142au Real-Time and in-Process Monitoring and Control of Polymerization Processes

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There is a significant demand in polymerization processes for in-line and real-time instruments that are capable of accurately and precisely measuring the desired polymer product quality and monitoring the reaction progress. Final monomer conversion and by-production formation, as well as minimizing runaway reactions, are several important factors to consider during polymerization reactions. It is difficult to monitor polymerization reactions due to sampling issues, such as temperature, preparation, or time delay, and limited measurement windows. In addition, safety is also a major concern as polymerization reactions are highly exothermic and highly viscous. Typically, off-line sampling of a polymerization process can be difficult, wasteful, and unsafe. Improper mixing or unexpected concentration gradients may lead to hot-spots or runaway reactions. Therefore, the inclusion of real-time instruments is advantageous to the user for safe production of polymer of desired quality or product specification. In situ attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectroscopy has been frequently used in polymerization processes. This measurement technique is insightful and information rich, since a fingerprint of the reaction is recorded. ATR-FTIR is also inherently safe; the probe is in intimate contact with the reaction. Therefore, there is no sample preparation and the reaction is monitored as-is.

The Mettler-Toledo ReactIR in situ FTIR probe has been successful at monitoring a diverse group of polymerization reactions, extending to both homogeneous (free radical and condensation) and heterogeneous (emulsion and microemulsion) reactions. Also, in situ FTIR has been used to determine and control the degree of polymerization and correlate to final product characteristics. As safety is a major concern with polymerization reactions, in situ FTIR eliminates exposure of the operator to toxic monomers due to sampling and reduces exposure to exothermic reactions.

This paper focuses on several applications in which real-time in situ measurements have been implemented in polymerization process to qualitatively track the product/by-product formation, initial charge ratio, and to determine the reaction end-point. Reaction end-point is very important as it could mean the difference between use in medical equipment or a consumer good.

In polyether polymerization, in situ ATR-FTIR is used to monitor the ethylene oxide and propylene oxide infrared profiles to understand the rates of monomer uptake. This technology is used to assist in controlling the feed rate and determining the end-point. Sample removal is hazardous and can lead to gaseous monomer loss and polymer oxidation which would significantly affect the sample. It is shown that the ethylene oxide consumption is more rapid than its feed rate. The propylene oxide uptake is slower than its feed rate. This fact is important for safety and control of the final material.

In polyurethane prepolymer formation, in situ FTIR is used to monitor the reaction of diisocyanate and polyol in order to minimize the occurrence of gel batches. Gel batches can occur when there is poor control of the diisocyanate/polyol ratio. FTIR is used to track the diisocyanate and polyol to assist in controlling the feed, detecting the reaction end-point, and reduce the dependency on time consuming, potentially hazardous off-line sample analysis. At the plant level, current in situ monitoring technology is temperature and pressure for process control.

In esterification, there are several reasons that in situ FTIR was implemented. Primarily, in-line monitoring was used for the detection of the initial charge ratio for faster response to the composition variance. In addition, it is important to monitor the reaction kinetics for efficient use of raw materials and process engineering overhead. Also, it is necessary that the reaction end-point can be detected for a consistent product quality and minimal batch cycle time. Finally, it is vital to monitor the chemical composition for quality of raw materials and diagnostic information from system disruptions, such temperature spike or impurities. In this example, the case study evaluated the monitoring technology, in terms of system compatability, performance, and stability. Also, FTIR was used to establish the monitoring feasibility for detecting the charge ratios and reaction end-point by tracking the alcohol, acid, and ester reaction components. A correlation was made between the spectral data and hydroxyl and acid numbers.

In heterorgeneous polyolefin polymerization it is necessary to monitor polymer swelling, catalyst fragmentation, and particle morphology. It is difficult to monitor polymerization reactions due to sampling issues, such as temperature, pressure, sample preparation, or time delay, and limited measurement windows. In addition, safety is also a major concern as polymerization reactions are highly exothermic and highly viscous. Typically, off-line sampling of a polymerization process can be difficult, wasteful, and unsafe. Improper mixing or unexpected concentration gradients may lead to hot-spots or runaway reactions. Therefore, the inclusion of real-time instruments is advantageous to the user for safe production of polymer of desired quality or product specification. Therefore, there is no sample preparation and the reaction is monitored as-is.

Three distinct scales are present in heterogeneous polymerization, such as polyolefin polymerization to produce Linear Low Density Polyethylene (LLDPE) or High Density Polyethylene (HDPE): micro-, meso-, and macroscale. The microscale involves the interaction of component species, such as monomer(s) and catalyst, nonlinear reaction kinetics, and polymer structure. The mesoscale involves growth of polymer particles, catalyst fragmentation, and intraparticle transport phenomena. The macroscale involves the overall transport phenomena (mass, energy, and momentum balances) in the reactor, the polymer particle size distribution, mixing, and temperature and concentration gradients.

The Mettler-Toledo Lasentec in-line Focused Beam Reflectance (FBRM) probe and Particle Vision and Measurement (PVM) in-process imaging system have been successfully implemented in the pharmaceutical world to monitor particle growth at the mesoscale and the particle size distribution at the macroscale. The FBRM probe is inserted into a flowing medium of any concentration or viscosity. A laser beam is emitted through the sapphire window of the FBRM probe and highly focused just outside the window surface. This focused beam is then moved so it follows a path around the circumference of the probe window. The focused beam is moving at a high rate of speed (2 m/s to 6 m/s, depending on the application) so that particle motion is insignificant to the measurement (i.e., the speed of the focused beam is significantly faster than particle motion). As particles pass by the window surface, the focused beam will intersect the edge of a particle. The particle will then begin to backscatter laser light. The particle will continue to backscatter the light until the focused beam has reached the particle's opposite edge. The backscatter is collected by the FBRM optics and converted into an electronic signal. FBRM uses a unique discrimination circuit to isolate the time period of backscatter from one edge of an individual particle to its opposite edge. This time period is multiplied by the scan speed and the result is a distance. The FBRM has a measurement range of 0.5-3000 ƒÝm. The PVM is a unique in-process imaging system capable of providing high-resolution images at most solids concentrations. With resolution below 3 microns and the ability to be inserted directly in a process line or reactor, the in-process video microscope provides an unsurpassed qualitative understanding of the change to particles and particle structures during the polymerization process.

LLDPE and HDPE are produced in isothermal and isobaric conditions in both catalytic slurry tank reactors and fluidized beds. The porous catalyst particles typically measure 10-50 ƒÝm in diameter. Initially, the porous catalyst structure fills with polymer, followed by submicron microparticle formation by fragmentation. The mechanism of catalyst fragmentation determines the final particle morphology.

The catalyst microparticles continue to grow (micron) and agglomerate as reactants diffuse and react at the catalyst surface. The final polymer particle size is 1-3 mm. The FBRM and PVM are capable of monitoring the particle growth and agglomeration during this polymerization process. The FBRM is sensitive to changes in the number of particles, such as a decrease in smaller particle and increase in larger macroparticles indicating agglomeration, and changes to particle shape. The PVM is capable of capturing in-process images of the polyolefin polymerization, allowing the user to monitor surface morphology.