LECTURE

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In-line process monitoring on polymer melts by NIR-spectroscopy

Abstract The application of near-infrared (NIR) spectroscopy to continuous monitoring of extrusion processes of polymers was demonstrated. NIR probes were adapted to the extruder outlet. The connection between probe and extruder was realized through a fiber-optic cable. The measurements utilized transmission or diffuse reflectance modes. Quantitative analysis was carried out using the chemometric methods of Partial Least Squares (PLS) and Principle Component Regression (PCR). Subjects of our investigations were the quantification of the composition of polymer blends (polypropylene/ethylene vinyl acetate copolymer) and the quantification of content of filler in polymer matrices (polypropylene/pulverized chalk) in the range of weight concentrations from 0 to 40%. The results show that NIR spectroscopy is suitable for quantitative in-line and real-time analysis of polymers.

1 Introduction

IR spectroscopy on polymer melts opens up new possibilities for process monitoring in the production and processing of polymers. Accurate information about product quality and product composition during the actual process in the extruder can be obtained immediately. Information about reaction kinetics, conversion, chemical equilibrium, and the thermal stability is derivable. Such detailed knowledge of the product composition makes it possible to respond to process variations directly.

In-line IR measurement technologies are finding increasing use in all steps of polymer production. A review about recent developments in mid-IR and NIR [1] and a comprehensive review of process NIR spectroscopy from 1980 to 1993 [2] also contain practical definitions of the

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terms at-line, on-line, in-line, etc. Common applications of on-line IR spectroscopy in the mid-IR are, for example, described in [3–5]. Unfortunately, the use of these systems leads to a time lag and it is presently not possible to use optical mid-IR fibers, because of their lack of stability and their high loss of energy. An alternative is the use of an ATR dipper system [6]. However, for an accurate quantification it is necessary to consider the wetting and adhesion processes between polymer melt and ATR crystal. NIR spectroscopy in the spectral range 4000 cm^{-1} (2.5 µm) to 10000 cm^{-1} (1.0 µm) is the method of choice because it ideally combines real-time analysis with quantitative analysis. NIR probes can be adapted in-line in the extruder. It is possible to separate the spectrometer from the extruder by up to 1000 meters by application of glass fibers. Over the past few years, some applications of in-line NIR analysis of polymers have been described [7–13]. All workers used in-line NIR transmission probes for the quantitative analysis of transparent systems. The advantages and disadvantages of process NIR systems are listed by Moessner [8]. Hall et al. [14], for example, used NIR reflectance spectroscopy for the quantification of additive powders in polypropylene, but not in-line.

2 Experimental

Extrusion monitoring system. The instrument system used for the NIR process spectroscopy consists of a co-rotating twin screw extruder (ZSK 30, Werner & Pfleiderer, Stuttgart) and an in-line NIR system. The NIR system used either a NIR-spectrometer BIO-RAD FTS 175 with a transmission probe, or a BRUKER VECTOR 22 N with a transmission or a diffuse reflectance probe. An additional in-line ATR system for complementary measurements in the MIR range was used and has been described in detail elsewhere [6].

Extrusion. The screw configuration is characterized by the alternation of several mixing and feeding zones. The processing of the polymer melts was carried out in a temperature range from 210 to 245°C. The filler and the blend components were proportioned gravimetrically. The residence time was 3 to 6 min.

In-line NIR System. The basic design of an in-line NIR system is illustrated in Fig. 1. We used a ceramic transmission probe with
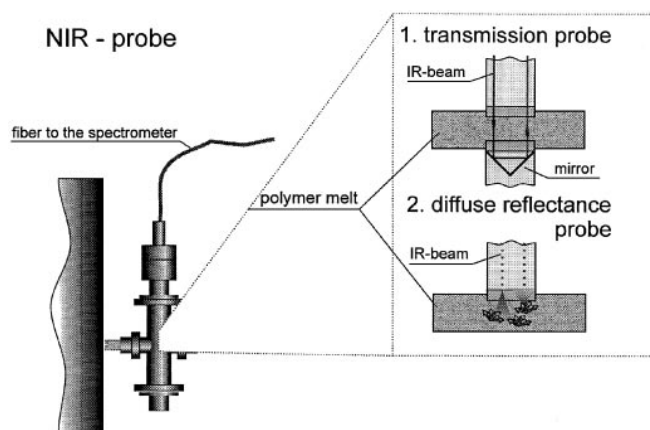
Fig. 1 Adaptation of NIR probes on an extruder (transmission probe and diffuse reflectance probe)

sapphire windows (O.K.Tec, Jena) with variable optical pathlength (1–10 mm). It was directly adapted to the extruding head as shown in Fig. 1. All transmission spectra were recorded automatically every minute with a resolution of 4 cm^{-1} and 64 scans.

The non-transparent polymer system was measured using a diffuse reflectance probe (Bruker, Karlsruhe), which was dipped in the freshly pelletized material collected in small portions under ambient conditions right next to the extruder in a real-time manner. Samples were taken at one minute intervals and the diffuse reflectance spectra were recorded with a resolution of 4 cm^{-1} and 64 scans.

3 Quantitative analysis

Quantitative analyses performed with transmission spectroscopy usually depend upon a linear relationship between band intensity and concentration.

For diffuse reflectance spectroscopy, Kubelka-Munk theory indicates that linear plots of band intensity versus concentration should result when intensities are plotted as the Kubelka-Munk function $F(R) = K/S$, where R is the absolute diffuse reflectance of the sample at infinite depth, K is the absorption coefficient and S is the scattering coefficient.

The use of the Kubelka-Munk equation for quantitative analysis by diffuse reflectance spectroscopy is common for measurements in the visible, mid-IR and far-IR regions of the spectrum, but not in the near-IR region. As has been pointed out in review articles [15, 16], almost all near-IR diffuse reflectance spectra have been converted to log (1/R) (R = reflectance). The use of log (1/R) values instead of the Kubelka-Munk function provide a more linear relationship between reflectance and concentration. Olinger and Griffiths [17] explain this behavior by the effective penetration depth of the beam, which is very short, when the absorption is strong.

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 refractive index of the sample. Therefore, the scattering is not equal over the whole spectrum. This appears as a baseline shift, as a tilt or as a curvature. Therefore, a Multiplicative Scatter Correction [18] was used before starting chemometrics. The MSC eliminates or reduces the difference in light scatter between samples before the calibration. This correction method assumes that the wavelength dependence of light scattering is different from that of the constituent absorbance. So it should be possible to separate the two dependences. This method attempts to remove the effects of scattering by linearization of each spectrum to a so-called ideal spectrum of the sample. All spectra are then corrected using the same ideal spectrum. As there is no way that a spectrum can be collected that perfectly represents all samples, an estimate was used instead. MSC calculates the average spectrum from all the data in the training set and uses it as the ideal spectrum. Then the spectral responses in each spectrum are used to calculate a linear regression against the equal points in the ideal spectrum. The slope value from this regression is ratioed and the offset value from this regression is subtracted from the original training spectrum to give the MSC corrected spectrum ($A = \log(1/R)$):

$$\text{Mean Spectrum}: \quad \overline{A}_j = \sum_{i=1}^{n} A_{i,j}$$

$$\text{Linear Regression}: \ A_j = m_i \, \overline{A} + b_i$$

$$\text{MSC Correction}: \ A_{i\,(MSC)} = (A_i - b_i)/m_i$$

where A is the n by p matrix of training set spectral responses for all wavenumbers; $\overline{A}$ is a 1 by p vector of the average responses of all training set spectra at each wavenumber; $\overline{A}_j$ is a 1 by p vector of the responses for a single spectrum in the training set; n is the number of training spectra; p is the number of wavenumbers in the spectra; m_i is the slope of the linear regression of the mean spectrum vector $\overline{A}$ versus the A_i spectrum vector; and b_i is the offset coefficient of the linear regression of the mean spectrum vector $\overline{A}$ versus the A_i spectrum vector.

By adjusting the slope and offset of the sample spectra to the ideal average spectrum, the chemical information is preserved while the differences between the spectra are minimized. MSC works very well with spectra of samples that are chemically similar.

Chemometrics

A chemometric evaluation of the measured spectra is necessary for fast and reliable quantitative analysis. The methods Principle Component Regression (PCR) and Partial Least Squares (PLS) were used (program PLSPlus [19]). A detailed description and a comparison of the chemometric methods can be found for example in [20–22].

Principle Component Regression (PCR)

The Principal Component Regression method combines Principal Component Analysis spectral decomposition with

Inverse Least Squares regression method to create a quantitative model for complex samples. The PCR method regresses the concentrations on the PCA factors. The eigenvectors of a PCA decomposition represent the spectral variations that are common to all of the spectroscopic calibration data. Therefore, by using that information to calculate a regression, a robust model is created for predicting concentrations of the desired constituents in complex samples. The combination of the concentration equation with the factors equation results in the final PCR model equation:

$$\mathbf{C}(k,n) = \mathbf{B}(f,p)\,\mathbf{A}(n,p)\,\mathbf{F'}(f,p) + \mathbf{E}_C$$

where $\mathbf{C}$ is the matrix of constituent concentrations, $\mathbf{B}$ is the matrix of the regression coefficients, $\mathbf{A}$ is the matrix of spectral absorbances, and $\mathbf{F}$ is the matrix of eigenvectors. The dimensions of the matrices are n for the number of samples (spectra), k for the number of components used for calibration, p for the number of data points (wavenumbers) used for calibration, and f for the number of PCA eigenvectors. The $\mathbf{E}_C$ matrix describes the errors in the model's ability to predict the calibration absorbances and has the same dimension as the $\mathbf{A}$ matrix. In the case of eigenvector analysis, the $\mathbf{E}_C$ matrix is often called the matrix of residual spectra.

Partial Least Squares (PLS)

PLS is a quantitative spectral decomposition technique that is closely related to PCR. However, in PLS, the decomposition is performed in a slightly different fashion. Instead of first decomposing the spectral matrix into a set of eigenvectors and factors, and regressing them against the concentrations as a separate step, PLS actually uses the concentration information during the decomposition process. This causes spectra containing higher constituent concentrations to be weighted more heavily than those with low concentrations. Thus, the eigenvectors and factors calculated using PLS are quite different from those of PCR. The main idea of PLS is to get as much concentration information as possible into the first few loading vectors. This generates two sets of vectors and two sets of corresponding factors; one set for the spectral data, and the other for the constituent concentrations. Presumably, the two sets of factors are related to each other through some type of regression, and a calibration model is constructed. PLS is therefore a one step process. PLS performs the decomposition on both the spectral and concentration data simultaneously. The newly reduced data matrices are then used to calculate the next factor, and the process is repeated until the required number of factors is calculated. The first minimum of a factor is usually the terminating criterion.

4 Results and discussion

Quantification of content of filler in polymers

The system polypropylene (matrix) and pulverized chalk (filler) was analyzed using the diffuse reflectance probe because this material is not transparent. Fig. 2 illustrates the real, time spectra of polypropylene with ascending concentration of pulverized chalk. As there are only slight visual differences in the spectra with different concentrations of pulverized chalk to analyze the system quantitatively, it was necessary to perform chemometric analysis.

A calibration model with 18 samples using three relevant spectral regions (5307–6275, 6838–7505, 7987–8894 cm^{-1})was developed. The PRESS (Prediction Residual Error Sum of Squares) factors are 4 for PCR and 6 for PLS. The SEP (Standard Error of Prediction) values are 0.815% for PCR and 0.935% for PLS. Fig. 3 represents the result of the chemometric analysis. Both methods perform approximately equally and the mean error between
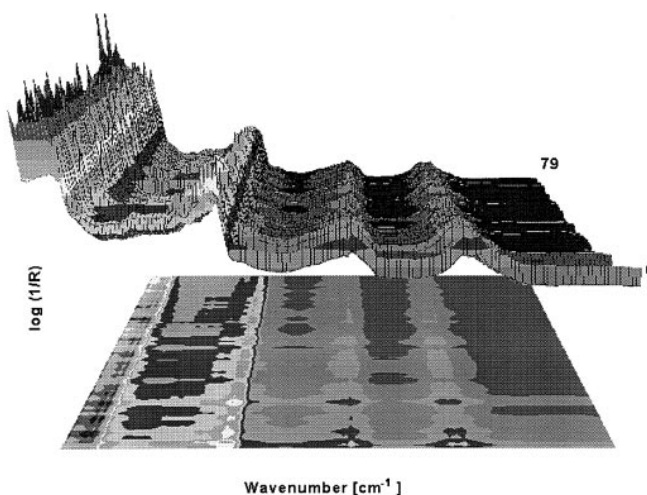

Fig. 2 NIR-spectroscopic scanning and contour plot of pulverized chalk in polypropylene
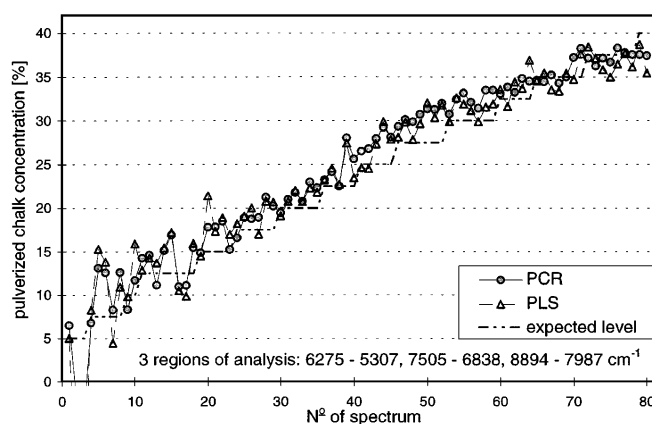

Fig. 3 Chemometric analysis of NIR spectra for the quantification of pulverized chalk in polypropylene
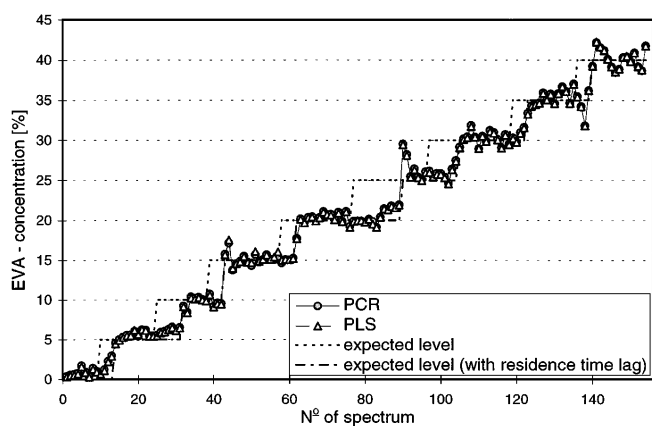
Fig. 4 Chemometric analysis of NIR spectra for the quantification of EVA copolymer in polypropylene

the chemometric values and the expected content of chalk is 3.9% for PLS and 2.7% for PCR.

Quantification of composition in polymer blends

The system polypropylene (matrix) and ethylene vinyl acetate (EVA) copolymer was measured in the melt using the transmission probe. A baseline correction of the measured absorbance spectra was performed before starting the chemometric analysis. A calibration model with 34 samples using the complete spectral range between 4425 and 9000 cm^{-1} was developed. The optimized PRESS factors are 2 for PCR and 2 for PLS. The SEP values are 0.992% for PCR and 0.994% for PLS. Fig. 4 shows the results of the chemometric analysis. There is an excellent agreement between PLS and PCR results and 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 delay in the EVA concentrations in Fig. 4 are traced to residence time lags (6 min) of the polymer blend in the extruder.

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