Determination of additives in polymer pellets by near-infrared spectroscopy

This Application note shows that NIR spectroscopy is an excellent tool for determining low levels of additives in finished polypropylene pellets. This is demonstrated by monitoring the UV stabilizer Tinuvin 770 and the antioxidant Irganox 225. Multiple linear least-squares regression (MLR) models compensate for pathlength variations and interferences in the polymer pellets.

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Method description

Introduction

Additive levels in finished product polymer pellets are measured in order to confirm that required product specifications are met.

Current methods of analysis require the pellets to be pressed into thin films or plaques before spectroscopic analysis. Alternatively, solvent extraction followed by chromatographic analysis may be used. A simpler, more direct, and less manipulative method of analysis is necessary for quality control laboratories.
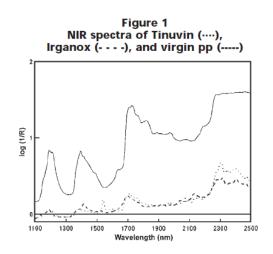
Near-infrared (NIR) spectroscopy has traditionally been used to nondestructively determine percent levels (> 0.1%) of constituents in highly scattering, strongly absorbing matrices, such as polymer pellets. However, through the use of sophisticated multivariate chemometric techniques, useful quantitative information can be more fully extracted from the NIR spectrum. As a result, low levels of additives can be estimated directly in intact polymer pellets. In this study, the levels of Tinuvin 770, a light stabilizer, and Irganox 225, an antioxidant, are determined in polypropylene pellets. Calibration models are derived using multiple linear least squares regression (MLR) analysis.

Experimental

Polypropylene samples (n = 9) having varying levels of Tinuvin 770 (0.05–0.4%) and Irganox 225 (0.1–0.45%) were collected. Seven samples were used for calibration development and two samples were used for validation. Ten replicates of each of the calibration samples were scanned giving 70 calibration spectra. For the validation data, 12 replicates were scanned for the two validation samples giving 24 individual spectra. Samples were analyzed using a NIRSystems Rapid Resin II Analyzer. Since this instrument is not available anymore, the NIRS XDS RapidContent Analyzer or the NIRS DS2500 Analyzer is recommended. The samples were analyzed in reflectance mode from 1100–2500 nm. Samples were simply pured into a hopper designed specifically for polymer pellets. This configuration diminishes the variations caused by nonhomogeneous sample packing and minimizes the within-sample variation.
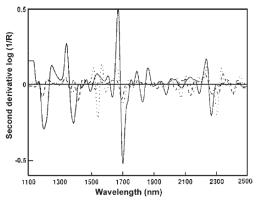
Results and discussion

To identify bands that may be suitable for quantitative purposes, the NIR spectra of Tinuvin 770, Irganox 225, and virgin polypropylene were compared (Figure 1). The baseline variations are due to differences in the scattering properties of the individual pure components and make isolation of unique spectral features difficult.

Figure 1
NIR spectra of Tinuvin (····),
Irganox (- - - -), and virgin pp (-----)

To enhance spectral features and reduce baseline offsets, the second derivative of the log(1/R) data was calculated (Figure 2).

Figure 2
NIR Second-derivative Spectra

In the second derivative spectra, log(1/R) maxima are inverted to peak minima.
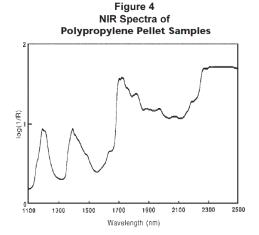
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Bands that may be used for quantitative analysis of Tinuvin 770 (1560 nm) and Irganox 225 (1390 nm) are identified in Figure 3.

Figure 3
Expanded NIR Second-derivative Spectra

Figure 4 shows representative spectra of polypropylene pellets containing various levels of Tinuvin 770 and Irganox 225. The corresponding second derivative spectra are shown in Figure 5. Figure 6 is an expanded view of the 1360 nm to 1600 nm region. Spectral differences can be seen at about 1540 nm deriving from variations in the Tinuvin 770 content.

A multiple linear least-squares (MLR) calibration approach is generally employed when unique spectral features are readily identifiable for major constituents. Although the additive levels are rather low, unique spectral features are readily identifiable. For Tinuvin 770, a two-term quotient model (1512 nm/1354 nm) yields a multiple correlation coefficient (R) of 0.998 and standard error of calibration (SEC) of 75 ppm.
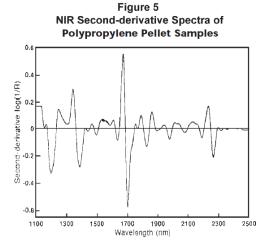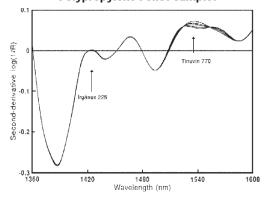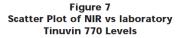
Figure 5
NIR Second-derivative Spectra of Polypropylene Pellet Samples

Figure 4
NIR Spectra of Polypropylene Pellet Samples

Figure 6
Expanded NIR Second-derivative Spectra of Polypropylene Pellet Samples

The weakness of the Irganox 225 band, coupled with its location on the shoulder of the very strong polypropylene band centered at 1400 nm (Figure 3) obscures spectral differences associated with variations in the Irganox 225 level. The variation is more easily seen upon greater expansion.
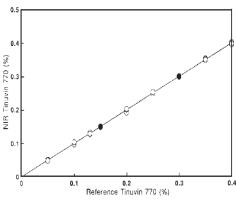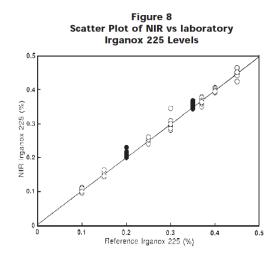
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The Tinuvin (analyte) wavelength (1512 nm) corresponds to a zero-crossover for Irganox 225 and polypropylene (Figure 3). The denominator term, 1354 nm, corrects for subtle differences in pathlength due to pellet shape and size. This wavelength corresponds to the positive side-lobe of polypropylene (Figure 3). Since the polypropylene content can be assumed to be constant, the selection of this wavelength for normalization of pathlength differences is justified. The scatter plot of NIR calculated results vs. laboratory reported results is shown in Figure 7.

Figure 7
Scatter Plot of NIR vs laboratory
Tinuvin 770 Levels

Figure 8
Scatter Plot of NIR vs laboratory
Irganox 225 Levels

Conclusions

This study demonstrates that NIR spectroscopy can be used to monitor low levels of additives in intact polypropylene pellets. Multilinear regression models were developed to account for pathlength variations and interferences in the polymer pellets.

For Irganox 225, the predominant source of error in the NIR assay is not due to effective pathlength differences but is due to the spectral interference from polypropylene (Figure 3). Therefore a two-term linear summation equation (1412 nm + 1352 nm) was derived that provides an R of 0.998 and SEC of 150 ppm. 1412 nm corresponds to the previously identified Irganox 225 band (Figure 3) and 1352 nm is the same side-lobe of the strong polypropylene band previously discussed. The scatter plot of NIR calculated results vs. laboratory reported results is shown in Figure 8.

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