Combination of NIR, Raman, Ultrasonic and Dielectric Spectroscopy for In-Line Monitoring of the Extrusion Process

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Summary: Determination of melt composition and/or morphology by fast, reliable and accurate in-line methods is highly desired in polymer industry. In-line spectroscopic methods like near infrared (NIR), Raman or ultrasonic spectroscopy are such reliable methods for process control without time consuming sampling and off-line analytics. As the number of in-line techniques available is increasing, it becomes increasingly difficult for manufacturers and plastic processors to choose the right method or combination of methods for their needs and to keep track of the growing amount of information. Therefore, we combined different in-line techniques in one slit die in order to compare their potential for various systems such as composites and blends. One installation consists of a combination of NIR and Raman spectroscopy, rheometry and ultrasonic measurements. Another installation bases on a slit die developed for rheology which was equipped with dielectric and ultrasonic sensors. The results of the applied in-line methods are compared and the specific advantages and drawbacks are discussed.

Keywords: additives; blends; chemometrics; composites; in-line process control

Introduction

Due to the increasing requirements with respect to productivity and quality, the field of real-time monitoring of polymer processing has been tremendously grown within the last years.[1,2] Special properties of the resulting end products are obtained by blending or by modification using additives or fillers. Since process control for more complex systems, such as composites or blends will provide the highest benefit, fast and accurate determination of melt composition and/or melt morphology is therefore highly desired. Besides classical methods like temperature and pressure measurements and melt rheology, a lot of new methods have emerged in the last decade. In this paper we will compare the advantages and drawbacks of three different spectroscopic methods for in-line control of the extrusion process: near infrared (NIR) and Raman spectroscopy,[3–5] and ultrasonic measurements.[6–8] Finally, we report on the application of in-line dielectric measurements to the extrusion of carbon-black filled polyethylene.

Measurement Setups

NIR, Raman and Ultrasonic Spectroscopy

A special measurement slit die is flange connected to an extruder immediately behind the screw tips. Within that die the melt is flowing through a channel with rectangular cross section (width 20 mm, height 4 mm). Fitted to that channel are near infrared transmission probes (or alternatively a reflectance probe), a Raman probe, and two ultrasonic transducers (Figure 1). Additionally, two pressure transducers provide the mean pressure and the pressure drop along the melt

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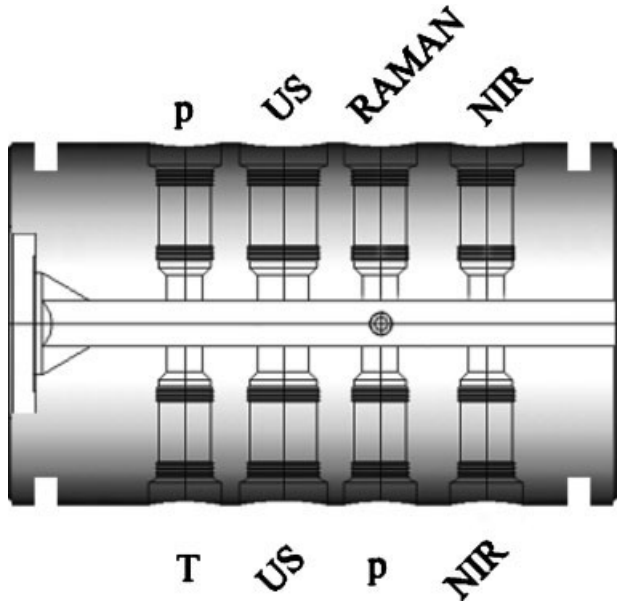


Figure 1.
Measurement slit die with borings for pressure (p) and temperature (T) sensors, NIR and Raman probes, and ultrasonic transducers (US).

channel. A temperature sensor is used to obtain the melt temperature.

Such dies are used in combination with different spectrometers and extruders. The NIR probes are connected to a diode array based spectrometer (SentroProc NIR or SentroProc NIR/Raman, Sentronic GmbH) using quartz glass fibres. The spectral range of the NIR spectrometer is 900 nm – 1700 nm. The NIR transmission probes are commercial probes (Axiom Analytical Inc.) with a sapphire window head which can withstand high temperatures (300 °C) and pressures (280 bar). This window has direct contact to the melt. The Raman probe is connected to a Raman spectrometer (SentroProc NIR/Raman, Sentronic GmbH, or HoloProbe 785, Kaiser Optical Inc.) by two quartz glass fibres. The excitation wavelength of the Sentronic spectrometer is 785 nm with a measurement range of 80–3700 cm^{-1}. The Raman probe is also a commercial one (Kaiser Optical Inc.) with a sapphire window.

The ultrasonic transducers (developed at Deutsches Kunststoff-Institut) are connected to ultrasonic PC plug-in cards, a pulser/receiver card and a digitizing card. The transmitted ultrasonic signal is Fourier transformed in order to calculate the amplitude and the phase spectrum. In this work only the ultrasonic attenuation spectra were used. The actual frequency range was 1 to 7 MHz. By comparison with a known reference spectrum (e. g. of polyethylene) one can obtain the sound attenuation spectrum and the sound velocity spectrum of the melt. The ultrasonic spectra were measured and analysed using measurement software (DKI_MEAS) developed at Deutsches Kunststoff-Institut.

Figure 2 shows the measurement slit die flange connected to a twin screw extruder (Micro Leistritz 27).

Dielectric Spectroscopy, Rheology and Ultrasonics

A measurement slit die equipped with dielectric sensors (see Figure 3 and Figure 4) was applied to monitor the extrusion of conductive polymer composites. An Agilent LCR bridge HP4284A was used to measure parallel capacitance C_p and $\tan(\delta)$ in a frequency range from 20 Hz to 1 MHz.

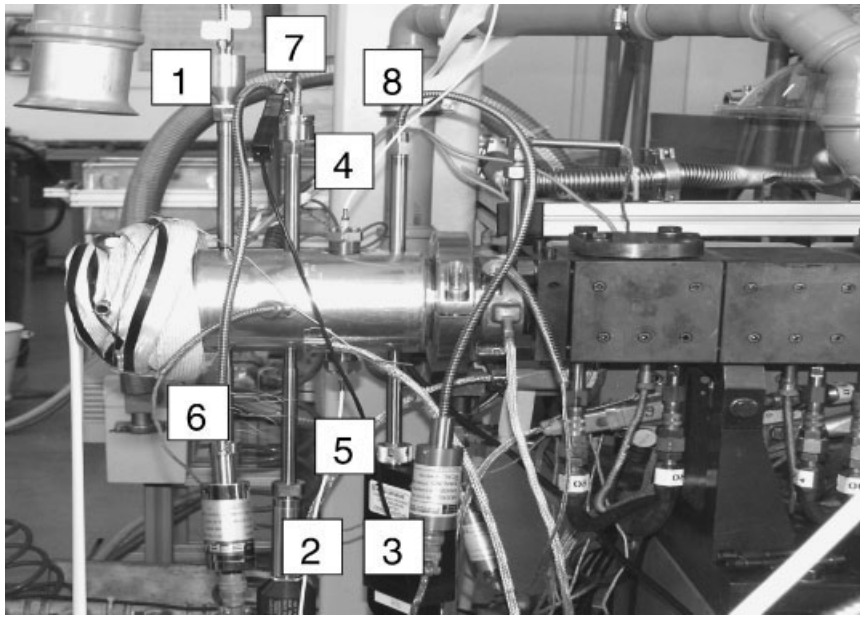


Figure 2.
Measurement slit die flange connected to an extruder with NIR reflectance probe (1), Raman probes (2, 3), ultrasonic transducers (4, 5) as well as temperature (6) and pressure sensors (7, 8).

The two sensors (NETZSCH Gerätebau GmbH) with electrode diameter of 8 mm were mounted face to face in the melt channel with a distance of 4 mm. The A/d-ratio (area by thickness) in this configuration is approx. 0.01 m, resulting in an air capacity of 0.09 pF. The A/d ratio was calculated by a finite element simulation of the electrical field for the actual sensor geometry. Permittivity ε and conductivity σ are calculated from the A/d-ratio and the measured values of C_p and $\tan(\delta)$, respectively. Additionally two pressure transducers determine the pressure drop along the slit, which is required for in-line rheometry. The design of the channel bases on a rheometric measuring die from Brabender (Germany). Two ultrasonic transducers

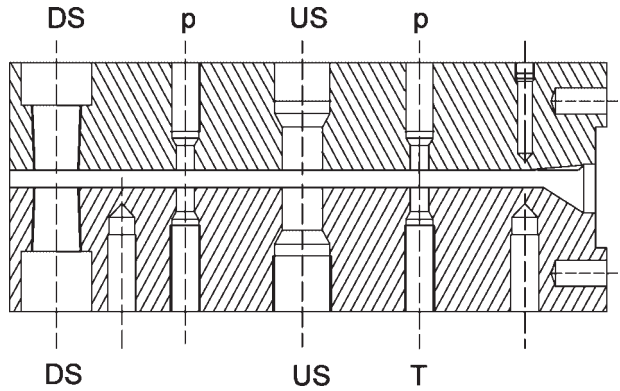


Figure 3.
Measurement slit die with borings for pressure (p), temperature (T), ultrasonic (US) and dielectric sensors (DS). In this study only the data from dielectric sensors were used.

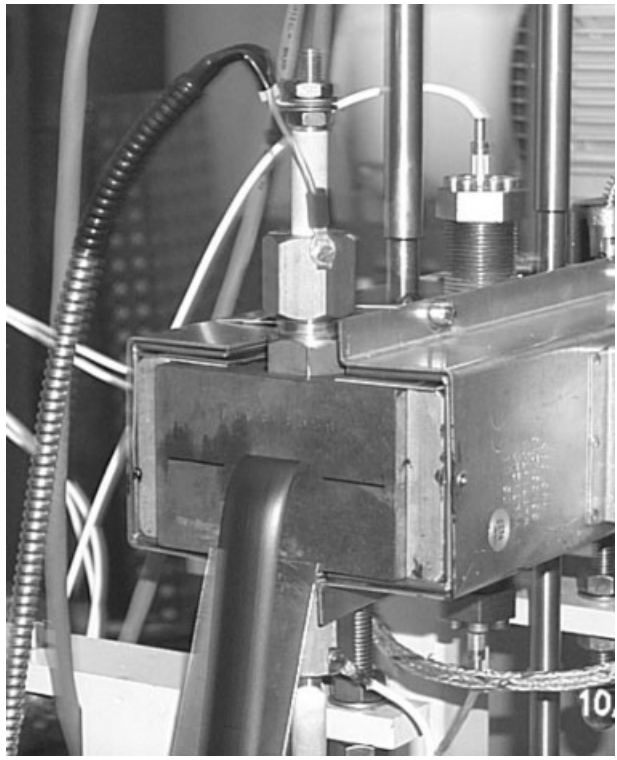


Figure 4.
Measurement slit die of Figure 3 equipped with two dielectric sensors, two pressure transducers and two ultrasonic transducers during the extrusion of a polyethylene/carbon black composite.

(not used in this report) are placed between the pressure transducers.

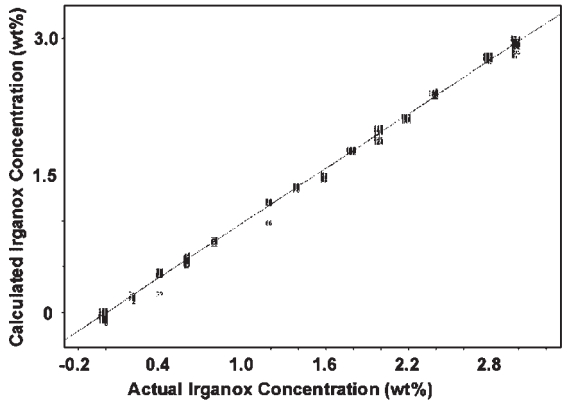
Examples

Polypropylene/Irganox

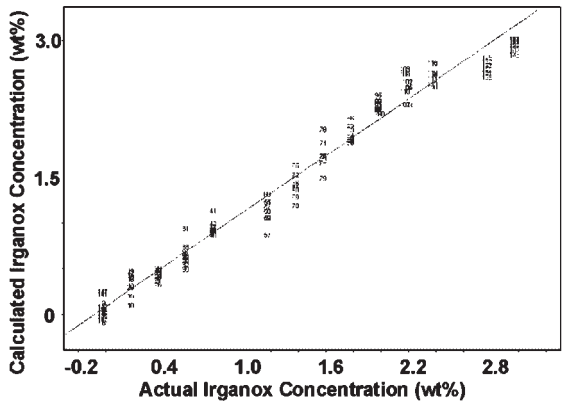
Polypropylene (PP) with Irganox was chosen as example to demonstrate the accuracy of detecting even small amounts of additives and to find the detection limit of optical spectroscopy (NIR and Raman) and ultrasonic measurements. The measurement die shown in Figure 1 was used. Irganox is widely applied as an UV stabilizer. With the aid of chemometrical methods we were able to determine the concentration of the Irganox additive in real time.

The PP/Irganox mixtures were prepared from Moplen HF500N (PP-powder, Basell Polyolefins) and Irganox 1076 (Ciba AG) using a twin screw extruder (Micro Leistritz 27). The installation was similar to that shown in Figure 2, but instead of two Raman probes only one was installed and the NIR-spectra were measured in transmission mode by two identical transmission probes. The calibration was done with 16 different concentrations of 0.2 wt% - 3 wt% Irganox and with pure PP.

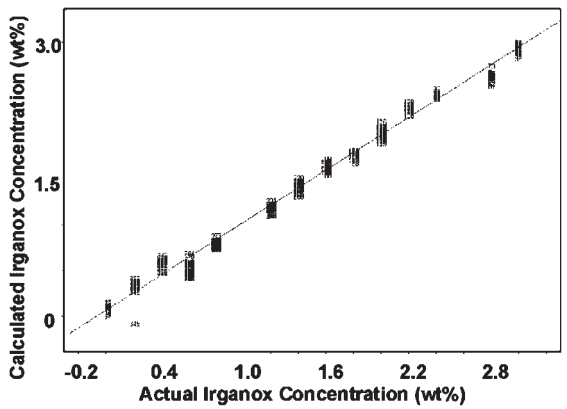
For the NIR and Raman measurements the spectrometers SentroProc NIR and HoloProbe 785 (Raman), respectively, were used. The data were processed by the vendor supplied software (WinSpec, Sentronic GmbH and HoloGrams, Kaiser Optical Inc). The ultrasonic attenuation spectra in the frequency range from 1 to 7 MHz were recorded using the measurement software DKI_MEAS. The ultrasonic attenuation in polymer composites is related to viscoelastic properties and/or sound scattering. Since Irganox is almost



a)



b)



c)

Figure 5.
Calculated vs. actual concentration plots obtained by PLS-analysis for the measured NIR- (a), Raman- (b) and ultrasonic attenuation spectra (c).

dissolved in the PP matrix scattering contributions are less probable and the concentration dependence of the sound attenuation bases therefore most likely on changes of the viscoelastic properties. The phase spectra, related to sound velocity, are

strongly depending on pressure and temperature and are therefore not used for chemometric analysis.

For calibration and validation of the spectra the partial least squares (PLS2) analysis[9,10] provided by the chemometric software GRAMS32/PLSplus/IQ (Galactic Ind. Corp.) was applied.

The predicted vs. actual concentration plots are shown in Figure 5(a–c) for all three methods. The correlation coefficient is 0.99% for the NIR and ultrasonic data, and 0.98% for the Raman data. The standard error of cross validation (SECV) for all data points is 0.05% (NIR), 0.15% (Raman) and 0.09% (ultrasonic).

A crucial criterion for the suitability in technical applications is the independent validation. The calculated calibration data sets were tested with the spectra of two additional mixtures, which were not included within the calibration data. We used mixtures with 1.0 and 2.6 wt% Irganox in PP. From the measured spectra of these validation mixtures the Irganox concentration was calculated. The result of this validation experiment is visualized for all three methods in Figure 6.

The mean value of the calculated Irganox concentration was 1.11 wt% and 2.60 wt% for the NIR spectra, 0.96 wt% and 2.59 wt% for the Raman spectra and 1.02% and 2.52% for the ultrasonic attenuation spectra. These findings show the suitability of all three methods for in-line process control of melt composition. The determination of additive concentration is accurate and can be done in real time. All three methods show adequate significance. In a technical application one might prefer the NIR or ultrasonic spectroscopy for expense reasons. In addition, the ultrasonic spectroscopy is preferable because of its robustness. It should be noted that is very important that the extrusion conditions (screw configuration, rpm, temperature, pressure) should be identical for the investigated process during calibration, validation and the later industrial use. For significant changes in these conditions, it is necessary to recalibrate the system.

We have also investigated PP/chalk composites with different chalk types.[11] It turned out that the ultrasonic attenuation spectroscopy was sensitive to the formation of aggregates and to the size distribution of the fillers.

Polyethylene/Carbon Black

Polyethylene/carbon black composites were extruded to test the applicability of dielectric spectroscopy. Different samples with a carbon black (CB) content ranging from 10 wt% to 30 wt% were obtained via dilution of a master batch (Polyblack 1423, A Schulman Inc.). Figure 7 shows the measured conductivity of the melt during the processing. The measurements were started with a CB concentration of 30 wt%, for which the melt is fairly conductive, i.e. this CB concentration is well above the percolation threshold. Feeding in the composite with 20 wt% CB content after approx. 100 sec process time, leads to a decrease of the conductivity. Changing the concentration to 10 wt% and finally to 0 wt% CB causes a further decrease of the conductivity. The drop in the conductivity is much smaller for these two changes compared to the change from 30 wt% to 20 wt%.

The following can be concluded: The composite with a CB content of 20 wt% is already below the percolation threshold and therefore a further reduction of CB content results only in a minor decrease of the conductivity. The fluctuation of the conductivity for 20 wt% CB is much higher than that for the 30 wt% and 10 wt% CB composites. This fluctuation indicates that the concentration of 20 wt% CB is near (but below) the percolation threshold, and small changes of the process parameters (temperature, pressure, screw speed) result in large variations of conductivity. The continuous decrease of the conductivity for this sample indicates the slow exchange of the material. From this experiment it can be concluded that dielectric spectroscopy is sensitive to the amount of conductive filler.

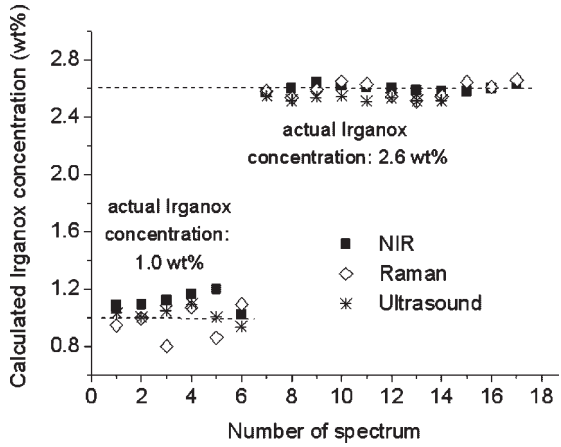


Figure 6.
Calculated Irganox concentration using the previously obtained calibration data set and the NIR-, Raman- and ultrasonic attenuation spectra of the two independent validation mixtures.

Conclusions

In-line NIR, Raman and ultrasonic spectroscopy are found to be well suited for quality monitoring and control of the extrusion process. It can be concluded that all of the three presented methods allow the determination of the concentration of additives being added by only small amounts of 1% or even less. The measurement setups combining different methods in one slit die give us the opportunity to choose the method be suited best or a combination of methods for a given problem or material.

A slit die with dielectric sensors was applied to monitor the extrusion of carbon-black filled polyethylene. The sensitivity of this method for determination of the carbon black content and its distribution was sufficiently high. Within the concentration range of the percolation threshold (approx. 20 wt%) fluctuations in the conductivity mirror small changes in the processing parameters.

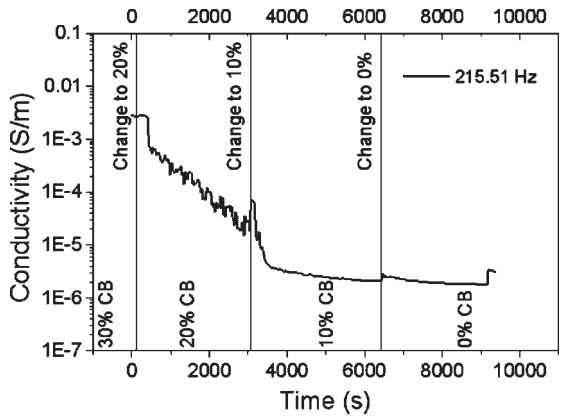


Figure 7.
Conductivity values during extrusion of Polyethylene/carbon black composites and pure polyethylene. The actual carbon black concentrations (wt%) are indicated in the figure.

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