



Application Note AN N517

Analysis of Polyethylene Density

The density of polyethylene is one of the key performance criteria used by suppliers and customers to determine.

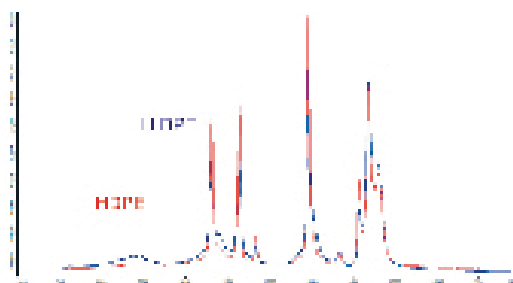
Resin suppliers typically use a density gradient column or a densimeter for this analysis. Both methods are generally slow, labor intensive and require samples to be collected and transported to the lab for measurement. With the trend to larger operation facilities, which produce more polymer per hour, a faster and less laborious method of determining the density of the polymer is needed.

Raman spectrometry offers the possibility of rapid determination of the density of polyethylene pellets or powder off-line in the Quality Lab by the lab tester, at-line by the production operator or actually on-line in the process itself.

Experimental

A Bruker Optics SENTINEL Raman spectrometer with a 500 mW 785 nm diode laser, 785 nm Unilab Raman probe, Rotating Stage, OPUS acquisition and chemometric software as well as OPUS Process software were used to obtain the spectra and build the calibration models. Samples of polyethylene pellets were obtained from a major polyethylene manufacturer.

Figure 1

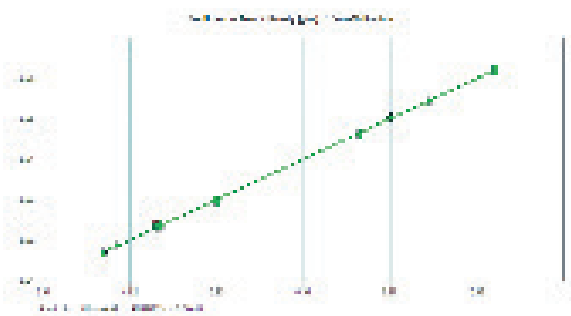


The Raman spectrum of a linear low-density and a high-density polyethylene.

Results and Discussion

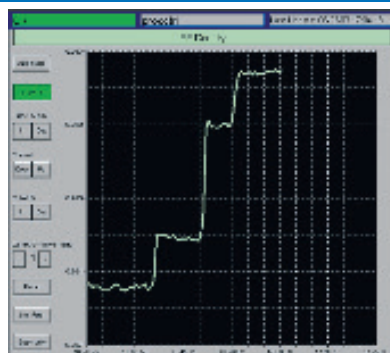
The Raman peak at 1416 Rcm^{-1} is indicative of the crystalline region of polyethylene and is much more intense in the spectrum of the high density (HDPE), $d = 0.9620 \text{ g/cc}$, sample than in the Linear Low Density Polyethylene (LLDPE), $d = 0.9170 \text{ g/cc}$, sample. The spectral peaks of the amorphous bands of polyethylene in the 886, 1082 and 1310 Rcm^{-1} regions are more pronounced in the LLDPE sample and the peak at 1416 Rcm^{-1} is lower in intensity than in the HDPE sample. Thus, the Raman spectrum is directly responsive to the semi-crystalline morphology of polyethylene.

Figure 2



Polyethylene Density Chemometric Calibration Model R2: 99.92 with RMSECV: 0.0004

Figure 3



High Power Sentinel, Unilab Probe and Rotating Stage Bruker OPUS Process Control Software

Figure 2 shows the results of the calibration model. Eight samples of polyethylene pellets across the density range of 0.9170 to 0.9620 g/cc were used for this study. The partial least squares calibration model used the spectral range 662 – 1596 cm^{-1} . Parameters of the model were Vector Normalization, Cross Validation and Mean Centering. Five spectra of each sample were included in the model. The Regression coefficient obtained was 99.92 with a Root Mean Square of Cross Validation of 0.0004 g/cc.

By use of the above model, OPUS Process software was used to monitor the density of polyethylene pellets. Figure 3 illustrates the results of the OPUS Process software, where samples of pellets in the density range of 0.918 – 0.962 g/cc were monitored. Because of the Bruker Optics Sure_Cal feature, the method was easily transformed to a second spectrometer.

Conclusion

These results show the SENTINEL can be used in the Quality Assurance laboratory with polyethylene pellets. The same Sentinel spectrometer can be coupled with a probe by means of fiber optics to provide at-line density analysis of pellets or powder. The Sentinel could be connected directly to a probe in the process to provide more continuous on-line density values.

● Bruker Scientific LLC

Billerica, MA · USA
Phone +1 (978) 439-9899
info.bopt.us@bruker.com

www.bruker.com/optics

Bruker Optics GmbH & Co. KG

Ettlingen · Germany
Phone +49 (7243) 504-2000
info.bopt.de@bruker.com

Bruker Shanghai Ltd.

Shanghai · China
Tel.: +86 21 51720-890
info.bopt.cn@bruker.com