Determination of percent ethylene in ethylene-propylene statistical copolymers

Analytical method

Polymers

Authors

Dr. Wayne Collins*, John Seelenbinder† and Frank Higgins†

Agilent Technologies
* Wilmington, DE, USA
† Danbury, CT, USA

Scope

This method is for the determination of the statistical or randomly distributed ethylene content of ethylene-propylene copolymers. The determination is specific for ethylene and cannot be applied for the quantitation of other comonomers. The method has been validated over the range of 0.3 to 3.5% statistical content and can be used for either powder or pellet samples. Certain sorbitol-based clarifiers have been found to interfere with the determination and therefore a correction factor is necessary for resins containing these additives. This method is generally not recommended for quantitation of ethylene in filled or pigmented resins.

Summary

This method describes a procedure for measuring the statistical ethylene contents in ethylene-propylene statistical copolymers. The procedure utilizes an absorption band at 733 cm^{-1} associated with statistically distributed ethylene for a Beer's Law type calculation.

An analytically representative sample of the copolymer resin is molded into a film of thickness between 0.5 and 0.7 mm. Molding conditions are not important to the results obtained by this method, as long as the resin is not subjected to temperatures of more than 250 °C for more than 2 to 3 minutes, and the films have a smooth, consistent surface. The sample is placed in the infrared spectrometer and the spectrum is obtained at a resolution of 4 wavenumbers or better. Using the Agilent DialPath or TumblIR accessories, the film or coupon can be inserted into the infrared beam path between the top and bottom crystals (Figure 1). Both these accessories are unique to Agilent and provide a revolutionary new way to measure thin polymer films or liquids. The horizontal mounting provides a simple, fast and reproducible mechanism to mount the sample by simply laying it down flat and rotating the crystal into position, eliminating errors and providing accurate and reliable answers — fast! The peak height of the absorbance band at 733 cm^{-1} is determined relative to a baseline drawn between 759 and 703 cm^{-1}. This value is divided by the peak height of the absorbance band at 1044 cm^{-1} relative to a baseline drawn between 1068 and 949 cm^{-1} to give the normalized absorbance at each wavenumber. The random ethylene concentrations can then be determined by comparing these values with a linear regression equation of normalized absorbance versus ethylene content for a set of standards of known ethylene content as determined by C^{13} nuclear magnetic resonance spectroscopy (NMR), which is a primary analytical technique. At least three separate films are analyzed and averaged for each sample analyzed.

Figure 1. The Agilent DialPath transmission cell used for polymer analysis of coupons or films

Apparatus

- Data is obtained using an Agilent Cary 630 FTIR spectrometer equipped with a DialPath or TumblIR sample interface with a 1000 µm path length. Equivalent FTIR spectrometers, such as the mobile or portable Agilent 5500/4500 Series FTIR, can also be used.
- Hydraulic press — with heated platens capable of maintaining 200 °C and a ram force of 25,000 pounds.
- Chase mold — to control thickness (optional).
- Aluminum sheet — 0.05–0.18 mm thick.

Calibration

Standards are prepared by measuring the statistical ethylene content of a series of copolymers covering the desired range using by NMR, which is a primary analytical technique. To perform the calibration, prepare and analyze at least three films for each standard resin in accordance with the requirements of this method. All absorbance values should be less than 1.6 units. Perform a linear least squares regression of the concentration of the analyte versus normalized absorbance using all data points; do not include the

origin as a data point. Divide the peak height of the statistical ethylene absorbance band by the peak height of the reference polypropylene absorbance band to normalize the result. The calibration equation obtained for the standards used in this study is:

$$\% \text{ Stat. ethylene} = M \times (A_{733}/A_{1044}) + N$$

Where:

% Stat. ethylene	= Weight % of statistically distritubed ethylene incorporated into the copolymer
A_{733}	= Peak height of absorbance band of statistical ethylene band at 733 cm^{-1}
A_{1044}	= Peak height of absorbance band of polypropylene reference at 1044 cm^{-1}
M	= Calibration constant
N	= Intercept

The calibration curve for the determination of statistical ethylene in ethylene-propylene copolymers for the standards used in this study is shown in Figure 2.

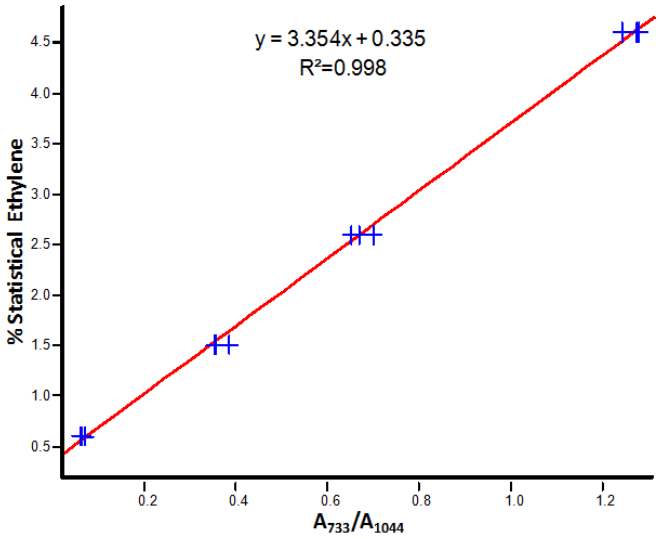

Figure 2. Calibration curve for % statistical ethylene in polypropylene

Procedure

Sample preparation

Obtain a representative sample of the resin to be analyzed; statistical sampling techniques are recommended (cone and quarter technique, chute splitter, rotary splitter, roto-riffler, and so forth). Molding conditions are not important to the results obtained by this method, as long as the resin is not subjected to temperatures of more than 250 °C for more than 2 to 3 minutes. A typical technique for preparation of these films is as follows:

Place the chase mold on a sheet of aluminum and slightly overfill each cavity in the chase with the resin. Another sheet of aluminum is placed on top and the stack is carefully placed in the press with the platens heated to 200 °C. The press is closed to apply minimal force for 1 or 2 minutes while the sample melts. The force is increased to at least 25,000 pounds, held for approximately 30 seconds and released. The stack is then removed from the press and allowed to cool on the benchtop or in a cold press. The aluminum sheet is stripped from the chase and the films are pushed from the cavities and trimmed to remove the flash.

Once the samples are prepared, each sample is examined for surface defects and checked to ensure that the thickness is between 0.5 and 0.7 mm. Samples with defects or thickness outside of the range are discarded; at least three suitable films are required for the analysis.

Operating conditions

The infrared spectrometer should be turned on for at least 15 minutes prior to analysis. The resolution should be set to at least 4 wavenumbers.

Collect for a minimum of 30 seconds (74 scans) for each of the triplicate film samples.

Method configuration

To determine the statistical ethylene concentration, measure the peak height absorbance for statistical ethylene at 733 cm^{-1}, measured by a vertical intersecting line to a baseline drawn between 759 and 703 cm^{-1}. The specified peak height and baseline points can easily be set in an Agilent MicroLab PC FTIR software method. Each peak measurement is called a component and the baseline limits are easily set as shown in Figure 3. The peak type of 'Peak Height with Duel Baseline' is first set. Then parameters for measurement of the peak height polypropylene absorbance band at 1044 cm^{-1} relative to a baseline drawn between 1068 and 949 cm^{-1} (Figure 4) are set. The 'Peak Stop' field is left blank for peak height measurements. The component is further configured to report the absorbance value to five decimal places as shown in Figures 3 and 4.

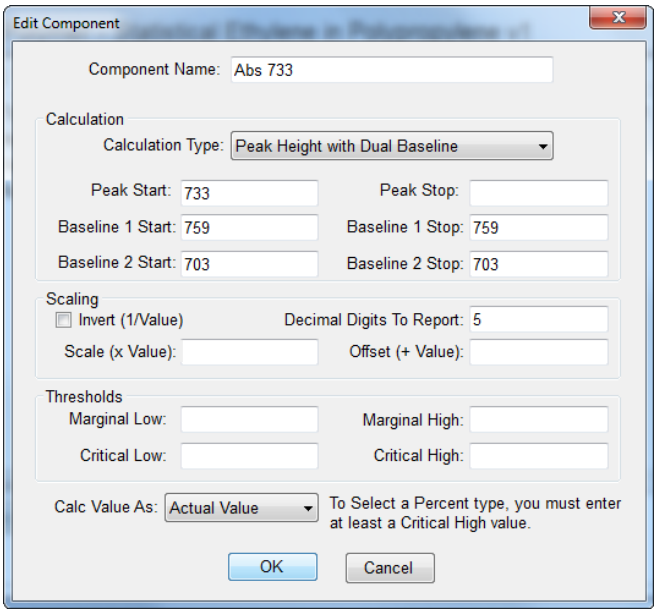

Figure 3. The statistical ethylene peak height absorbance (component) measurement at 733 cm^{-1} in the MicroLab PC FTIR software. The peak start refers to the peak maxima position from which the peak height is measured. Single point baselines should be set up with the same baseline start and stop points.

A ratio of the analyte band absorbance to the reference band is used for this analysis.

$$\% C_2 \text{ (stat.)} = M_s \times (A_{733}/A_{1044}) + N$$

with M and N as determined in the the Calibration section.

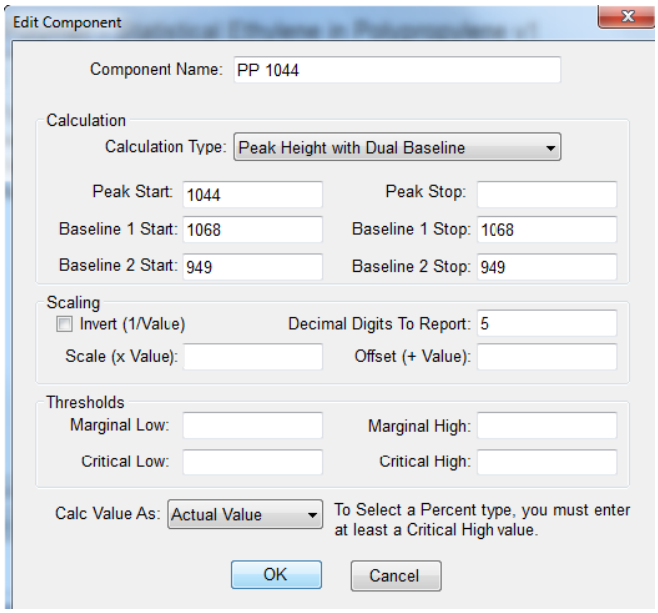

Figure 4. The polypropylene reference peak component addition in the MicroLab PC FTIR software

The MicroLab PC FTIR software makes the peak ratio calculation easy to set up. Simply edit the method by selecting the 'Peak Ratio' calculation type and the peak components that are to be ratioed (Figure 5).

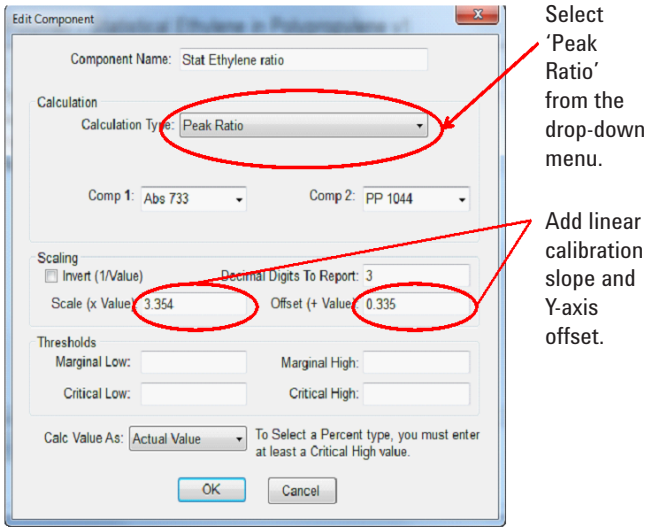

Figure 5. The peak ratio component addition in the MicroLab PC FTIR software. After plotting the calibration data, the resulting linear regression line's slope is entered in the 'Scale' field and the Y-axis offset in the 'Offset' field.

Analysis

The specimen is placed in the sample compartment and the spectrum is recorded; a typical spectrum is shown in Figure 6. The presence of an absorption band at 695 cm^{-1} suggests that the resin contains a sorbitol-based clarifier that can interfere with the statistical ethylene measurement at 733 cm^{-1}. If the presence of this clarifier is confirmed, the statistical ethylene measurement must be corrected to compensate for the absorbance of the clarifier. Certain anti-acid additives can also have an effect on the measurement but are usually ignored since these compounds are present at very low concentrations.

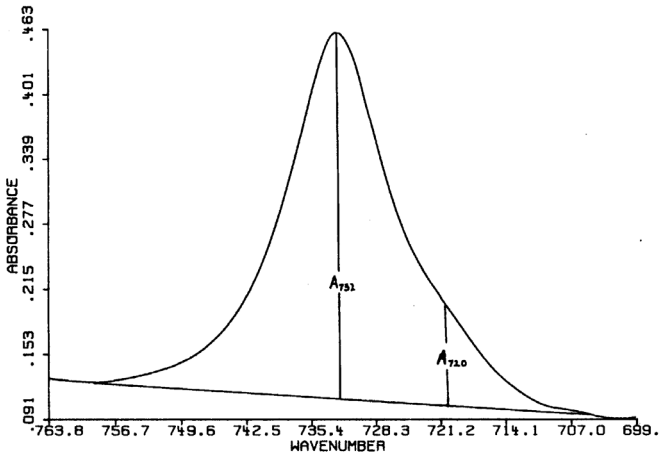

Figure 6. Typical absorption bands for statistical and block ethylene

With the ratio defined from the Method Configuration section, the new method is ready to be used to obtain at least triplicate measurements of each calibration standard. Unknown polymer coupons should also be run with a minimum of three measurements around the coupon. This process is made simple and convenient with the DialPath or TumblIR transmission cells. Users can see the exact point of measurement in real time, and quickly reposition the sample for the replicate measurements.

Plot the values measured for the ratio relative to the statistical ethylene concentration (Figure 2), and insert the slope and offset values back into the method as shown in Figure 5. Once the slope and offset values have been entered, the MicroLab PC FTIR software method will report the statistical ethylene concentration.

The MicroLab PC method, Polymer – Statistical Ethylene in Polypropylene v1, includes the calibration data from Figure 2. This calibrated method is available with the Agilent 5500 and 4500 Series DialPath or TumblIR FTIR spectrometers, as well as the Cary 630 FTIR spectrometers. This method and software performs all the calculations automatically and reports the final value as % statistical ethylene (Figure 7).

The values obtained from triplicate determinations should be averaged to give the final reported concentration.

Conclusion

This analytical method demonstrates how the Agilent Cary 630 FTIR can be used to easily and accurately measure polymer thin films. The unique sampling capabilities of the DialPath and TumblIR provide a simple mechanism to mount your sample, while the step-by-step method-driven software with color-coded, actionable results guides you through your analysis to ensure that your samples are measured with minimum effort and highest accuracy.

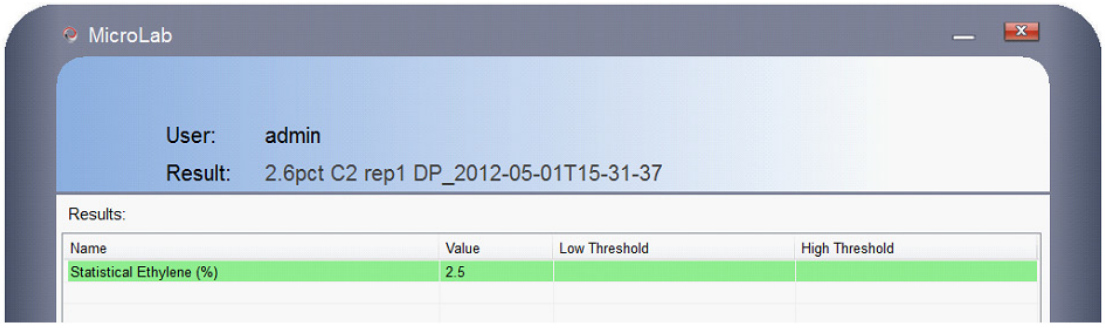

Figure 7. The MicroLab PC software prediction result for a 2.6% statistical ethylene in polypropylene sample

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