Measuring Where It Counts

Real-Time Monitoring of Polymers during Extrusion for More Effective Compounding

Quality assurance during polymer extrusion requires continuous and reliable measurement. In two European research projects, three robust, practical and relatively simple online measurement techniques for material characterization have been developed. This paper will discuss the current state-of-the-art in the real-time monitoring of extrusion processes.

Material characterization during the compounding process avoids defective batches and enables the cost- and time-saving development of new materials. Quality fluctuations within the process can be identified and corrected at an early stage using online measurement methods. In the production of "conventional" polymer compounds, the most common technique of monitoring the pressure and temperature, combined with subsequent offline analysis, can lead to a high rejection rate. For this reason the Fraunhofer Institute for Chemical Technology ICT in Pfinztal, Germany, is investigating new characterization methods that can be adapted to compounding processes. Various processes are being validated for the potential application of this method, such as the reactive extrusion of PLA or the manufacture of nanocompounds. **Table 1** provides an overview of the three investigated measurement techniques and the associated measurement values, which are discussed in further detail below.

Reliable Data Sets from Spectroscopic Measurements

Spectroscopy enables inferences to be made concerning particular material properties, as the electromagnetic radiation applied to the material mix is absorbed differently by different substances. An evaluation of the frequencies of the reflected radiation provides information about the specific properties of the material investigated. The different types of spectroscopy vary in terms of the wavelength of the radiation used and consequently the information that can be obtained. For example, near-infrared spectroscopy (NIR) and Raman spectroscopy are most frequently used for process analysis.

Once the technology is optimized, data evaluation can be carried out in real-time using specific analysis routines, reducing the quantity of information recorded in the spectra to an easily understandable conclusion concerning quality. This can be illustrated with reference to three current examples of spectroscopy used for specific tasks at Fraunhofer ICT.

Constant Input Quality Is Not Guaranteed

Analyses carried out early in the process can help to ensure the quality of the »

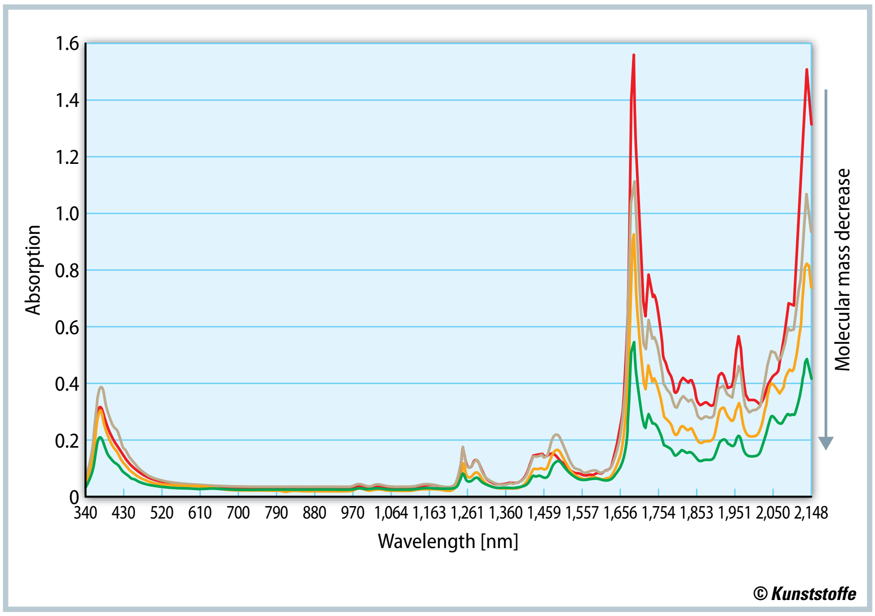

Fig. 1. NIR spectra measured during the process with decreasing molecular weight of the product (source: Fraunhofer ICT)

Measurement technology	Application
Spectroscopy (NIR/Raman), dielectric measurement	Input/reaction monitoring, formulation, dispersion
Viscometry	Viscosity, input/reaction monitoring, material degradation
Electrical resistance	Conductivity of the melt

Table 1. Online characterization methods and corresponding measurement values for the compounding process (source: Fraunhofer ICT)

Collaborative Projects

Within the scope of the European collaborative project **InnoREX**, an online characterization technique for reactive extrusion was developed that shortened the development times of new polymers. Researchers in the consortium carried out a real-time evaluation of the polymerization of polylactic acid (PLA) in a continuous twin-screw extruder using viscosity and spectroscopic measurements. Technologies providing fast elaboration of research tasks are able to provide real-time in-spec/out-of-spec in day-to-day production. For the processor this means less discarded material and consistent product quality even when the educt quality fluctuates.

The same applies to the processing of nanocomposites. Within the European collaborative project **NanoOnSpect**, an analysis tool was developed which enables the characterization of polymer compounds in terms of their target properties during the production process, and which is suitable for industrial application.

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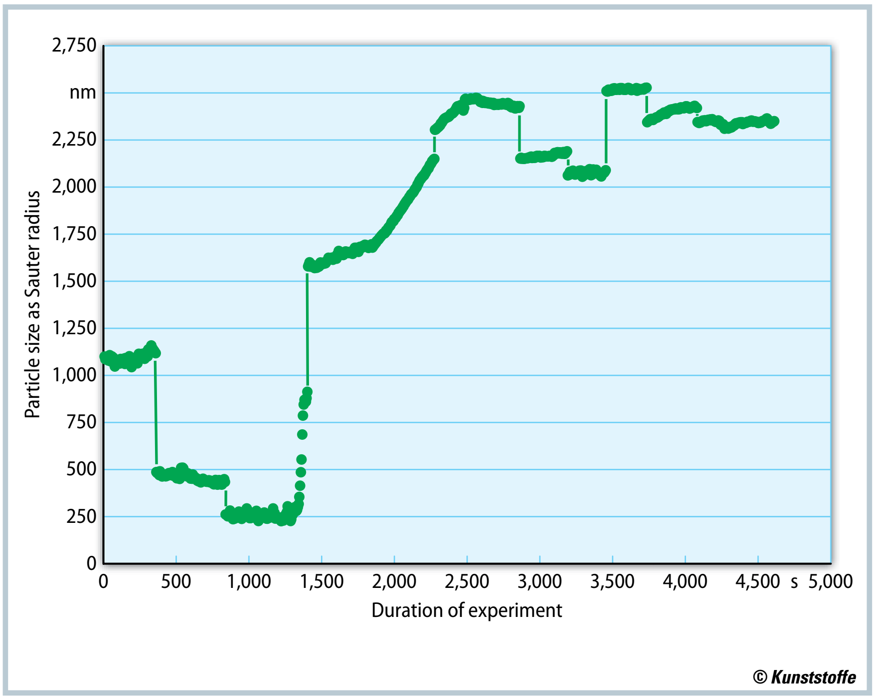

Fig. 2. Visualization of clay particle size for various processing parameters in polypropylene with the process aid additive Priex (source: Fraunhofer ICT)

input. Depending on the material to be processed, moisture, for example, can be a critical factor. The spectroscopic process applied enables the detection of fluctuations in moisture content of 300 ppm in commercial PLA systems. Besides the quality of the material input, the correct functioning and implementation of upstream drying processes must be ensured in day-to-day production. NIR spectroscopy can provide similar information concerning recyclates or natural materials used in manufacturing processes. Both these precursor materials can exhibit significant fluctuations in input quality, and these can only be tolerated and compensated in the process to a certain extent. Here, too, material analysis conducted early in the process can help to prevent defective batches.

The final product composition can also be validated and documented continuously using spectroscopic measurement methods. It has been demonstrated that a deviation as small as 0.25 % from the prescribed additive content can be detected using spectroscopy. Monitoring of the composition of polymer blends, i.e. measurement of the relative quantity of different polymers within the entire system, has also been demonstrated. This flexibility means that spectroscopic quality measurements are suitable for a wide range of applications to ensure and document the product quality.

Spectroscopy Reveals Chemical Changes

Chemical changes within a compound can also be observed using spectroscopic methods. A current example is the monitoring of (undesired) degradation of the polymer. Particularly in recyclate systems with a high residual moisture, the material quality can decrease significantly under harsh processing conditions. The residual moisture attacks the polymer chains, splits them and shortens them in an uncontrolled reaction, leading to lower viscosity and melt strength as well as a deterioration of the material properties. It was shown that the degradation of polymer chains, and consequently the molecular weight, can be measured directly online and in real time in the extrusion process. For this purpose, reactive extrusion is used to degrade various polyester systems and damage the polymer in a targeted way, imitating the undefined and undesirable degradation occurring when the processed material is too moist. **Figure 1** illustrates changes in the spectra as the molecular weight decreases. These changes can be quantified using mathe-

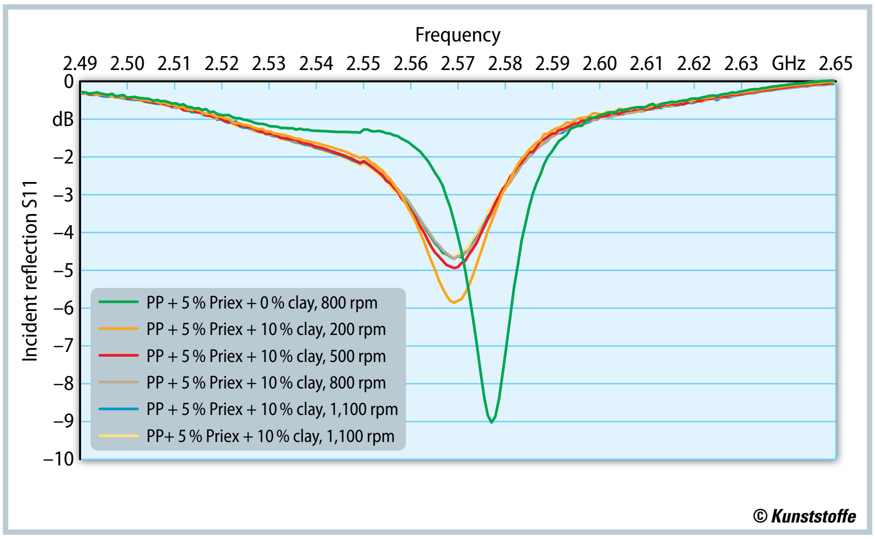

Fig. 3. Microwave reflection in correlation with shear energy (source: Fraunhofer ICT)

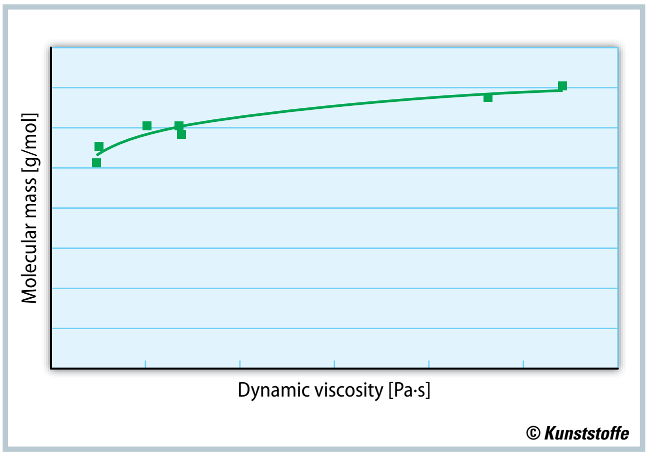

Fig. 4. Dynamic viscosity measured during the process and plotted against the molecular weight of the investigated material (source: Fraunhofer ICT)

matical data processing, and converted into a predictive model.

The reverse process – i.e. gains in molecular weight – can also be monitored. In the European research project InnoREX (see **information box**), the polymerization of the biopolymer PLA is observed in real-time at different points in the reaction pathway within the extruder, providing a deeper understanding of the process and also ensuring the success of the reaction and the quality of the product. Spectroscopic methods were used to demonstrate that one characteristic change in the spectrum occurred for each material in a range of different material systems, enabling direct calculation of the molecular weight.

Measurement of the Dispersion of Additives

Where a new functionality is added to a polymer compound through the additive, the even distribution and dispersion of this additive is essential to ensure a homogeneous product quality. This can also be measured during the compounding process using NIR spectroscopy or dielectric measurement. NIR spectroscopy is used to observe the decrease in intensity or the self-reflection of the IR radiation as it passes through the compound.

Mie-theory, for example, can then be applied to the NIR spectra to calculate an average particle size. **Figure 2** shows a sample evaluation of an NIR spectrum for a compound consisting of organically modified layered silicate (nanoclays) in polypropylene. Various process parameter settings (throughput, concentration, screw speed) and the resulting particle size (as a Sauter mean diameter) are shown. As a result, the most effective process window for the desired particle size could quickly be determined in each case.

Where dielectric measurement is used to determine the homogeneity of the product quality, a change in the distribution of the filler leads to a change in the dielectric properties of the compound, which in turn alters the reflection, transmission and absorption of the input microwave signal. Unlike the optical spectroscopy methods established in industry, the use of dielectric measurements for quality control during compounding is still under development. In the project NanoOnSpect (see **information box**), clear correlations could be observed between the screw speed (which determines the shear energy introduced into the material) and the microwave reflection signal of the applied material ("nanoclay in polypropylene"). This is shown in **Figure 3**. A decrease in the signal intensity and shift of the minimum with increasing shear energy can be observed.

Measuring Viscosity with Capillary Methods

Using real-time viscometry, it is possible to continuously monitor the dynamic viscosity of the polymer melt during production. Robust capillary measurement methods are especially suitable for this kind of process analysis. During the measurement, a gear pump presses a partial stream of the polymer melt from the main melt channel through a defined slit capillary, in which the melt temperature and pressure are then measured at two different sites. Following the Hagen-Poiseuille equation, this data can then be used to calculate the dynamic viscosity of the material. The calculation takes place immediately, and the dynamic viscosity is provided to the user as an output parameter.

Viscometry can also help to answer complex questions in the context of scientific research. In the InnoREX project, high-molecular PLA was synthesized using reactive extrusion in a twin-screw extruder. In this case, online viscometry showed that material viscosity is affected by both the molecular weight and the residual monomer content, which in this context acts as a plasticizer. In this project, real-time viscometry thus enabled the optimization of processing parameters during testing, and facilitated the quick evaluation of experimental results without the need for time-consum- »

ing wet-chemical analytics. **Figure 4** illustrates the correlation between material quality and viscosity determined during this process.

Development of Measurement Devices for Monitoring Electrical Conductivity

One research area at Fraunhofer ICT is the development of electrically conductive nanocomposites. For rapid material and process optimizations, an online measurement device was developed that measures the electrical resistivity of the melt. Here the electrical resistivity of the material stream is measured using two sensors that face each other. In a series of comprehensive tests, a method was developed that enables calculation of the electrical conductivity of the cooled material based on the electrical resistivity of the melt. This enables the targeted optimization of processing parameters to achieve the desired electrical conductivity, or the investigation of process stability. **Figure 5** shows the operational principle of the measuring method.

Summary

There are multiple ways to monitor the compounding process using robust, practicable online quality control. The technical feasibility study must be followed by an individual, company-specific economic evaluation which compares the purchasing price of the sensors with the amount of resources saved. In the EU-funded projects it could be shown that the complexity of analysis technologies can be reduced significantly when specific signals provide key information enabling quality evaluation. This leads to lower costs and makes it possible to analyze the data without having extensive knowledge in this field. ■

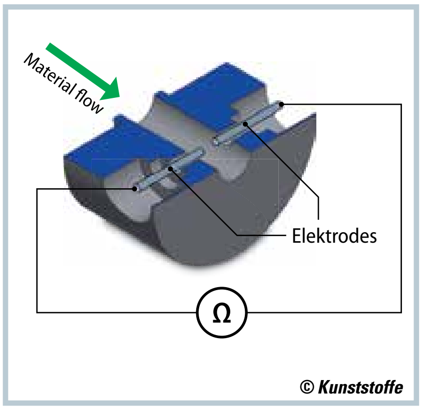

Fig. 5. Measurement of the electrical resistivity of the melt (source: Fraunhofer ICT)