid and alkalinity numbers of polyols
- Determination of acidity as Acid Number (AN) for polyether polyols

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