Determination of the vinyl content of polyethylene resins

Analytical method

Polymers

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Scope

This method is for the determination of the number of vinyl groups (C=C) in polyethylene resins by infrared spectroscopy. The test is used primarily for resins made with chromium catalyst technology, which gives a vinyl group at the end of each polymer chain, rather than resins made with titanium-based catalysts, which have few unsaturation sites. The method is applicable to powder, pellets or pieces cut from finished parts, but cannot be used for filled or pigmented samples.

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Summary

This method determines the number of sites of unsaturation per 1000 carbon atoms by relating the intensity of the infrared absorption vinyl band at 908 cm^{-1} to a calibration curve for standards derived from nuclear magnetic resonance (NMR) measurements, which is the primary measurement technique.

An analytically representative sample of the polyethylene resin is molded into a film with a thickness of 0.4 to 0.5 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 film is placed in the infrared spectrometer and the spectrum is obtained at 2 wavenumber resolution. Using the Agilent DialPath or TumbIIR 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 absorbance of the band at 908 cm^{-1} is measured and corrected to a baseline drawn between 950 and 875 cm^{-1}. This absorbance value is divided by the absorbance of a reference band at 2019 cm^{-1} relative to a baseline drawn between 1981 and 2108 cm^{-1}. Substitution of this ratio into the linear regression calibration equation derived from similar measurements on the standards gives the vinyl content in units of number of vinyl groups per 1000 carbon atoms. The vinyl content of a polyethylene sample is primarily determined by the catalyst used to manufacture the resin. Generally, resins made with a chromium catalyst will have significant vinyl content, greater than 0.5 vinyls/1000 carbon atoms, while resins from titanium catalysts typically have low vinyl content, less than 0.5 vinyls/1000 carbon atoms.

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 TumbIIR 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

To perform the calibration, a spectrum is obtained for three films prepared from each standard resin. Determine the area of the analytical absorbance band relative to the baseline at 908 cm^{-1} and the area of the reference band at 2019 cm^{-1} following the same procedure as for samples described in this method. All absorbance values should be less than 1.6 units. Perform a linear least squares regression of the known vinyl content versus the ratio A_{908}/A_{2019} using all data points; do not include the origin as a data point.

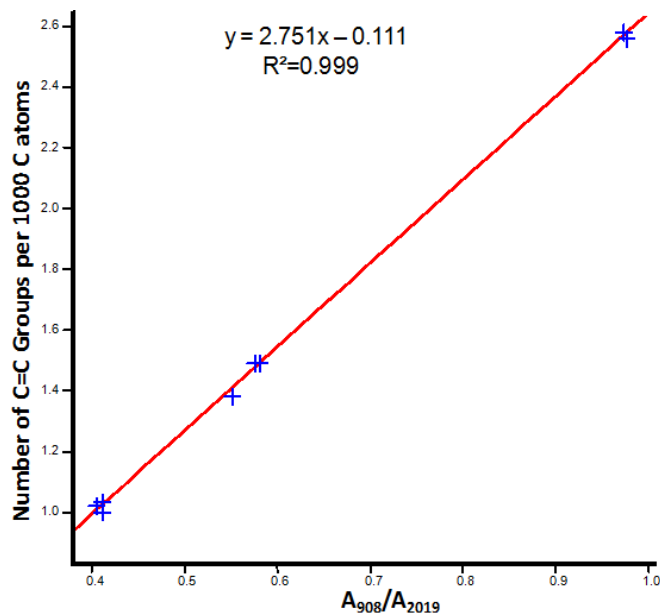The calibration curve and equation obtained for this method is shown in Figure 2.

$$y = 2.751x - 0.111$$
$$R^2 = 0.999$$

Figure 2. Calibration curve for the number of vinyl C=C groups per 1000 C atoms in polyethylene. The correlation coefficient, R^2, was 0.999 and the 95% confidence interval was ±0.1 C=C per 1000 C atoms.

Vinyl C=C groups per 1000 C atoms = M x (A_{908} / $_{2019}$) + N

Where:

Vinyl C=C groups per 1000 C atoms	= Vinyl C=C groups per 1000 C atoms in the polyethylene
A_{908}	= Peak area absorbance of vinyl group at 908 cm^{-1}
A_{2019}	= Absorbance of polyethylene reference band at 2019 cm^{-1}
M	= Calibration constant
N	= Intercept

The vinyl content of each standard is typically determined by multiple analyses by C^{13} NMR spectroscopy.

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 exposed to temperatures of more than 250 °C for more than 2 to 3 minutes. A typical preparation technique 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 hydraulic 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 0.4 and 0.5 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 and allowed to stabilize for at least 15 minutes prior to analysis. The resolution should be set to 2 wavenumbers or better.

Collect for a minimum of 30 seconds (37 scans) for each of the triplicate film samples.

Method configuration

To determine the vinyl concentration, measure the area under the absorbance band for the vinyl CH wag group at 908 cm^{-1} relative to a baseline drawn between 926 and 898 cm^{-1}. A typical spectrum is shown in Figure 3. The specified peak areas 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 4. The peak type of 'Peak Area with Duel Baseline' is first set. Then parameters for measurement of the area under the reference polyethylene absorbance band at 2019 cm^{-1} relative to a baseline drawn between 2097 and 1987 cm^{-1} (Figure 5) are set. The component is further configured to report the absorbance value to five decimal places as shown in Figures 4 and 5.
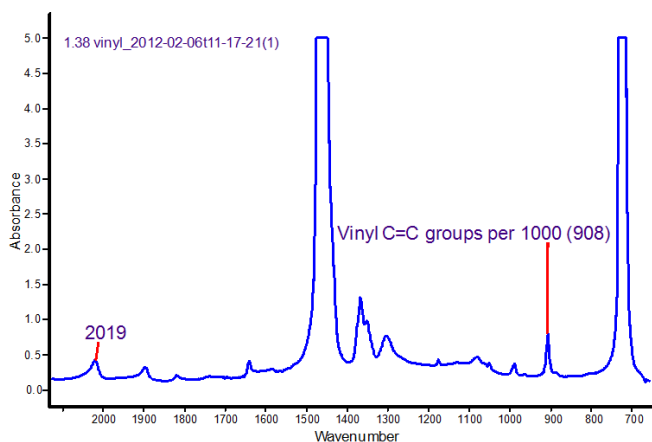

Figure 3. Typical spectrum for the measurement of the vinyl group (CH wag) in polyethylene

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

Number C=C per 1000 C atoms = M x [A_{908} / A_{2019}] + N

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

The ratio calibration equation for this analysis is:

Number C=C per 1000 C atoms = 2.751 x [A_{908} / A_{2019}] − 0.111

Figure 4. The vinyl peak area absorbance (component) measurement at 908 cm^{-1} in the MicroLab PC FTIR software. The peak start and stop refers to the area under the peak to be integrated. Single point baselines should be set up with the same baseline start and stop points

Figure 5. The polyethylene 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 6).
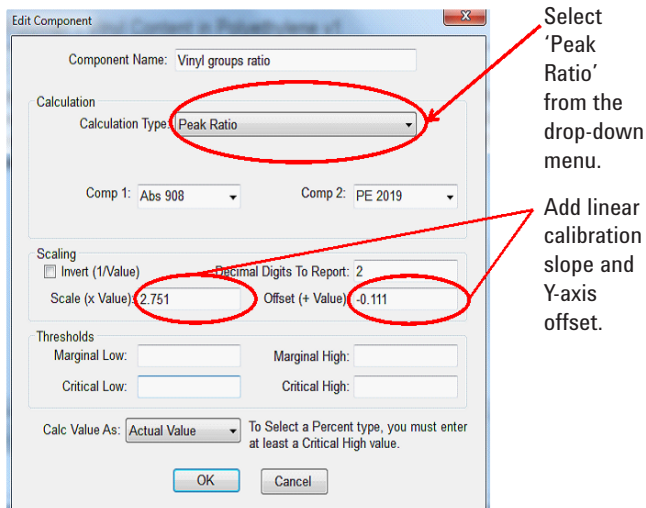
Select 'Peak Ratio' from the drop-down menu.

Add linear calibration slope and Y-axis offset.

Figure 6. 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

With the ratio defined, 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 vinyl group concentration (Figure 2), and insert the slope and offset values back into the method as shown in Figure 6. Once the slope and offset values have been entered, the Microlab FTIR software method will report the vinyl group concentration.

The MicroLab PC FTIR software method, Polymer – Vinyl Content in Polyethylene 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 Number C=C per 1000 C Atoms (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.
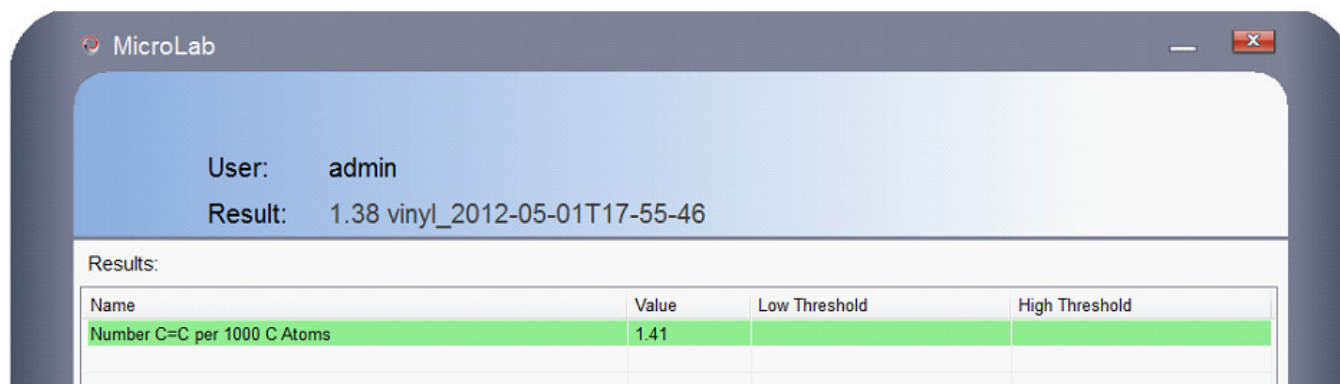

Figure 7. The MicroLab PC FTIR software prediction result for a 1.38 vinyl C=C groups per 1000 C atoms in polyethylene sample

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