

In-line monitoring of polymer extrusion processes by NIR spectroscopy

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NIR spectroscopy has become an analytical tool frequently used in many chemical production processes. Its use in polymer processing applications such as polymer extrusion would greatly increase product quality. Parameters of interest in this application are composition of the processed polymer, moisture or reaction status in reactive polymeric systems, as well as rheological parameters such as melt flow index (MFI) or viscosity. The measurement of NIR spectra could provide a way to control the processes. For this purpose a transmission sensor was developed for the application of NIR spectroscopy to extrusion processes. This sensor includes fibre optical probes and a measuring cell that can be adapted to the various extruders for in-line measurements. In contrast to mid-infrared sensors, it uses optical quartz components, which provides a low-cost solution. Extrusion processes at temperatures up to 300°C and pressures up to 35 MPa have been investigated. The application of multivariate analysis for PE/PP blending demonstrated the performance of the system with respect to process monitoring. In this case deviations between predicted and actual polymer composition were below 2%. Together with an AOTF spectrometer that was also developed, the complete system is suitable for harsh industrial environments and could lead to improved extrusion processes.

Keywords: polymer, extrusion, sensor, fibre optic probes, in-line, AOTF spectrometer.

Introduction

In the last few decades near infrared (NIR) spectroscopy has become an intensively used analytical tool for many applications in very different fields of application.^{1,2} A very promising field is process analysis leading to improved processes in many areas.^{3–5} Especially in the field of polymer processing NIR spectroscopy has opened new possibilities for process control.^{6–13} These new control concepts can be used, for example in extrusion processes, to enhance knowledge about the processed polymer melt. At present, mainly spot check off-line measurements are implemented, e.g. composition, mechanical properties, moisture, MFI etc. In-/on-line measurements have been introduced only for a few process parameters such as melt temperature or pres-

sure, if they are implemented at all. Other parameters are neglected. This low level of information about the processed product can lead to huge losses due to the time lag between detection of insufficient product quality in the laboratory and the reaction in the process itself. This time lag can exceed several hours and would lead to the production of up to several tons of polymeric waste, because products not fulfilling the quality demands of customers cannot be reprocessed in many cases. So, the parameters measured on-line at present are not sufficient for adequate description of the polymeric melt. NIR spectroscopy can solve this lack of knowledge by in-line measurements of the melt. Results of in-line NIR spectroscopy can be, for example, moisture or composition of the melt.¹⁴ With these and other parame-

ters it could be possible to control the complete extrusion process automatically. The result will be a new measurement method and a new process control concept for future manufacturing design.

There are many problems in realising this measurement technology:

- probes are exposed to hot and pressurised polymer melts, which can be corrosive;
- the spectrometer used has to withstand harsh industrial environments;
- data handling has to be fast and reliable;
- the complete system has to be economic and very robust.

These demands are not easy to meet. But a polymer melt analyser overcoming these problems would bring great benefit to real-world extrusion processes using continuous quality control (especially interesting with respect to ISO 9000) or to fully automated extrusion lines producing high quality plastics. This is of interest especially for small and medium enterprises, who change their extrusion processes often. Thus, the time to change process parameters could be reduced by effective process control. A reduction of costs and plastic waste (due to insufficient product quality) would be the result.

In this paper a measurement system for in-line transmission NIR spectroscopy of polymer extrusion processes is presented. Application to the determination of polymer melt composition is demonstrated for a PE/PP blend.

Method and materials

Equipment

A 20 mm single-screw extruder (Haake Rheomex 252) with length to diameter ratio of 25 is used to melt particulate solid polymers. Maximum torque is 100 Nm, maximum melt pressure is 7 GPa. Temperature profile can be adjusted with four independent temperature zones (including the nozzle). Maximum wall temperature at the cylinder is 400°C. A control unit regulates the extrusion conditions and automatically records the torque and speed of the screw.

Between the end of the screw and the nozzle there is an adapter, which has been transformed to a flow cell combining an adapter and insertion for probes (Figure 1). Hence, molten polymer passes the mea-

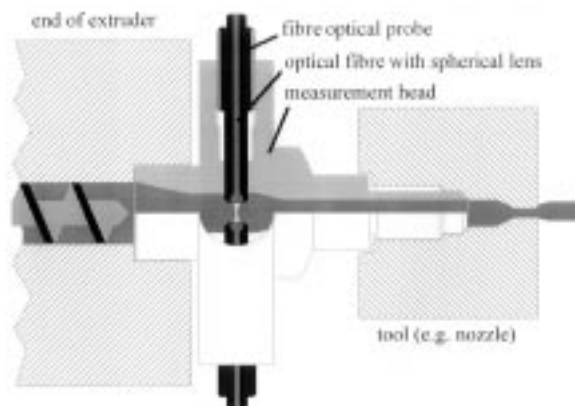


Figure 1. Scheme of measurement head with integrated fibre optical probes for in-line measurement.

suring zone still inside the extruder, where the two probes are installed facing each other. Fibre optic probes are used to transmit light through the polymer stream. The distance between these probes can be varied by insertion of spacers, and consequently pathlength ranges from 0 to 10 mm can be obtained. Fibre-optic probes installed in the flow cell are connected to an AOTF-NIR spectrometer via optical fibres. This spectrometer had been developed at the Fraunhofer-Institut für Chemische Technologie (ICT) and uses a tungsten halogen lamp, a germanium detector and an acousto-optic tunable filter (AOTF) as the dispersive element (Figure 2). The control and acquisition unit consists of a personal computer, a voltage controlled oscillator (VCO) and a power amplifier. Details of the spectrometer are given below.

Probes

Fibre-optic probes for use for in-line monitoring of polymer extrusion processes have to fulfil various demands. First of all they have to cope with different adverse conditions such as high temperature, high pressure, high viscosity and corrosiveness of the polymer melt. Thermal cycling due to process start-up and shutdown is another difficulty in developing a usable probe. For measuring these probes have to transport radiation effectively, so damping of optical components has to be low. The chemical effect of the probe on the polymer melt must be considered: it

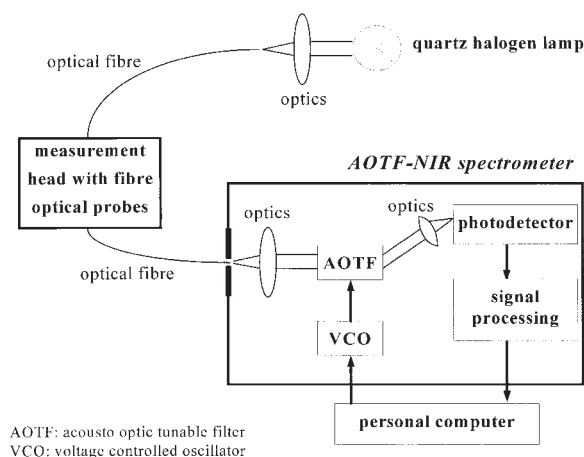


Figure 2. Scheme of in-line measurement system consisting of illumination unit, measurement head with integrated probes, and AOTF-NIR spectrometer.

must be guaranteed that probes do not affect polymeric properties negatively. On the other hand, for industrial use it is also important to meet several additional demands: probes have to be robust and inexpensive to achieve wide acceptance for industrial applications.

The probe design is shown in Figure 3 and can be divided into two main parts. The first part consists of a spherical lens, which is welded onto an optical fibre. Both components are made of quartz. This central optical component is embedded in a sleeve made of stainless steel. The space between the sleeve and the optics is filled with a high temperature resistant glue. A protective housing in the form of a sleeve is the second part of the probe. It contains the first part and has an opening for the spherical lens, so that only part of the lens has contact with the polymer melt. On the other side of the housing there is a standard SMA connector for an optical fibre. Connection between the two parts is made again by a glue.

This design was selected for several reasons. Use of spherical lenses reduces intensity losses compared to a simple installation of two optical fibres opposite each other. This results in an overall transmission ratio of 12%. Quartz was chosen as the lens material since its use gives no problems due to temperature, because quartz withstands up to 800°C, which is much higher than normal extrusion temper-

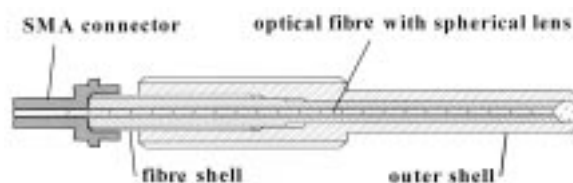


Figure 3. Scheme of fibre optical probes.

atures. The difference between the thermal coefficient of expansion of quartz and the housing material is quite high ($0.5 \times 10^{-6} \text{ K}^{-1}$ compared to $16 \times 10^{-6} \text{ K}^{-1}$), but because of the glue there are no internal tensions. On the other hand coefficients of expansion of the housing and the flow cell material are the same, so that there is a gap between these two parts. This gap is sealed by a special sealing mass withstanding temperatures of up to 1100°C. The result of this arrangement is an effective gasket.

The usefulness of this probe design is obvious. There is no by-pass used, so no waste appears and the processed material itself is measured without extra processing (e.g. by transportation with a gear pump). The cost for one probe is low, because no expensive materials are used (e.g. diamond or sapphire windows). Handling of these probes is easy, because they only have to be screwed into the right borehole. Adaptation to other extruders is also easy, because probes do not need very much space (only an M10 borehole). All in all these advantages make this probe design suitable for use in an industrial environment.

AOTF-NIR spectrometer

The AOTF-NIR spectrometer in use had been developed at ICT as well.¹⁵ It consists of a halogen light source, quartz fibre optics, the AOTF (made of TeO_2), germanium photodetectors (1,000 to 1,800 nm) and a control and data acquisition unit (Figure 2). Scan speed of the spectrometer is $1,000 \text{ nm ms}^{-1}$ with a time delay of 0.01 ms between two spectral scans. A wavelength resolution of 2 to 3 nm can be obtained for lower scan speeds.

The control and data acquisition unit consists of a personal computer with data acquisition card, a voltage controlled oscillator (VCO) and a power ampli-

fier. It controls AOTF operation by the output of a voltage via a D/A converter fed to the VCO. The VCO supplies the corresponding frequency to the piezoelectric transducer of the AOTF crystal and generates a propagating acoustic wave. This acoustic wave diffracts incoming light and produces three output beams, where only the first order beam is used. The wavelength of the diffracted beam corresponds to the frequency of the acoustic wave and hence to the voltage fed to the VCO. Details concerning operation of an AOTF are described elsewhere.¹⁶

AOTF-NIR spectrometers have the necessary properties for use in an industrial environment:

- robustness
- acceptable costs
- high scan speeds (up to 1,000 spectra per second)
- resistance to disturbances because of the use of fibre optics
- fast data acquisition and processing via PC.

All these advantages have already been proven for plastic identification processes in recycling applications.^{17,18} Therefore, the developed spectrometer seems to be best applicable for industrial use in the field of polymer processing.

Materials

The materials used are polyethylene (PE-LD) and polypropylene (PP). The polyethylene is low-density ESCORENE from EXXON Chemical and has an MFI (190°C; 2.16 kg) of 0.3 g 10 min⁻¹ (highly viscous). The polypropylene used for these investigations is Hostalen PP from Hoechst AG with an MFI (230°C; 2.16 kg) of 47 g 10 min⁻¹ (low viscosity). These materials are widely used in extrusion applications. Materials were used as the pure material and as mixtures for blending. The mixtures were produced by weighing with an accuracy of ±0.01 g. So, all mixing ratios are given in weight percent.

Experimental

The extruder is heated to a predefined temperature profile corresponding to the processed material

and afterwards it is filled with polymeric material. After processing inside the extruder NIR spectra of the polymer melt are taken while it is passing the measurement head. The recorded spectra are stored and evaluated on a separate personal computer. During the measurement, the melt temperature, melt pressure and torque of the screw as well as the spectrometer adjustments are documented. Measurement time for one spectrum (including averaging of 500 single spectra) is only a fraction of a second.

It was investigated whether it is necessary to clean the extruder after measurement of different material mixtures. For this purpose a few mixtures were selected and extruded in two different ways: 1) cleaning the extruder after each mixture, 2) one mixture after another, i.e. 1 kg of material was filled into the funnel of the extruder and extruded until the funnel was empty and then the funnel was re-filled with the next material mixture. The result of this pre-investigation was that there is no noticeable difference in the spectra between the two procedures. This can be explained by the self-cleaning effect of the extruder, i.e. the screw not only homogenises and transports the polymer melt to the nozzle, but also cleans the walls from remaining material. So, the second procedure was chosen for all experiments.

Data analysis

The recorded spectra were processed, evaluated and analysed with the Unscrambler® (CAMO Inc.) software package. Common statistical analysis [e.g. principal component analysis (PCA), principal component regression (PCR), partial least squares analysis (PLS)] can be carried out with it. For the investigations on polymer blends only PLS analysis¹⁹ was used. The PLS model was generated with one set of spectra and the prediction ability of this model was tested with another set of spectra. These sets were recorded one after the other, so that spectra of the same mixture were recorded within the extruder. So, the spectra for the calibration set and the validation set are collected in the same extrusion run. For generation of the PLS model 20 spectra of each mixture have been used. This calibration might not be applicable for another extrusion process, where pressure and temperature might change. This question will be investigated in the future.

Results and discussion

Technical results on the developed probes

The developed probes withstand the normal extrusion environment. Melt temperature of 300°C and pressure of up to 35 MPa did not cause any problems. The complete measuring head was sealed, so that no melt could leave the melt channel. A change of transmission distance between the two probes by simple screwing did not influence this result: the measurement head was still sealed without any damage to the probes. Although the sensors are within the melt channel the melt flow is essentially not disturbed with respect to throughput and obvious flow inhomogeneities.

The optical properties of the probes are sufficient for the described application. Light leaving the probe forms a cone with a focal point at about 2.5 mm, i.e. illuminating light is not parallel at all. Therefore these probes are not applicable for sophisticated spectroscopic measurements intended to determine correct extinction values. But for spectroscopic measurements for use in coming to the relative simple statement whether an observed process is running well or badly, the probes described here are sufficient. For such applications the overall maximum light transmission of 12% is more important than high quality spectra, because high transmission allows longer absorption pathlengths, e.g. to go to higher extruder diameters or to decrease surface effects on the probes.

Hence, it can be concluded that the developed probes are appropriate sensors for in-line observation of polymeric melts in an extruder leading to quality statements concerning actual process status and actual processed material.

PE/PP-blends

Different PE/PP-blends have been mixed and measured as stated above, varying the content of PE (PP respectively) from 0 to 100% in different percentage steps. In Figure 4, spectra are shown as examples for 20% steps. It is obvious that the main spectral information concerning the composition of the blend is in the second overtone of the C–H stretching band around 1.21 μm (Figure 5). Transmission in the area of 1.21 μm decreases if the PE content is increased. A contrary effect can be ob-

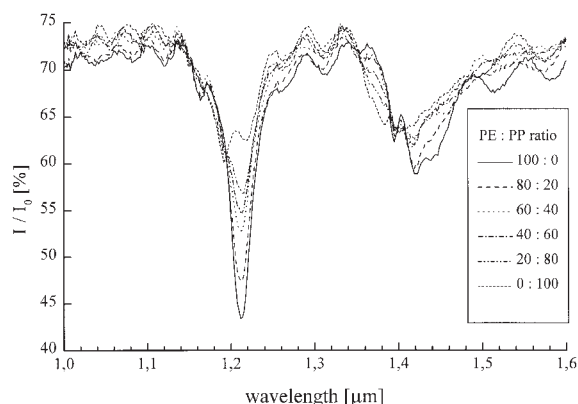


Figure 4. Spectra of PE/PP blends with different mixture ratios varying from pure PE to pure PP in steps of 20%. (PE/PP blend was extruded at 240°C and 50 rpm. Number of averaged spectra. 500, scan frequency: 100 spectra s^{-1} , spectral resolution: 2 nm at 1.523 μm).

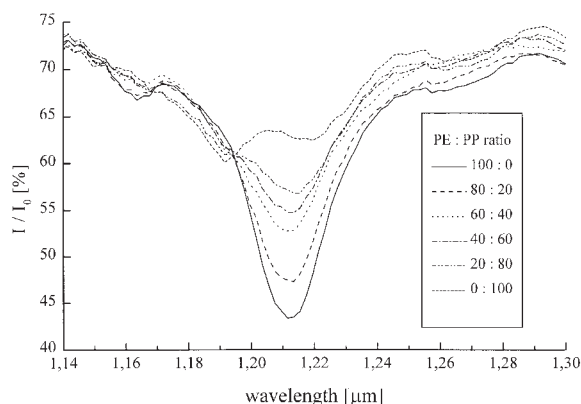


Figure 5. Spectra of PE/PP blends (detail).

served in the wavelength area of 1.19 μm where a shoulder develops to a side maximum with increasing PP content. This side maximum of PP can be explained by the fact that besides C–H vibrations of CH_2 groups, vibrations of CH and CH_3 groups also appear, which are slightly shifted compared to CH_2 group vibrations. This leads to band splitting and displacement of the band centre.

A PLS1 (PLS from now on) model was applied for prediction of a polymer mixture, i.e. the ratio of PE to PP. Mixtures used for PLS were varied between pure PE and 90% PE + 10% PP in steps of 1%. These mixtures were chosen to simulate a) different

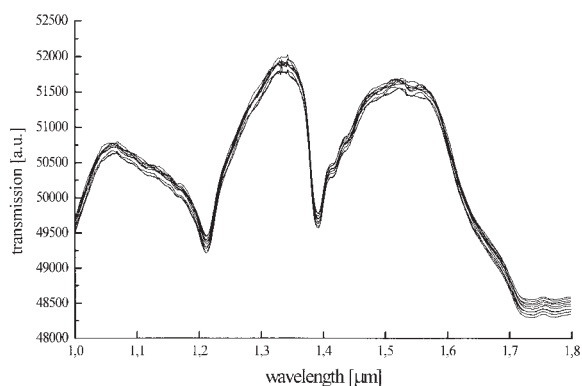


Figure 6. Averaged transmission spectra of calibration set.

amounts of an additive in a polymer matrix and b) blending of two different polymers. So, the PLS model covers 11 different PE/PP blends, with 20 spectra of each mixture used for calibration and 20 spectra of eight mixtures for validation. Averaged spectra of the calibration set are shown in Figure 6. For a first estimation of the mixture ratio it was sufficient to use these original raw spectra (without any further data processing) and the limited number of spectra.

For the PLS model four principal components were enough, since 95% of the spectral variance explain 99% of the compositional variance of the PP/PE system (Table 1). A model with more principal components would result in overfitting of the model, i.e. more noise would be modelled by the PLS regression. As it can be seen from Figure 7, the loadings become more and more noisy from PC1 to PC4. The loadings of PC1 and PC2 show some characteristic peaks around 1.2 μm , which reflects the overtone stretching mode of the C–H groups in the PE/PP blends. In Table 1 it can also be seen, that the modelled compositional variance increases from PC1 to PC2 and then decreases again from PC2 to PC3 and PC4, i.e. there is a local maximum. This usually happens when there are outliers in the calibration set. That could also be the reason why the prediction results are constantly over the measured ones, as shown in Figure 8. The root mean square error of prediction of the PLS model is 0.402, which is normally a quite good result for such rough modelling. The samples with 1% and 8% PP content show

Table 1. Explanation of spectral and compositional variance by the principal components.

Principal component	Spectral variance	Compositional variance
PC1	82%	40%
PC2	11%	44%
PC3	1%	10%
PC4	1%	5%

stronger deviations from prediction, which can be a hint that the measurement of the PP content in these calibration samples had a higher failure than the rest, or that the mixing of PE and PP in the extrusion process was not homogeneous enough.

The measurements and the PLS modelling can be improved if the PP content of the output material is also measured. As shown in Figure 7, the C–H stretching occurs in the loadings of the PCs. Consequently, an improvement can be achieved if data are reduced to a more narrow band around this wavelength region.

Nevertheless, the PLS model gave a good result and demonstrates that this new measurement system together with a sophisticated PLS model can strongly optimise the prediction of blend ratios during extrusion processes in the future.

Conclusion

A measurement system for in-line NIR spectroscopy for polymer extrusion processes had been developed at Fraunhofer ICT. It consists of a measurement head adapted to a single screw extruder with integrated fibre optic probes and an AOTF-NIR spectrometer. Transmission measurements at typical extrusion conditions (temperature 300°C, pressure 35 MPa) yielded good results with respect to mechanical and optical properties of the probes. The developed system is capable of measuring different polymer compositions as demonstrated for PE/PP blends. In this case the prediction ability of a

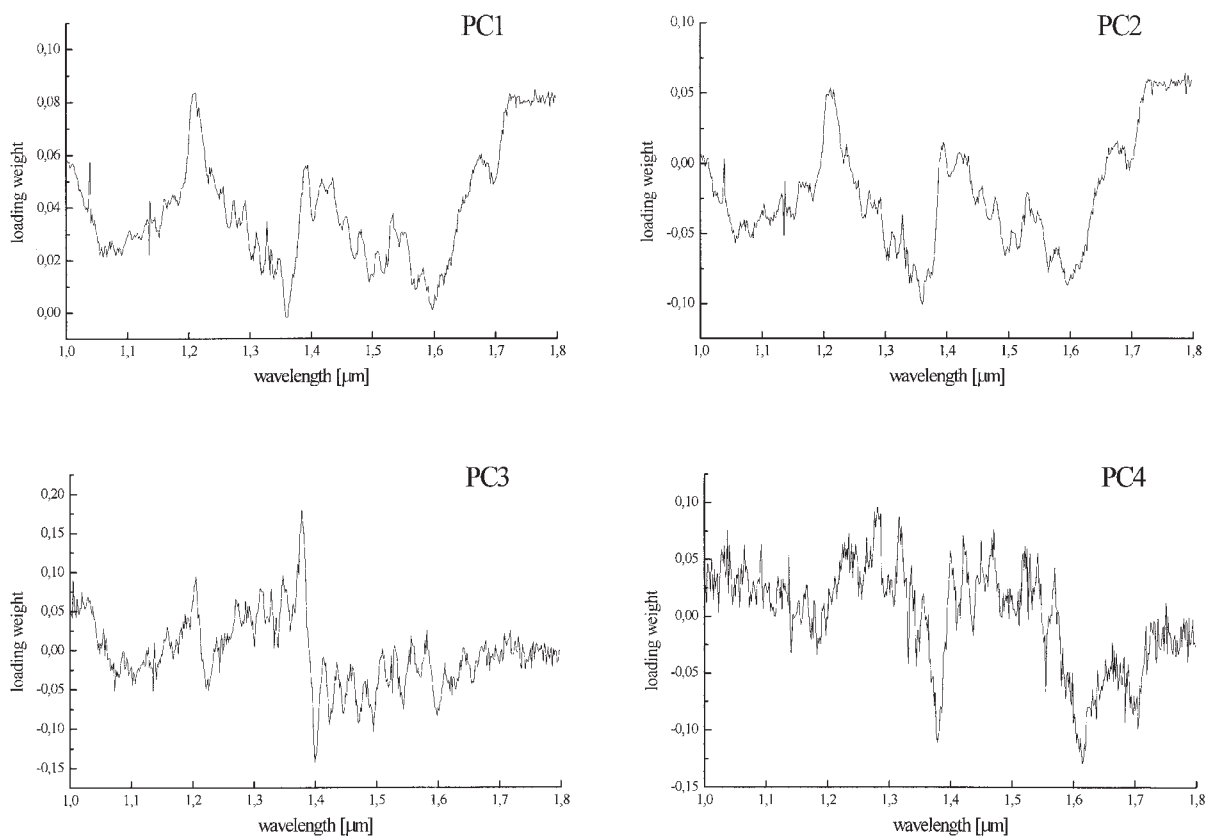


Figure 7. Principal components used for PLS model. Especially the second overtone of the C–H stretching band around 1.2 μm is most important for the explanation of the spectral variance (see PC1 and 2).

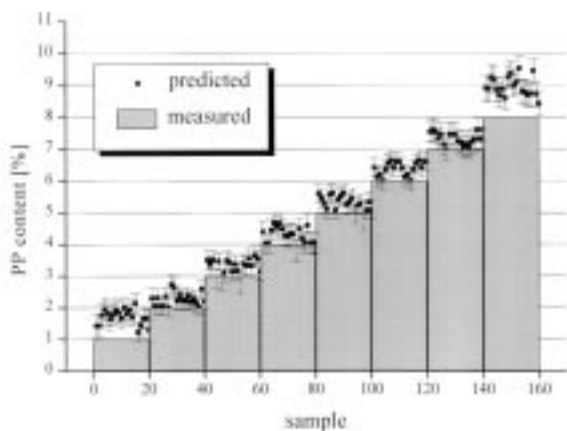


Figure 8. Validation plot: predicted (dot with error bar) and measured (column) value of PP content in PE/PP blend for spectra of validation set.

partial least squares (PLS) model was in the range of 1–2%.

It was shown that the speed and non-intrusive nature of in-line NIR spectroscopy make it perfectly suited to polymer extrusion processes. Deviations in the process can be detected in time to allow corrections to the process to be made. This could result in improved product quality and overall process efficiency.

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