Process analysis of polymers by NIR spectroscopy

D. Fischer and K.-J. Eichhorn

Institute of Polymer Research Dresden, Hohe Str. 6, D-01069 Dresden, Germany

The possibility of in-line NIR process spectroscopy on polymers opens up new perspectives of process analysis in the production and processing of polymers. Polymer melts, e.g. in extrusion processes, can be investigated in-line by transmission spectroscopy for transparent melts and diffuse reflectance spectroscopy for opaque melts. The quantitative analysis is carried out using chemometric methods, e.g. the Partial Least Squares method (PLS) and Principle Component Regression (PCR). Our results show, that NIR spectroscopy with transmission and diffuse reflectance probes is suitable for quantitative in-line process analysis of multicomponent polymer mixtures.

Overview: On-line and in-line process analysis of polymers

The field of process analysis is expanding due to the economic benefits achieved by using fast and reliable information. Classic textbooks about process analysis are [1,2]. In the literature there are five terms for process analysis. Callis et al. [3] describe these terms as off-line, at-line, on-line, in-line and non-contact. The last three terms are very on-line methods. The difference between on-line and in-line is clearly defined. An *on-line* system is an automated sampling system, which is used to extract the sample and present it to an analytical instrument for measurement *or* it is a continuous method that permits the sample flow continuously through the instrument. In contrast to on-line an *in-line* system contains an analysis, which is done directly in the process line, using a probe. The *non-contact* mode is a special case of in-line and on-line where the probe does not physically contact the sample. Both methods have advantages and disadvantages. For *in-line* systems the sampling delays are non-existent. However, an in-line probe can interfere with the main process stream, and the measurement is dependent on temperature and pressure variations during the process. For *on-line* systems, the sampling delays can be significant, because of the transport of the sampling stream to the measurement system, mostly by a gear pump. On the other hand, on-line systems are isolated from the process stream, so the temperature and pressure can be controlled.

All modern product philosophies, like “Just in time manufacturing”, “Total Quality Management” and “Zero defect product” have the same aim: the reduction of the cycle time from raw material to the 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, provides results more rapidly and, above all, it decreases costs in process analysis. However, a realistic view of the sensitivity of NIR as an in-line technique is important. It is also not an easy process to install an NIR analysis system. 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 staff, to design the interface for the link between the spectrometer and the NIR probe and to choose the spectrometer. Important is the development of a good calibration method and its validation. After the test and the introduction of the method in process it is necessary to maintain the monitoring 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. Besides NIR further techniques are available. These methods differ in precision, speed, complexity and 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 [4,5] and quoted papers therein. A short review about recent developments in mid-IR and NIR is in [5] and a comprehensive review of process NIR spectroscopy from 1980 to 1993 was given in [6].

Common applications of on-line mid-IR spectroscopy in the range from 4000 to 400 cm^{-1} (2.5 – 25 µm) are, for example, described in [7-9]. This is the range of the fundamental vibrations, which provides powerful information both on the concentration and chemical composition of the investigated system. However, due to strong absorption in this range, the transmission measurements must be done on very thin samples, mostly less than 100 µm. The use of an on-line system is often connected with a time lag problem, because the molten polymer is diverted from the process stream and passed through a heated bypass to a melt flow cell. It is not possible to use optical mid-IR fibres in an industrial environment, because of their lack of stability and their high loss of energy at present time. An alternative is the use of an ATR dipper system [10]. In this case for an accurate quantification it is necessary to consider the wetting and adhesion processes between polymer melt and ATR crystal.

One can overcome all these problems by NIR spectroscopy, which covers the range from 10 000 to 4 000 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, among 1 and 10 millimetres. A further important advantage 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 of in-line NIR analysis of polymers have been published [11-17]. All workers used in-line NIR transmission probes for the quantitative analysis of transparent systems.

There are five technologies used in NIR process spectrometers [6,18]. They 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 probes are available for measurements in transmission mode and in diffuse reflectance mode.

A disadvantage of NIR is that the information of the NIR spectrum in comparison to mid-IR is less detailed. There are only distinct bands from certain groups; normally OH, CH, NH, CO, and, the bands overlap. Therefore it is necessary for a quantitative analysis to perform a chemometric analysis. 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 [19,20]. For quantitative analysis it is necessary to carry out a careful and extensive calibration, which is frequently considerable complex and a time consuming process.

Example: Extrusion monitoring of polymer melts by NIR spectroscopy

Experimental

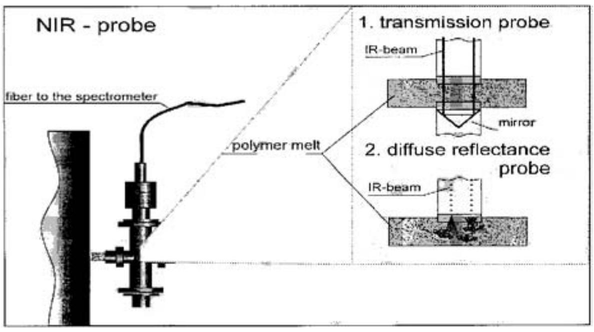

Figure 1. Adaptation of in-line NIR probes on an extruder (transmission probe and diffuse reflectance probe).

We apply transmission spectroscopy to transparent melts and diffuse reflectance spectroscopy to opaque melts in various extrusion processes. Two different co-rotating twin screw extruders (ZSK 30 by Werner Pfleiderer and Viskosystem by DAVO/Reifenhäuser) were used. The NIR probes were adapted in-line at the end of the extruders. The connection between the NIR probes and the NIR spectrometer were realised through quartz fibres. We used FT-NIR spectrometers of different producers (Bio-Rad FTS 175, Bruker Vector22N, Bran&Luebbe InfraProver).

The processing of the polymer melts was carried out in a temperature range from 190 to 245 °C. The various components were proportioned gravimetrically. The residence time was 3 to 6 minutes. The basic design of our experimental system is illustrated in figure 1. We used a transmission probe (O.K.Tec, material: ceramic with sapphire windows) with variable optical length of path (1 – 10 mm) for the transparent polymer melts. We recorded all transmission spectra automatically every minute with a resolution of 4 cm^{-1} and 64 scans. The non-transparent polymer systems were measured with a diffuse reflectance probe (Axiom FDR 520, material: stainless steel with sapphire windows). The diffuse reflectance spectra were measured in an interval of two minutes with a resolution of 25 cm^{-1} and 15 scans. The chemometric evaluations of the measured spectra, necessary for a fast and reliable quantitative analysis, were carried out with PCR and PLS with the program PLSplus [21].

Results

1. The system polypropylene (matrix) and ethylene vinyl acetate (EVA) copolymer was investigated in the molten state with the transmission probe. A baseline correction of the measured spectra was performed before starting the

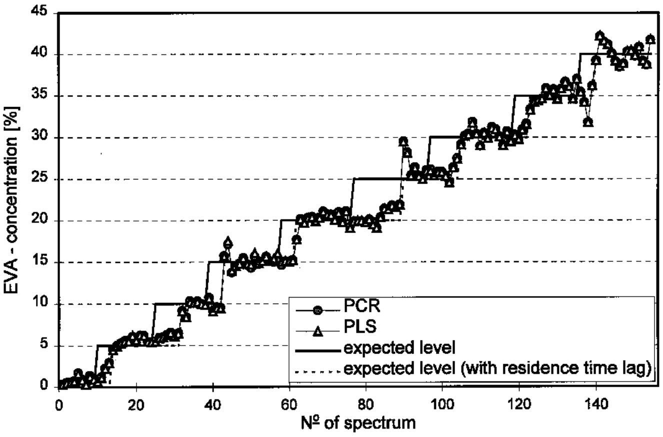

Figure 2. Chemometric analysis for the quantification of EVA copolymer in polypropylene.

chemometric analysis. A calibration model with 34 samples was developed. The optimised PRESS (Prediction Residual Error Sum of Squares) factors are 2 for PCR and 2 for PLS. The SEP (Standard Error of Prediction) values are 0.99% for PCR and PLS. Figure 2 shows the result of the chemometric analysis. We get an excellent agreement for both, PLS and PCR, with the expected values for the EVA copolymer. The mean error between the chemometric rated values and the expected level for the EVA copolymer is 1.1% for PLS and PCR. The marked delays in the EVA concentrations in figure 2 are traced to the residence time lag (6 minutes) of the polymer blend along the extruder.

2. A further subject of our investigation was the simultaneous quantification of the content of several additives, modifiers and lubricants in polyvinyl chloride (PVC). In the extrusion process it is necessary to monitor the actual concentration of these loadings. Figure 3 shows as an example the NIR spectra of 4 individual components of an industrial PVC. We have monitored the content of the lubricant from 3 to 6% and the content of the modifier from 8 to 13%. This system is opaque, so we used a diffuse reflectance probe. Samples that are measured using diffuse reflectance exhibit at times significant differences in the spectra due to the non-homogeneous distribution of the particles. The degree of scattering is dependent on the wavelength of the light, the particle size and the refractive index of the sample. The scattering is not equal over the whole spectrum. Due to this reason it is necessary to carry out a data pre-process for pathlength correction before starting chemometrics. We used the Multiplicative Scatter Correction (MSC) [22]. MSC eliminates or reduces the difference in light scatter between samples before the calibration. A more detailed description of MSC can be found in [23] and in the bibliography therein.

We performed a chemometric analysis with PLS and cross-validation. A calibration model with 110 samples using the complete spectral range from 4500 to 9000 cm^{-1} was developed. The correlation coefficient is 0.97 for the lubric and 0.95 for the modifier. Figure 4 shows the results of the chemometric analysis for the content of the lubricant and the modifier. There is a sufficient agreement between the PLS results and the dosed values. The mean error between the chemometric rated values and the expected level is for the lubricant ± 0.27% and for the modifier ± 0.89%. These results are sufficient for an effective process analysis.

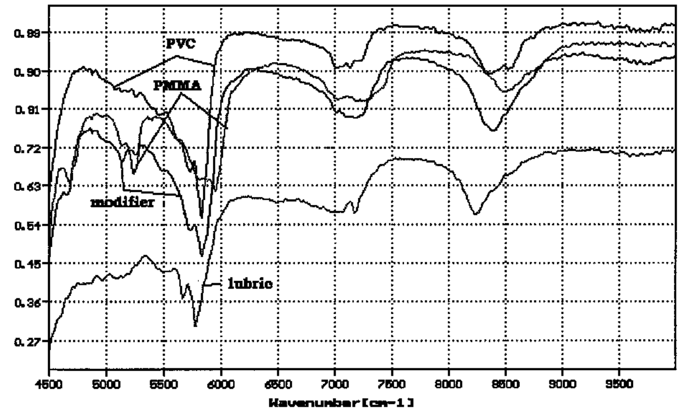

Figure 3. NIR spectra of pure PVC and of 4 components of an industrial PVC.

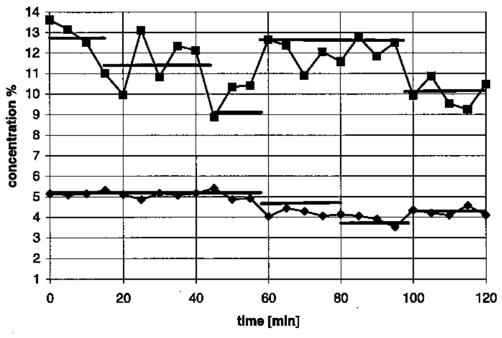

Figure 4. Chemometric analysis of the content of a lubricant and a modifier in PVC,
■ modifier, measured with NIR probe, calculated with PLS,
◆ lubricant, measured with NIR probe, calculated with PLS,
— expected (dosed) value.

Conclusion

Comparing the disadvantages and advantages of in-line NIR process analysis, given in this paper, the advantages predominate clearly.

By application of diffuse reflectance as measurement principle it is necessary to take into consideration that the investigated systems are nearly homogeneous blended and, that the calibration blends have the same scattering properties as the investigated real system. Our results show, that in-line NIR spectroscopy with both, transmission and diffuse reflectance probes and the use of chemometric calibration is suitable for quantitative in-line process analysis of multi-component polymer melts.

Acknowledgements

The authors thank the German Federal Ministry for Education, Science, Research and Technology for promoting the studies conducted within the project on the application of innovative methods for characterising polymers. We also are grateful to B. Kretzschmar at the Institute of Polymer Research Dresden who contributed valuable suggestions on the problems represented.

References

1. Clevett, K. J. Process Analyser Technology, John Wiley & Sons, New York, 1986.
2. Nichols, G. D. On-line Process Analysers, John Wiley & Sons, New York, 1988.
3. Callis, J. B.; Illman, D. L.; Kowalski, B. R. *Anal. Chem.* **1987**, *59*, 624A.
4. Xanthos, M.; Patel, S. H. *Adv. Polym. Techn.* **1995**, *14*, 151-157.

5. Dumoulin, M. M.; Gendron, R.; Cole, K. C. *TRIP* **1996**, *4*, 109-114.
6. Workmann, Jr. J. *J. Near Infrared Spectrosc*. **1993**, *1*, 221-245.
7. Stengler, R.; Weis, G. *Kunststoffe* **1989**, *79*, 955.
8. Fidler, R. A; *Plastics Compounding* **1992**, *15*, 47-50.
9. McPeters, L. H. *Anal. Chim. Acta* **1990**, *238*, 83-93.
10. Jakisch, L.; Fischer, D.; Stephan, M.; Eichhorn, K. J. *Kunststoffe* **1995**, *85*, 1338-1344.
11. Sohl, C. H. *SPE ANTEC* **1991**, 846-849.
12. Moessner, R. C. *Proc. Cont. Qual.* **1992**, *2*, 237-247.
13. Hansen, M. G.; Khettry, A.; Batra, J.; Stewart, D. A. *SPE ANTEC* **1993**, *39*, 1437.
14. McPeters, L. H.; Williams, S. O. *Proc. Cont. Qual.* **1992**, *3*, 75-83.
15. Hansen, M. G.; Khettry, A. *Pol. Eng. Sci.* **1994**, *34*, 1758-1766.
16. Batra, J.; Khettry, A.; Hansen, M. G. *Pol. Eng. Sci.* **1994**, *34*, 1767-1772.
17. Eschenauer, U.; Henck, O.; Hühne, M.; Wu, P.; Zebger, I.; Siesler, H. W.; Chapter 2 in: Introduction to Near Infrared Spectroscopy, Horwood, Chichester, 1992; pp 11-18.
18. Coates, J. *NIR News* **1994**, *5*(2), *7+5*(3), 7.
19. Martens, H.; Naes, T. Multivariate Calibration, John Wiley & Sons, Chichester, 1989.
20. Henrion, R.; Henrion, G. Multivariate Datenanalyse, Springer, Berlin, 1994.
21. PLSplus V. 2.1 for GRAMS/368 (1993) Galactic Industries Corporation.
22. Geladi, P.; Mac Dougall, D.; Martens, H. *Appl. Spec.* **1985**, *39*, 491.
23. Fischer, D.; Bayer, T.; Eichhorn, K. J.; Otto, M. *Fresenius J. Anal. Chem.* **1997**, *359*, 74-77.