Quantitative analysis of copolymers using the Cary 630 FTIR spectrometer

Application note

Materials testing and research

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Introduction

FTIR spectrometers employing attenuated total reflectance (ATR) sampling interfaces are a proven and powerful tool for the analysis of polymeric materials. Because of its unique combination of features and class-leading performance, the new Agilent Cary 630 FTIR spectrometer makes quantitative analysis of polymers especially fast and easy.

In this application note, the amount of key components in two important copolymeric materials are measured — the styrene content in styrene butadiene rubber (SBR) and the ratio of polyethylene to vinyl acetate in polyethylene vinyl acetate (PEVA) polymer. The Cary 630 FTIR equipped with its single reflection Diamond ATR sampling accessory (Figure 1) is used for these measurements.

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Figure 1. Agilent Cary 630 FTIR spectrometer equipped with single reflection Diamond ATR sampling accessory

Styrene concentration in SBR polymer

Styrene butadiene rubber (SBR) is the most common synthetic rubber material and its main use is in the manufacture of tires, which accounts for nearly 70% of its production. The properties of SBR rubber can be altered by varying the ratio of styrene to butadiene monomers in the manufacturing process. The normal ratio is 3:1 butadiene to styrene (25% styrene). Higher styrene concentrations make the material harder, but less elastic. Most performance industries, such as racing tires and specialty military applications, are requiring more consistent SBR product, which drives the need for better quality assurance and control by both end users and manufacturers.

The measurement of a polymer sample by the Cary 630 FTIR equipped with an ATR accessory is extremely straightforward. The polymer material is placed on the diamond crystal and the sample pressure press is rotated downward until adequate pressure is placed on the sample to observe a spectrum in the Cary 630's real-time analysis MicroLab FTIR software (Figure 2). The real-time analysis mode provides instantaneous spectral update and makes it easy for even novice users to get highly repeatable results. The sample press on the Cary 630 is designed so that it cannot be over-tightened, thus protecting the diamond crystal against over-pressure.
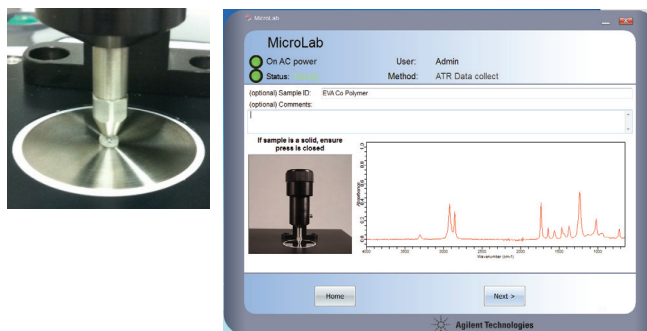

Figure 2. Polymer is placed directly on ATR sampling accessory. Uniform, constant pressure is provided by the sample press, ensuring that high quality spectra are obtained. Real-time analysis software provides an immediate indicator of spectral quality

To develop a quantitative FTIR method, four commercial SBR calibration standards, with polystyrene concentrations of 0%, 5%, 23%, and 45%, were measured in triplicate using the Cary 630 FTIR. The spectra reveal the expected polystyrene (PS) absorbance bands (Figure 3) at 699 cm^{-1}, 759 cm^{-1}, and a weaker band at 1031 cm^{-1}. Spectral bands at 911 cm^{-1}, 964 cm^{-1}, and 995 cm^{-1} arise from unsaturations (*vinyl* and *trans* CH wag) in polybutadiene, which decrease as the PS bands increase. The exception is the pure polybutadiene, which has far more *cis* unsaturations relative to the other polymers, since it is not cross-linked and in liquid form. The PS absorbance bands appear to follow Beer's Law by increasing proportionately with concentration, and therefore are excellent candidates for quantitative analysis.

The plot of the peak height absorbance for the strongest IR band of PS at 699 cm^{-1} as a function of concentration indicates great linearity and a strong correlation coefficient of R^2=0.999 in the calibration (Figure 4). Using the linear regression slope and offset from this calibration, a method is added to the MicroLab FTIR software that enables the polystyrene percentage in an unknown sample to be automatically displayed. The limit of detection for the quantitative analysis of PS in SBR is 0.09%, calculated as three times the standard deviation of the 0% replicate data (StDev= 0.03% PS).
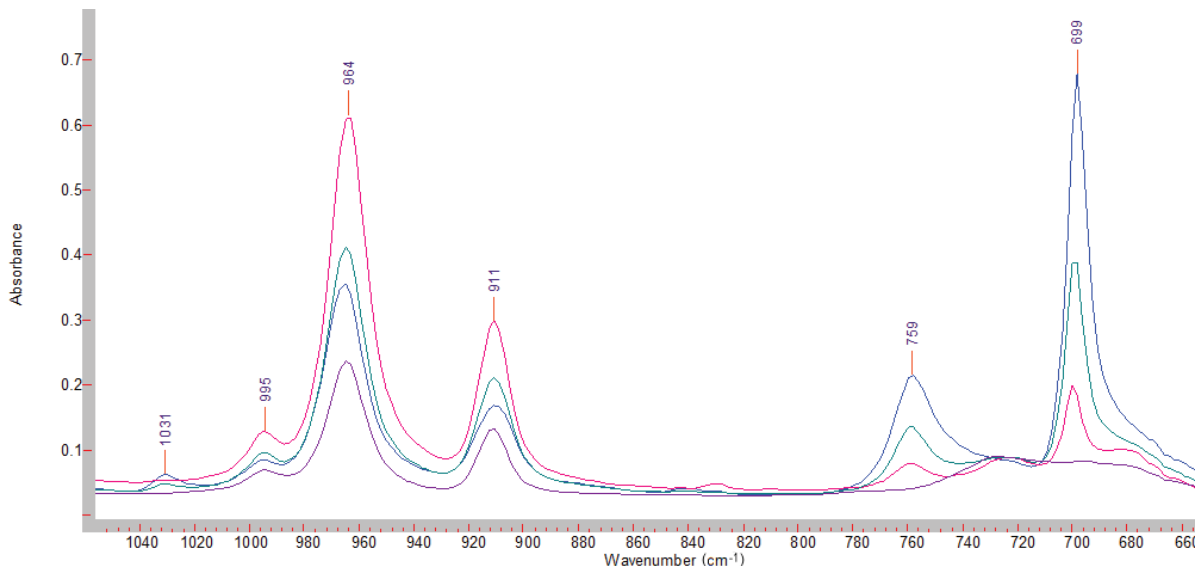
Figure 3. The FTIR spectra of four SBR rubber standards with increasing polystyrene concentrations: 0% (purple), 5% (red), 23% (green), and 45% (blue)
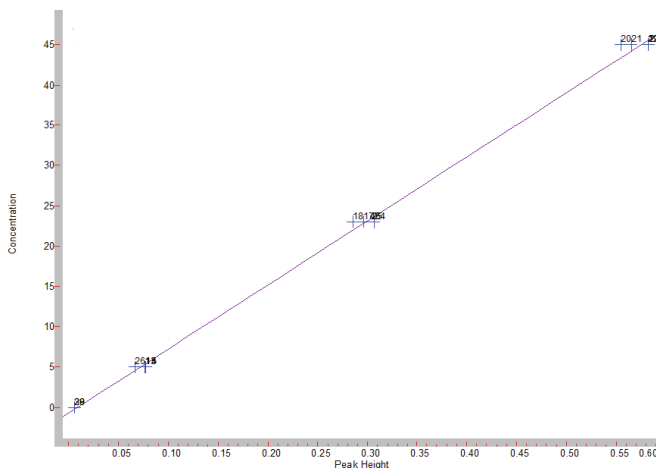
Figure 4. FTIR calibration curve for polystyrene in SBR rubber using the 699 cm^{-1} peak height absorbance; R^2=0.999.

## Ratio of polyethylene to vinyl acetate in PEVA

Polyethylene vinyl acetate (PEVA) is very common in everyday products used in the home, sports equipment, industrial and medical applications. In the latter applications, medicines can be mixed in solution with PEVA and then the mixture dried to produce biologically-inert, slow-release plastic implants and transdermal patches.

Since the ratio of polyethylene (PE) to vinyl acetate (VA) in PEVA can affect the physical properties of the final product, it is important for manufacturers to have a fast, easy measurement procedure for these components. As in the previous example, the Cary 630 FTIR spectrometer with single reflection diamond ATR is ideal for this measurement.

In this example, seven commercially-available standards of PEVA were measured with the Cary 630 FTIR system. The calibration standards used were:

- Polyethylene, low density (0% vinyl acetate)

- Ethylene/vinyl acetate copolymer #506 (9 wt% vinyl acetate)

- Ethylene/vinyl acetate copolymer #243 (14 wt% vinyl acetate)

- Ethylene/vinyl acetate copolymer #244 (18 wt% vinyl acetate)

- Ethylene/vinyl acetate copolymer #245 (25 wt% vinyl acetate)

- Ethylene/vinyl acetate copolymer #316 (28 wt% vinyl acetate)

- Ethylene/vinyl acetate copolymer #326 (40 wt% vinyl acetate)

3

The calibration samples were measured with one minute collection times, at a resolution of 4 cm^{-1}. The FTIR spectra exhibit strong acetate ester carbonyl bands at 1737 cm^{-1} and an ester C-O stretch band at 1236 cm^{-1} (Figure 5) arising from polyvinyl acetate (VA). Both of these bands are ideal for quantitative analysis of the VA in the polyethylene (PE) matrix. The characteristic PE absorbance bands are located at 2921cm^{-1}, 2852 cm^{-1}, 1467 cm^{-1} and 720 cm^{-1}. The best calibration is obtained by a peak area ratio of the 1236 cm^{-1} VA absorbance band ratioed to the PE absorbance at 1467 cm^{-1}. This IR absorbance ratio technique corrects for random variables that may affect the measurement, such as contact pressure or contact area of the polymers on the ATR diamond crystal. This is important since reliable ATR measurements require the sample to make good optical contact with the diamond, and hard, round polymer beads may not contact the whole diamond surface.
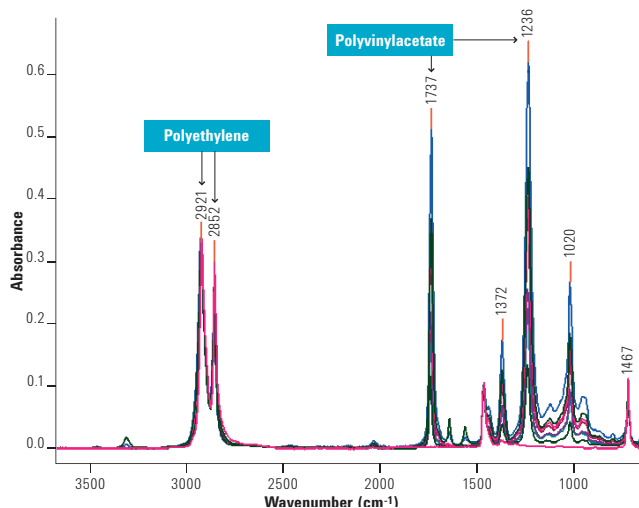

Figure 5. Spectral overlay of the calibration standards for polyethylene vinyl acetate). The spectra are all scaled to the polyethylene absorbance. The blue spectrum is 40 wt% VA, and the red spectrum is 0% VA

The resulting linear regression calibration curve from the above peak area ratio is excellent (Figure 6) with a correlation coefficient of $R^2 = 0.999$. The slope and offset for the linear regression is easily inserted into the MicroLab FTIR method editor (Figure 6), and the resultant method is now permanently calibrated. To test the robustness of the method, validation standards

were made by diluting (by weight) the 9% VA with the pure PE (0% VA) standards to make 1% and 0.55% VA samples. The polymer validation samples were then dissolved in toluene and heated to 75 °C until all the polymer dissolved. The toluene mixtures were then cast as thin films onto aluminum foil over a 60 °C hotplate and allowed to dry. The resulting polymer validation samples were then measured with the stored method. These validation samples were measured with a much shorter scan time (5 seconds) than the calibration set of spectra (60 seconds). This allows for multiple measurements of incoming raw materials in a very short time; this fast sample analysis is important for quality assurance and quality control (QA/QC) analysis. The speed of this analysis is also a benefit for incoming raw materials analysis in which a batch of PEVA can have some uniformity differences, requiring sampling from multiple areas of the container or on a molded part. The results of this fast analysis (5 second) yield exceptional repeatability and accuracy (Table 1) on the validation samples. A standard deviation of nominally 0.01% VA was obtained with limits of detection (LOD) and limits of quantitation (LOQ) of 0.03 wt% VA and 0.10 wt% VA, respectively. When a sample is run using this calibrated FTIR method, the results can also be displayed in color-coded format (Figure 7), indicating that the sample is in-spec (green), marginal (yellow), or out of spec (red). This enables an operator to get a rapid, visual indicator of the quality of the material.

Table 1. VA prediction values from the calibrated VA FTIR method for validation standards at 0.55% VA and 1.00% vinyl acetate in polyethylene. These validation samples were run with only 5 second collection times

Validation sample	0.55% VA	1.00% VA
Rep 1	0.53	0.97
Rep 2	0.54	0.96
Rep 3	0.55	0.96
Rep 4	0.56	0.96
Rep 5	0.55	0.99
Standard deviation	0.0114	0.0130
Average	0.55	0.97
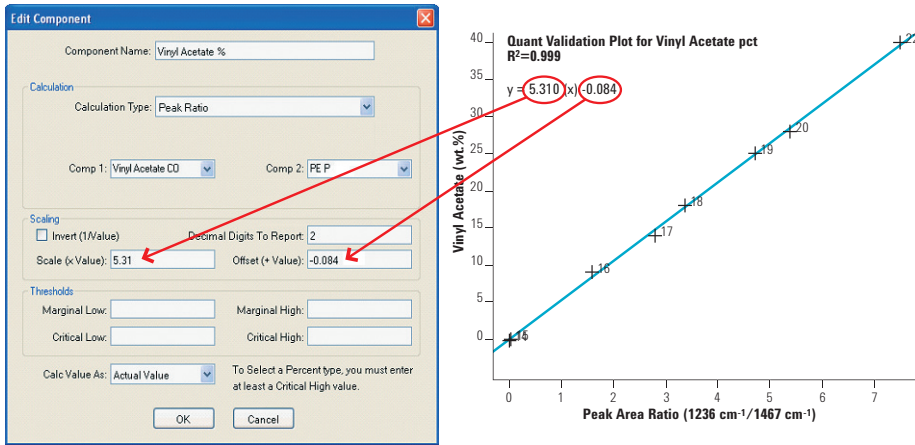
Figure 6. The method editor in the MicroLab FTIR software and the
calibration plot for VA in PE
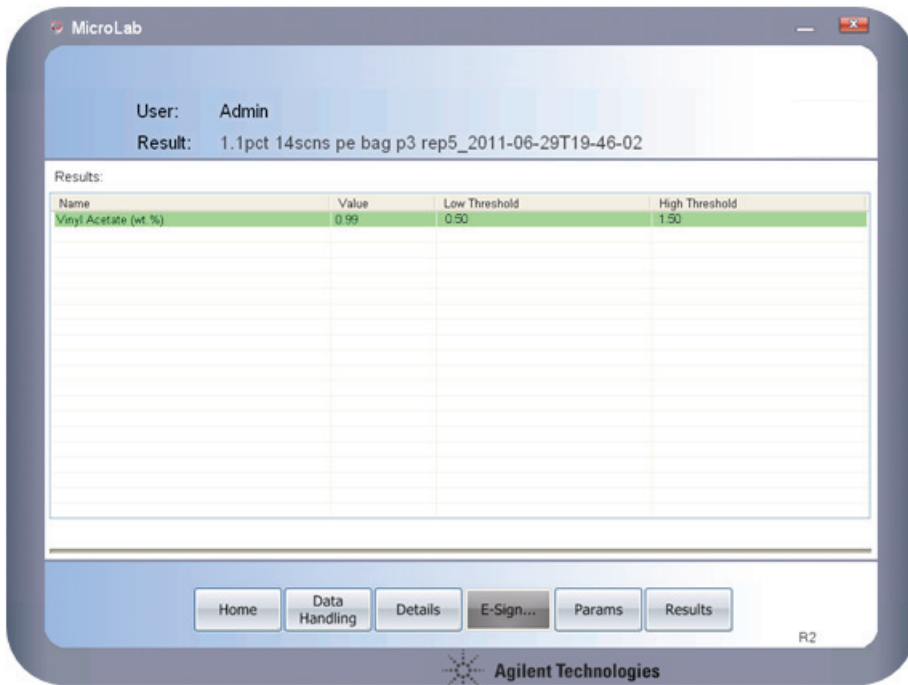
Figure 7. The result for the 1% VA validation standard — green color
indicates an in-spec sample

Conclusion

The Agilent Cary 630 FTIR equipped with ATR sampling technology is an exceedingly effective spectrometer for analyzing copolymer blends. The combination of its compact size, sampling technology, performance, speed of analysis, and intuitive software enables quantitative methods for polymers to be rapidly developed and deployed in quality assurance and quality control applications. The measurement of both SBR and PEVA copolymers yields highly linear calibrations with excellent quantitative accuracy and reproducibility.

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