Process Monitoring by Spectroscopic Methods in the Polymer and Plastics Industry

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1. Introduction

In recent years, real time monitoring of chemical reactions and product streams has become more and more important in the polymer and plastics industry. This is due to the growing economic and legislative demands on product quality and the environmental protection. The industry needs rapid, reliable, non-invasive and cost effective analytical methods for process control. Spectroscopic techniques can meet these demands. Vibrational spectroscopy is ideally suited to qualitative analysis of starting materials and end products and to quantification of polymer mixtures. Spectroscopic methods can also give valuable information at the molecular level about the extent of polymerisation reactions and the quality of the produced polymer.

Recent developments of modern fiber-optic-based spectrometers, especially for the near infrared and Raman spectroscopy, opened up new perspectives for process analysis in the polymer and plastics industry. The use of probes connected to spectrometer via optical fibers allows direct measurements in the product stream without interference in the production process.

This article gives an overview of the use of the vibrational spectroscopy techniques, near infrared (NIR) and Raman, for process control in the polymer and plastics industry.

2. Process analysis techniques in the polymer and plastics industry

Conventional process analysis techniques in the polymer and plastics industry are physical measurements such as temperature, flow, pressure and others. The obtained data give information about the physical conditions during the production process and they are permanently compared with set parameters. But these physical parameters do not supply all the necessary information to control the process.

The field of on-line and in-line analysis of polymer processing has a significant growth because of increased demands on quality of polymeric products and reduction of costs by avoidance of polymers of insufficient quality. Beside NIR further techniques are available. These methods differ in precision, speed, complexity, the amount of information gained and in the commercial availability. Commercial on-line and in-line instruments are available for rheometry, UV-, IR- and NIR-spectroscopy. Further techniques, presently still at the research level, are Raman-spectroscopy, ultrasonics, optical microscopy and light-scattering. Reviews about rheometry, UV-and Raman-spectroscopy, ultrasonics, optical microscopy and light-scattering are described in [1, 2] and quoted papers therein. A short review about recent developments in mid-IR and NIR is in [2] and a comprehensive review of process NIR spectroscopy from 1980 to 1993 was given in [3].

Chemical measurements such as spectroscopic techniques are used to qualitative analysis, e. g. the identification of raw materials, intermediate products and end products, and to quantitative analysis, like monitoring of polymerisation reactions and determination of the composition of polymer melt streams.

They are mainly used for:

1. real time monitoring of polymerisation reactions to stop the reactor as soon as a satisfactory end-point has been reached
2. quantitative compositional analysis of polymer melt streams in extruders
3. plastic identification in recycling processes

The term "process control" is very often associated with "on-line analysis". But in praxis one has to differentiate between several types of process analysis (Table 1).

The **off-line** technique has been used in connection with spectroscopic methods for many years. Samples are taken from reaction mixtures or finished products and analysed in a laboratory. The evaluation of the product composition and the concentration of the constituents can take from one to two hours. Meanwhile, the production of a product of unknown quality continues. Due to a large lag time of quality control, tons of off-spec products could be produced. Therefore, it is desireable to reduce the time between sampling and analysis results. One way is to bring the spectrometer to the production line and to do the analysis **at-line** immediately after the sampling.

But the best way is to do the analysis directly in the process stream. In the **on-line** technique a small part of the product stream is diverted from the main stream (by-pass) and presented continuously to a spectrometer. But, the adaptation of a by-pass at the production line is sometimes difficult or even impossible. Furthermore, there is still a time lag, though not that much, between sampling and analysis.

In-line measurements present the ideal form of process analysis. A probe is located in the process line itself and connected to an automated spectrometer. The measured spectra give immediate information about a reaction or the actual composition of a product stream without any lag time. By choosing the right positon of the probe and by careful design of the probe head the interference of the probe with the product stream can be minimised or totally avoided.

All modern product philosophies, like „Just in time manufacturing“, „Total Quality Management“ and “Zero defect product“ have the same aim; the reduction of cycle time from raw material to the final product. NIR process monitoring can be a very powerful tool in the chemical industry for reaching this aim. NIR offers improved measurement precision compared to previous methods. NIR can provide results more rapidly and, above all, NIR can decrease costs in process analysis. But, a realistic view of the sensitivity of NIR as an in-line technique is important. The implementation of a Process Control System for Quantitative Analysis is not an easy process. One needs, after a clear formulation of the problem, a feasibility study and the determination of the cost-benefit ratio. Furthermore, it is necessary to provide resources and manpower, to design the interface for the link between the spectrometer and the NIR probe, to choose the spectrometer and important is the development the calibration and the validation. After the test and the introduction of the method in process it is necessary to maintain the monitoring process.

Table 1:

Common definitions used to describe process control

off-line -	Manual sampling with transport to the laboratory
at-line -	Manual sampling with transport to an analyser near the production line
on-line -	Automated sampling and transport through a sample line (by-pass) to an automated analyser
in-line -	A fiber optic probe is located in the process line itself and connected to an automated analyser

3. Near-infrared spectroscopy for process control

Mid-Infrared (MIR) spectroscopy covers the range of electrochemical radiation from about 2500 nm (400 cm^{-1}) to 25,000 nm (4000 cm^{-1}). It is mainly used as an off-line technique in a laboratory to derive qualitative as well as quantitative information to control product quality.

NIR spectroscopy covers the range from 10000 to 4000 cm^{-1} (1 - 2.5 µm). This is the range of the overtone and combination vibrations, which are 10-100 times less intensive than the fundamental vibrations in the mid-IR. So we can use longer path lengths, between 1 and 10 millimetres. An important advantage of NIR is the application of optical fibres and sapphire windows. Both are robust, cheap and widely used. The distance between probe and spectrometer can be up to 1000 m. Over the past years, some applications in in-line NIR analysis of polymers have been published [4-10].

The intensities of the bands in pure components and in mixtures are proportional to the concentrations of the component/s. The relation between measured intensities and concentration is expressed in the Lambert-Beer law.

Absorbance = absorption coefficient x concentration x sample thickness

Thus it is possible to carry out quantitative analysis by methods based on band maxima, methods based on integrated intensities, single component analysis and multicomponent analysis by multivariate methods

There are five technologies used in NIR process spectrometers [3,11]. The differ in operating principle, range of application, robustness, speed and price. There are:

1. Filter spectrometer, based on optical (interference) filters.
2. Scanning grating monochromator spectrometer.
3. Photodiode array spectrometer with InGaAs(Indium Gallium Arsenide)-detector.
4. FT(Fourier-Transform)-NIR spectrometer.
5. AOTF (acousto-optical tuneable filter) spectrometer, based on internal crystals.

NIR in-line probes are available for measurements in transmission mode and in diffuse reflectance mode for reactors, extruders and pipelines. These probes can withstand the harsh conditions in these environments, e. g. 300 °C and 350 bar. Especially the development of diffuse reflectance probes opens up new possibilities for chemical process applications. Many process applications are too highly scattering to be amenable to transmission analysis.

4. Raman spectroscopy for process control

The Raman effect is a light-scattering effect. Raman scattering is the change in frequency for a very small percentage of the intensity in a monochromatic beam as the result of interacting with a compound. The frequency changes occur as the result of coupling between the radiation and vibrational energy levels of molecules. The region in which the Raman effect is observed depend on the energy of the incident radiation. This can be in the visible region, the UV region and in the NIR region. The condition for a molecule to be Raman active is a change in the deformation (polarisation) of the electron cloud during the interaction with the incident radiation. In case of Raman scattering is this interaction modulated by the molecular vibrations. So the Raman method is the complementary method to IR spectroscopy. The qualitative analysis by group frequencies and the quantitative analysis procedures for single and multicomponent analysis are in principal the same like in IR.

The limitation of Raman is the fluorescence phenomenon. Fluorescence is 10^7 times stronger than Raman scattering. Trace impurities may fluoresce so strongly that is often impossible to observe the Raman spectrum. The use of UV or NIR excitation is a possibility to overcome this problem.

There are three technologies used in Raman spectrometers. The differ in the exciting radiation and detection. There are:

1. Raman spectrometer with excitation in the visible range (488 nm – 694 nm) and a photomultiplier as detector
2. Raman spectrometer with excitation by diode lasers at 785 nm and a CCD detector
3. Raman spectrometer with excitation in the near infrared by a Nd:YAG laser at 1064 nm and a Ge semiconductor detector

The fiber-optic coupling of remote probes to Raman spectrometers provides real experimental versatility and stability. The use of probes is ideally suited for screening potential applications, routine troubleshooting, and methods development work in the laboratory or the pilot plant. So one can use a non-contact optic for measuring samples in bottles, vials, or through a site glass window. Alternatively, an immersion probe can be used to contact a sample directly in a stream or batch reactor or extruder. Such probes must be designed to withstand the very harsh conditions in the reactors or extruders.

5. Miniaturising of the spectrometers

Miniaturised spectrometers with line detectors measure a wavelength spectrum in the shortest possible time. As they are constructed without mechanically-moved parts, their characterising features are long-term stability and maintenance-free operation. The spectrometers are usually coupled with optical fibres. This gives a high level of modularity. Measuring configurations can be realised which are specifically suited to the object being measured and the measuring requirements. It is therefore possible to construct distributed measuring systems for process control as well as off-grid manual measuring devices. This shows the range of innovations which can be implemented by this future-oriented technology.

The revolutionary development of small and affordable spectrometers opens the door for many applications in the field of optical spectroscopy. These units will allow applications in process measurement as well as for mobile uses. Fibre optics give an unknown flexibility and a variety of probes for transmission and diffuse reflection.

Common properties of the miniature spectrometers are that they can be installed in a PC-slot (plug-in), the use of an InGaAs-Diode-Array detector, the thermo-electrical cooling of the optical bank and the use of SMA-connectors to connect an SMA-fibre directly to the spectrometer. The high sensitive and cooled detector allows very fast measurements within a few milliseconds. A mobile version of this NIR miniature spectrometer uses a PCMCIA board for notebook applications.

6. Quantitative analysis

6.1. Calibration

Vibrational spectroscopy is only an indirect method for the quantitative analysis of chemical mixtures. To use vibrational spectra for quantitative analysis it is necessary to find a relationship between the measured data and the concentrations. The most common model to express this relationship is a linear regression containing first-order or higher-order polynominals. These polynominal models are often termed calibration curves. They relate the concentration of the analyte to the response of the spectrometer. A linear regression model is an iterative process. After the construction of a model it is necessary to assess the model quality through observation of model parameters and to validate the model with independent data.

6. 2. Chemometrics

The chemical information of vibrational spectra are hidden in the band positions, the band intensities and also in the band widths. The band positions give information about the appearance of certain chemical compounds in a mixture. The intensities of the bands are related to the quantitative content of these compounds via the Beer-Lambert Law. The band widths can give information about the thermodynamics and kinetics of chemical molecules. The easiest way to determine the content of a chemical compound is to measure the change of the intensity of a well resolved band that clearly belongs to this compound. But this case is very rare. More often, the mixture of different chemical compounds give complex spectra with overlapping bands and the changes in intensities are not always related to the content change of only one compound. For these cases is it necessary to use chemometric methods to extract the qualitative or quantitative information from the spectra.

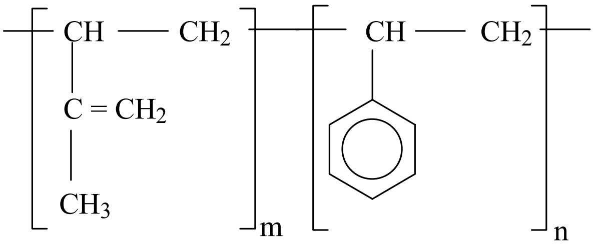
Chemometrics is the combination of mathematics, statistics and computer science to reach information from chemical data. In all cases the aim is the chemical interpretation of data. The quantitative chemometric method used is the Principal Component Analysis (PCA). This is a data reduction method, which separates data into the independent spectral variations. These individual spectrum scaling factors can be directly related to properties of the investigated systems, e. g. concentrations of components. PCA allows the use of the entire spectrum for the quantitative analysis. Quantitative models based on PCA are Principal Component Regression (PCR) and Partial Least Squares (PLS). A detailed description and a comparison of the chemometric methods can be found in [12,13]. It is necessary to carry out a careful and extensive calibration for a good quantitative analysis, which is frequently considerable complex and time consuming. But, only a good calibration which is reliable and robust, garantees a long-term stability of the process control system.

7. Applications in process control by infrared and raman spectroscopy in the polymer and plastics industry

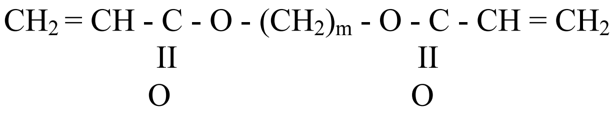
7. 1. Quantitative process analysis of acrylate monomers in SIS-block-copolymer melts by in-line NIR and Raman spectroscopy

The aim of this process analysis was the quantitative determination of the content of two acrylate monomers SIS-blockcopolymer melts.

SIS-blockcopolymer:



Acrylat-monomer:



$$CH_2=CH-\underset{\underset{O}{\|}}{C}-O-(CH_2)_m-O-\underset{\underset{O}{\|}}{C}-CH=CH_2$$

We investigated this melt by near infrared (NIR) spectroscopy in a corotating twin screw extruder (ZSK 40, Werner & Pfleiderer, Pressure: 145 bar, temperature: 139°C). Furthermore we used Raman spectroscopy to the determination of the monomers in solutions.

Experimental

NIR:

Probe: diffuse reflectance fiber optic probe FDR 520 (Axiom Analytical Inc., USA) with sapphire-window in a melt-at-die interface on the end of the extruder

Spectrometer: InfraProver II (Bran+Luebbe GmbH, Germany)

Chemometrics: Program ICAP (Bran+Luebbe GmbH, Germany), PLS-method,

Spectra pretreatment: Absorption, normalisation

Wavelength regions: 4620 - 5088 cm^{-1}, 6084 - 6288 cm^{-1} and 6504 - 7500 cm^{-1}

Raman:

Probe: fiber optic probe (Kaiser Optics Systems Inc., USA)

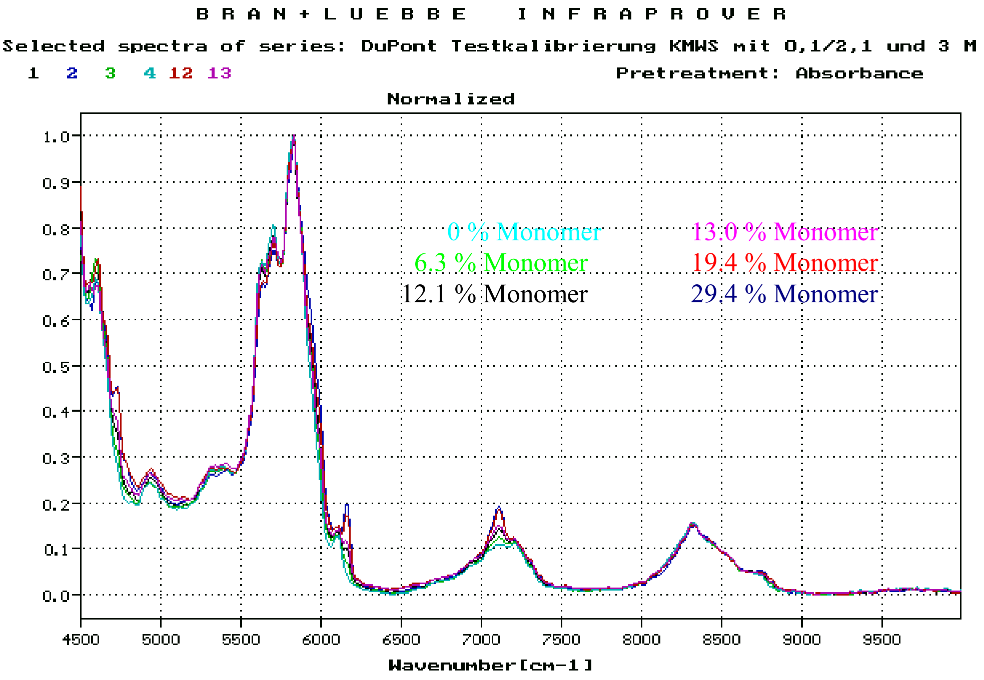
Spectrometer: HoloProbe 785 nm (Kaiser Optics Systems Inc., USA)

Chemometrics: Program GRAMS32/IQ-PLSplus (Galactic Industries Corp., USA), PLS-method, Spectra pretreatment: Multiplicative scatter correction (MSC)

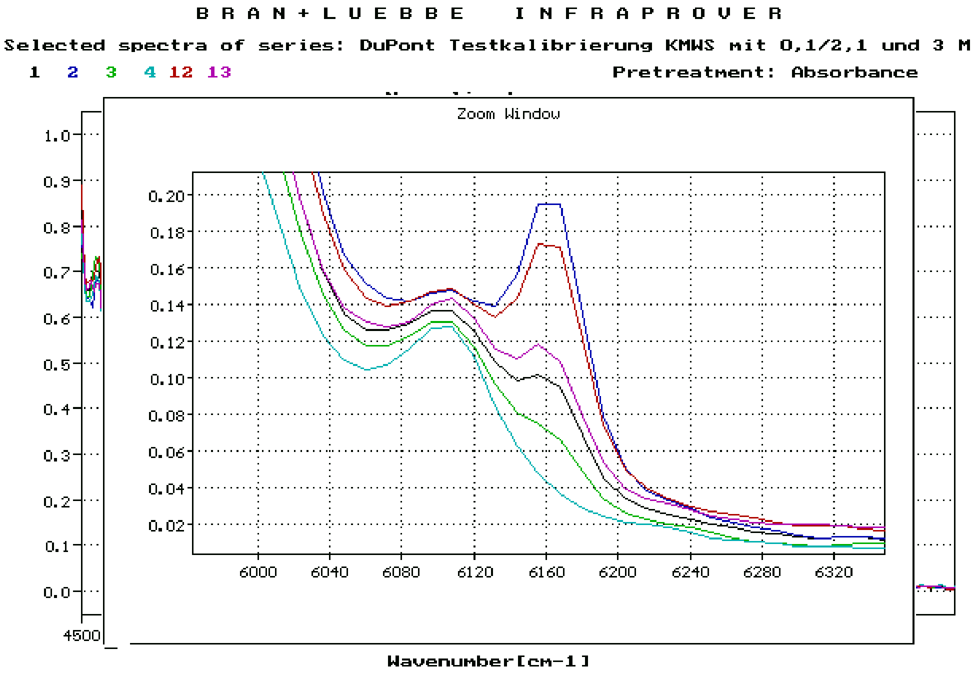
Wavelength regions: 3140 -2800 cm^{-1} and 1500 - 300 cm^{-1}

NIR results

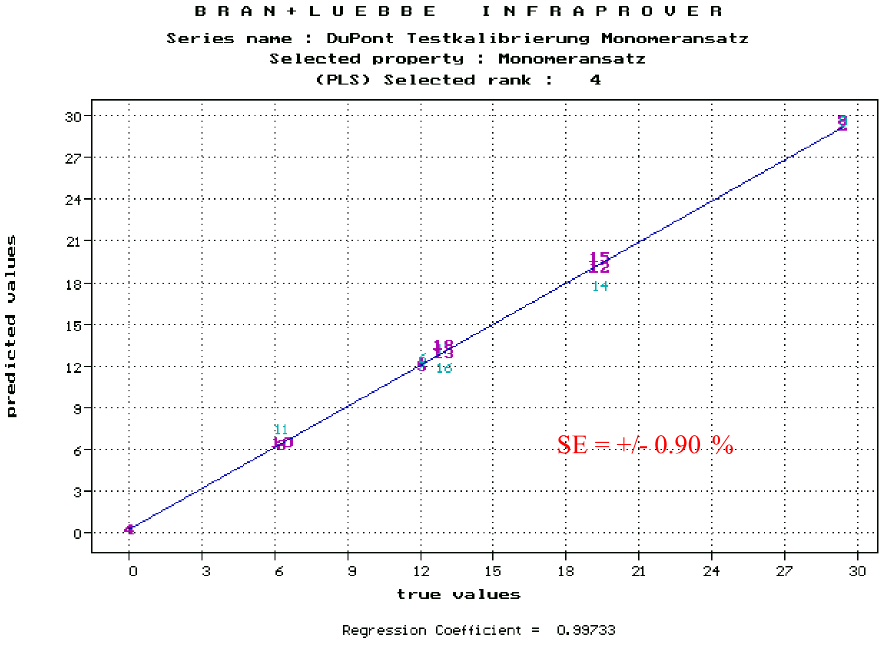
In-line NIR Spectra of SIS Block Copolymer with Different Acrylate Monomer content



In-line NIR Spectra of SIS Block Copolymer with Different Acrylate Monomer content



NIR-Calibration Curve for the Quantification of the Monomer content in a SIS Block Copolymer

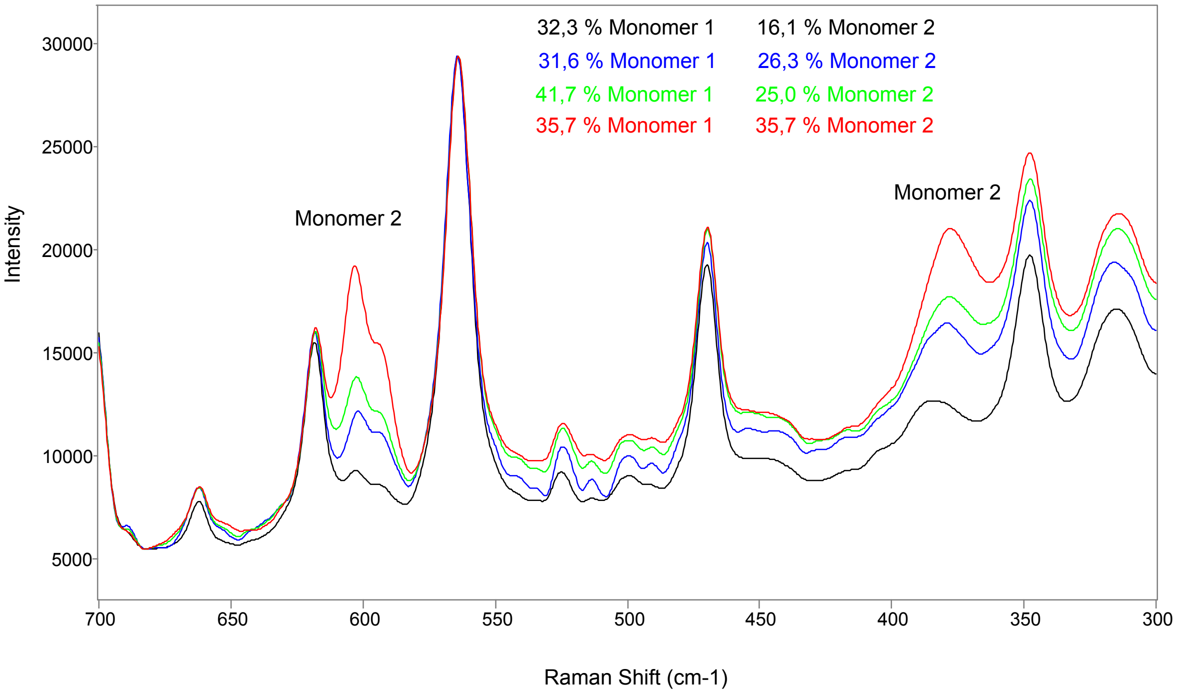


Tab. 2: True and with the NIR calibration model calculated values for the monomer content in the validation spectra

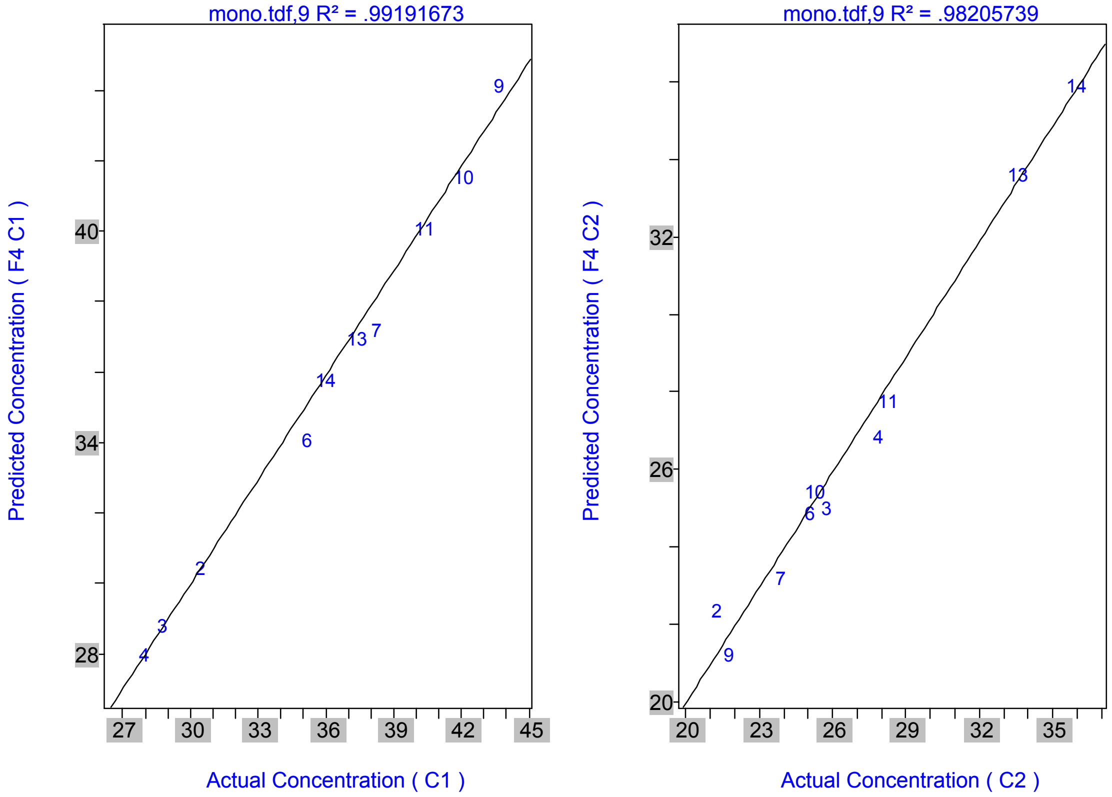
Test spectra	True value	Calculated value	error
6	12,1 %	12,2 %	+ 0,1 %
7	12,1 %	11,0 %	- 1,1 %
9	29,4 %	29,7 %	+ 0,3 %
11	6,3 %	7,4 %	+ 1,1 %
14	19,4 %	18,5 %	- 0,9 %
18	13,0 %	13,3 %	+ 0,3 %

Raman results

Raman spectra of Different Mixtures of Acrylate Monomer 1 and 2



Raman Calibration Curve for the Quantification of the Contents of Monomer 1 + 2



Tab. 3: True and with the Raman calibration model calculated values for the monomer 1 and Monomer 2 in the validation spectra

	Monomer 1			Monomer 2		
Spectra	True value	Calculated value	error	True value	Calculated value	error
5	31,6 %	31,4 %	- 0,2 %	26,3 %	26,6 %	+ 0,3 %
8	40,9 %	40,6 %	- 0,3 %	22,7 %	22,4 %	- 0,3 %
9	38,5 %	38,5%	0	30,6 %	30,6 %	- 0,2 %

Summary

The quantitative determination of the content of two different acrylate-monomers in SIS-Blockcopolymer melts in real time is practicable with NIR- and Raman-Spectroscopy.

Concerning the accuracy of the measurement and the differentiability of the two monomers is Raman spectroscopy the more appropriate method.

7. 2. Quantitative process analysis of additives in PVC melts by in-line NIR spectroscopy

The aim of this process analysis was the quantitative determination of the content of the main component PVC and two additives in an industrial PVC melt.

We investigated this melts by near infrared (NIR) spectroscopy in a twin screw extruder (Viskosystem, Reifenhaeuser, pressure: 50 – 270 bar, temperature: 200 °C) with an in-line diffuse reflectance probe.

Composition of an industrial PVC blend:

PVC	76 %
Recycling material	10 %
modifier	5 %
lubricant	4 %
TiO_2	3 %
$CaCO_3$	2 %

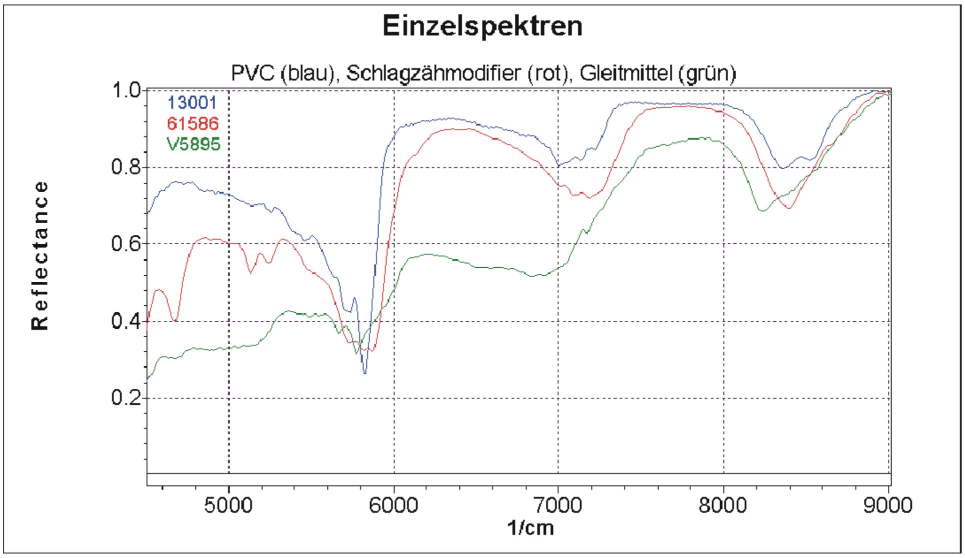
We monitor the content of the modifier from 3 to 7 % and the content of the lubricant from 2 to 6 %. The contents of PVC vary from 74 to 78 %.

Experimental

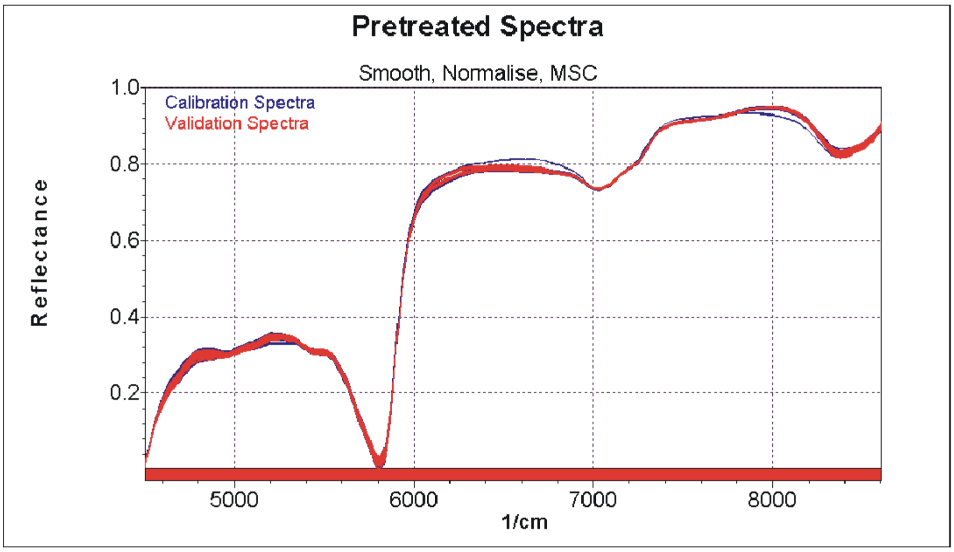
Probe: diffuse reflectance fiber optic probe FDR 650 (Axiom Analytical Inc., USA) with sapphire-window in a melt-at-die interface on the end of the extruder (fig. 3)
Spectrometer: NIRVIS (Büchi Labortechnik AG, Germany)
Chemometrics: Program NIRCAL (Büchi Labortechnik AG), Germany), PLS-method,
Spectra pretreatment: Smoothing, normalisation, MSC
Wavelength region: 4500 - 8600 cm^{-1}

Results

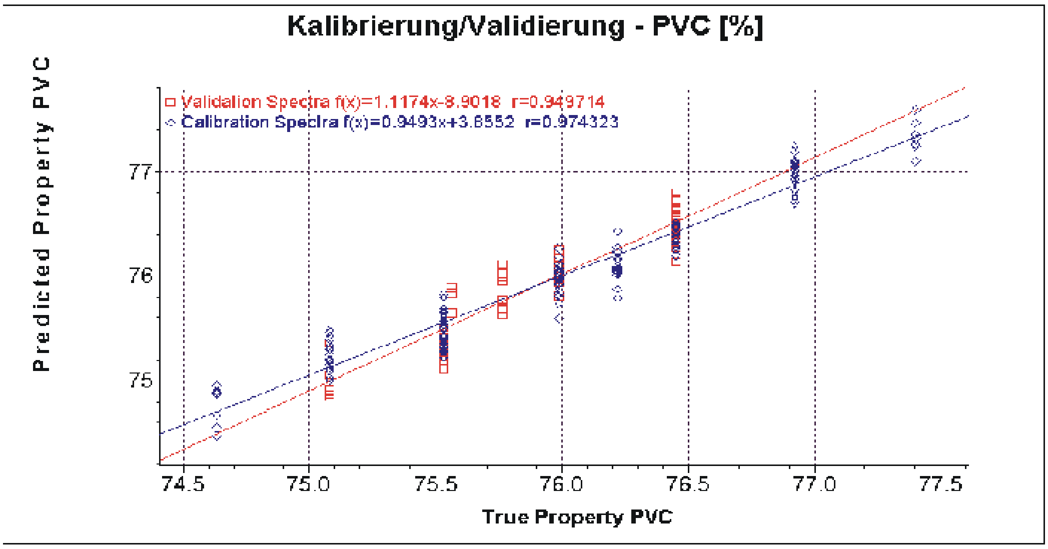
NIR Spectra of the components of an Industrial PVC measured with a Diffuse Reflectance Probe; PVC (blue), modifier (red), lubricant (green)



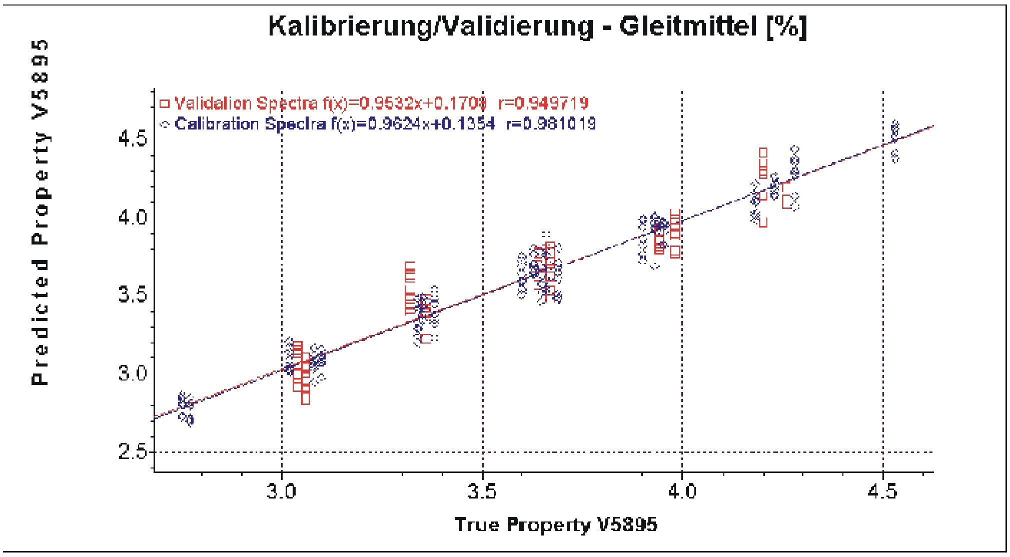
NIR Spectra of an Industrial PVC melt measured in-line with a Diffuse Reflectance Probe



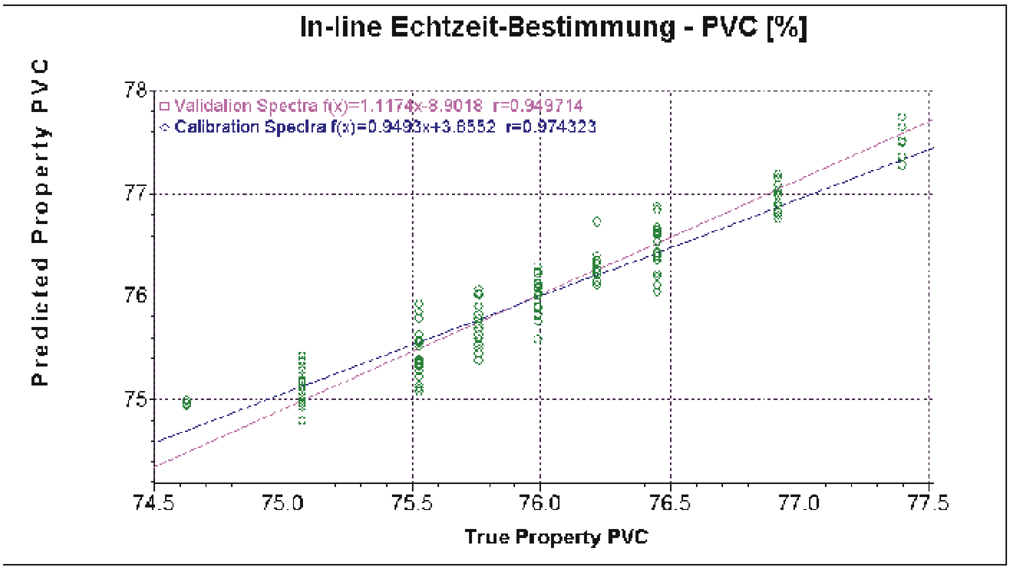
Calibration and Validation of the Content of PVC



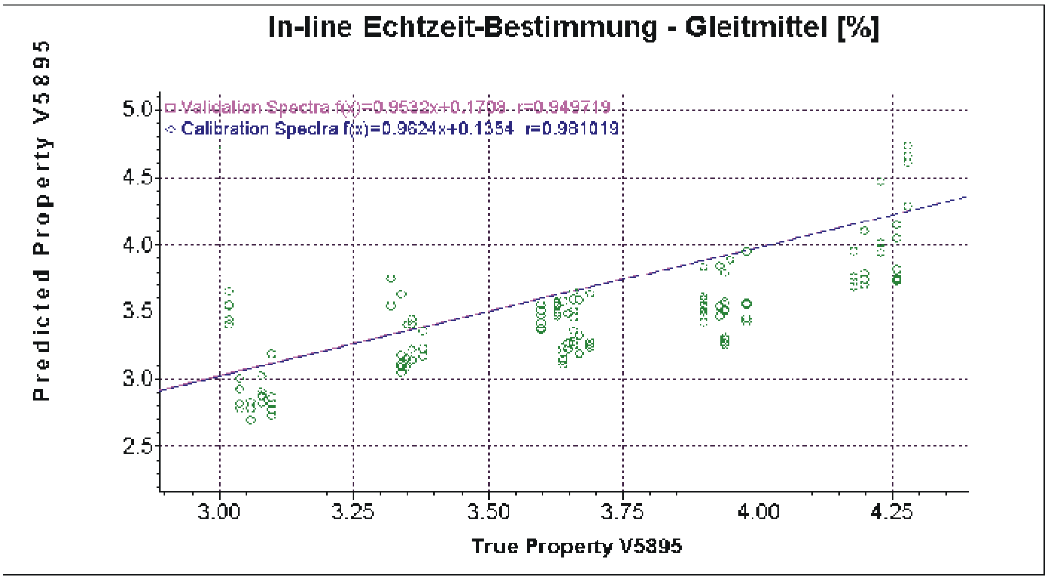
Calibration and Validation of the Content of the lubricant



Results of the in-line real time determination of PVC in the industrial PVC melt, calculated with the calibration model



Results of the in-line real time determination of the lubricant in the industrial PVC melt, calculated with the calibration model



Summary

The standard errors of Prediction (SEP) for the validation of the calibration model are

PVC 0.18 %
Modifier: 0.18 %
Lubricant : 0.13 %

The application of this calibration model for the quantitative in-line analysis for real industrial PVC melts show the following SEP:

PVC 0.20 %
Modifier: 0.28 %
Lubricant: 0.26 %

The quantitative determination of the main component PVC and the modifier and lubricant content in a industrial PVC melt mixture in real-time is with in-line NIR spectroscopy practicable.

8. References

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