Determination of percent glycerol monostearate in polypropylene by infrared spectroscopy

Analytical method

Polymers

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Scope

This method is for the determination of the glycerol monostearate (GMS) content and chemically identical antistatic additives in polypropylene where the additive package is known. The method utilizes a characteristic ester carbonyl band associated with the additive that is common in many other additives. Therefore, the total additive package must be known to confirm that other additives present do not contain bands that would interfere with the measurement. The method is typically used for process control of additive addition and is not recommended for filled or pigmented resins. The method has been validated over the range of 0.05 to 0.8% GMS content and can be used for either powder or pellet samples. Certain ester-based antioxidants, such as Irganox 1010 and Irganox 3114 have been found to interfere with the determination and therefore a correction factor is necessary for resins containing these additives. The purity of GMS additive for polymers ranges from 40 to 95% monoglyceride content. A correction to account for the purity must be made to determine the quantity of raw additive incorporated into the polymer. The sample must be pressed into a film or coupon prior to the analysis.

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Summary

An analytically representative sample of the polypropylene resin is molded into a 0.4 to 0.7 mm thickness film. 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 to obtain the spectrum at 4 wavenumber resolution or better. 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 ester absorbance of the GMS additive band is measured at 1739 cm^{-1} and the absorbance is measured for the reference polypropylene band at 1044 cm^{-1} to provide a path length or film thickness correction. To obtain the additive concentration in the sample, the ratio of the ester GMS band to the reference band is substituted into a linear regression calibration equation, constructed from measurements of prepared standards with known concentrations of additive. This Beer's Law calibration is linear through the 0.05 to 0.8% GMS range, however, non-linearities have been observed due to surface residues. Simply cleaning the film samples with a dry lint-free wipe removes the surface residues. Triplicate films are averaged to obtain a result.

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, 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 blending known amounts of GMS with polypropylene powder, and compounding under a nitrogen blanket until thoroughly mixed. 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 in the calibration and prediction measurements should be less than 1.6 absorbance 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 GMS ester 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:

$$Wt\% \ GMS = M \times (A_{1739}/A_{1044}) + N$$

Where:

Wt% GMS	= Weight % of GMS in the polypropylene
A_{1739}	= Absorbance of GMS at 1739 cm^{-1}
A_{1044}	= Absorbance of polypropylene reference band at 1044 cm^{-1}
M	= Calibration constant
N	= Intercept

The calibration curve for the determination of GMS in polypropylene for the standards used in this study is shown in Figure 2.
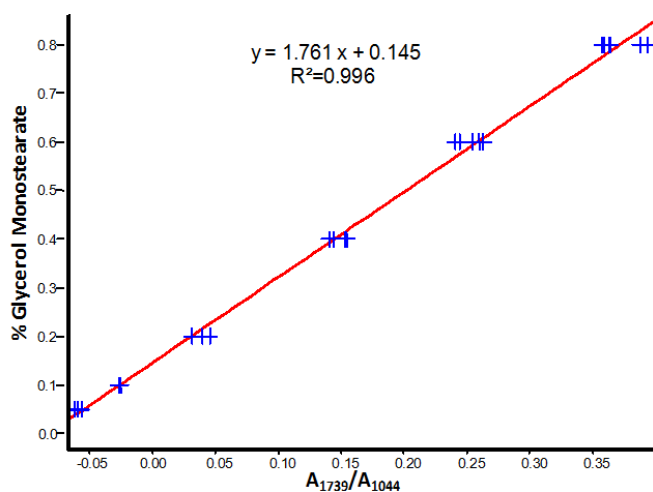

Figure 2. Calibration curve for % GMS in polypropylene.

Procedure

Sample preparation
Molding techniques and conditions used to prepare the sample do not significantly influence the results, as long as the resin is not subjected to temperatures of more than 250 °C for more than 2 to 3 minutes, and the prepared films have a smooth, consistent surface. A typical preparation procedure is as follows:

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). 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. The aluminum sheet is stripped from the chase and the films are pushed from the cavities and trimmed to remove the flash. Examine the sample for surface defects and check to ensure that the thickness is between 0.4 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 GMS concentration, measure the peak height absorbance for GMS at 1739 cm^{-1} measured by a vertical intersecting line to a baseline drawn between 1764 and 1722 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.
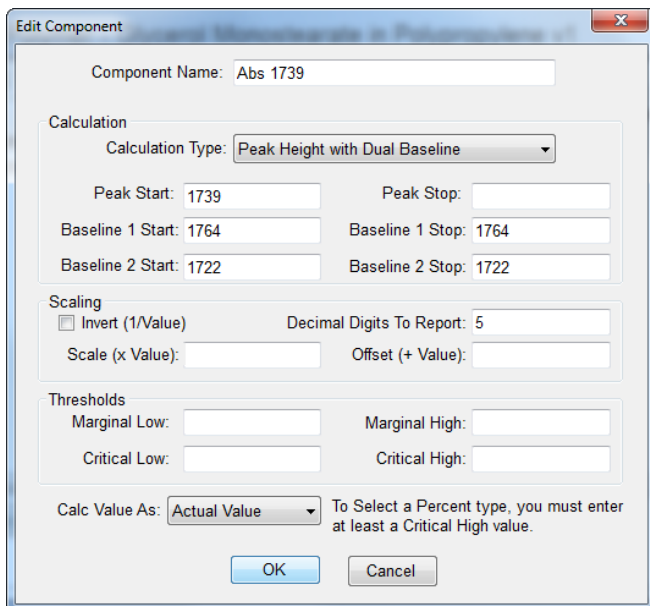
Figure 3. The GMS peak height absorbance (component) measurement at 1739 cm^{-1} in the MicroLab PC FTIR software. The peak start refers to the peak maxima position from which the peak height is measured. Single-point baselines should be set up with the same baseline start and stop points.
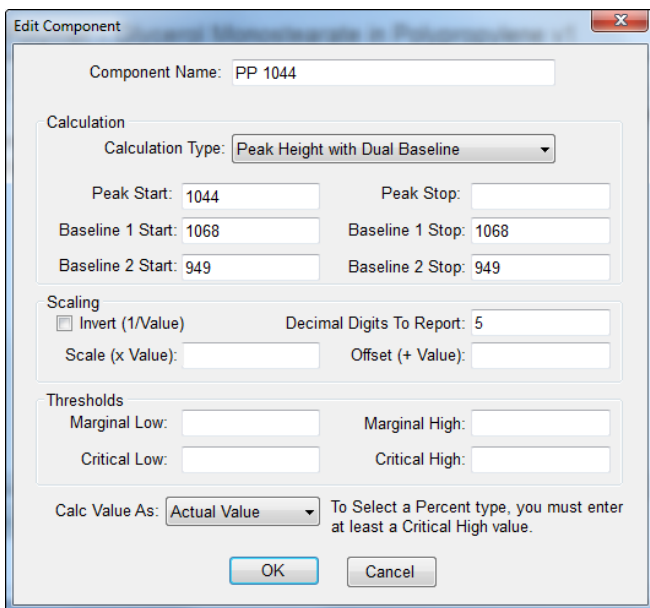

Figure 4. The polypropylene reference peak component addition in the MicroLab PC FTIR software.

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

GMS equation:
Wt% GMS = M x (A$_{1739}$/A$_{1044}$) + N

GMS resulting calibration values:
Wt% GMS = 1.761 x (A$_{1739}$/A$_{1044}$) + 0.145

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

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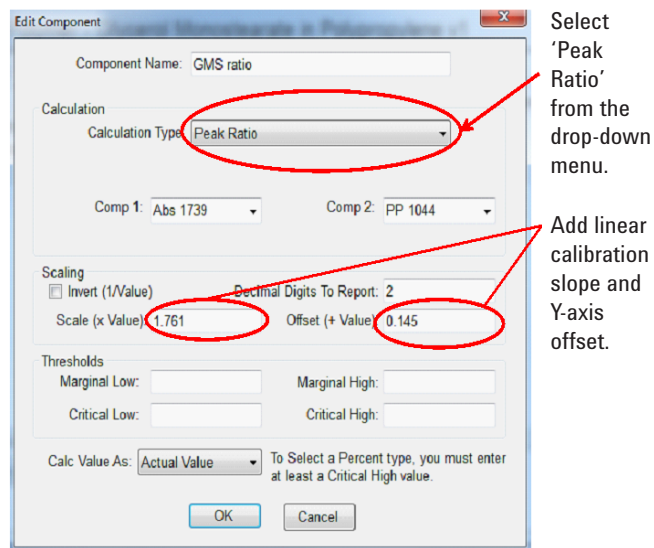

Select 'Peak Ratio' from the drop-down menu.

Add linear calibration slope and Y-axis offset.

Figure 5. The peak ratio component addition for the calibration in the MicroLab PC FTIR software. After plotting the 0.05– 8% GMS 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; the typical spectra in the 2200–1500 cm^{-1} range are overlaid in Figure 6. The presence of an absorption band at 1745 cm^{-1} suggests that the resin contains an ester-based antioxidant such as Irganox 1010 or Irganox 3114. If the presence of these antioxidants is confirmed, the GMS measurement must be corrected to compensate for the absorbance of the antioxidants.
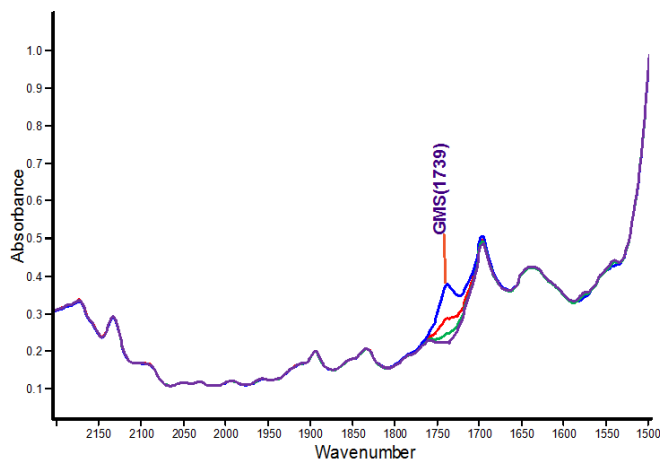
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Figure 6. Typical ester carbonyl absorbance for glycerol monostearate in polypropylene

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 GMS concentration (Figure 2), and insert the slope and offset values back into the method as shown in Figures 5 and 6. Once the slope and offset values have been entered, the Microlab PC FTIR software method will report the GMS concentration.

The MicroLab PC FTIR software method, Polymer — Glycerol Monostearate 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 % Glycerol Monostearate (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.
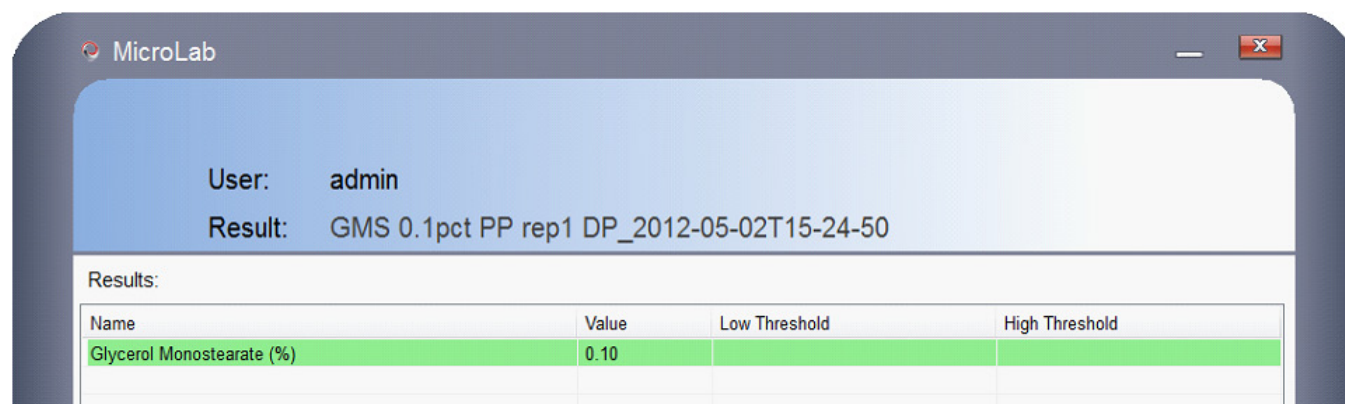

Figure 7. The MicroLab PC FTIR software prediction result for a 0.1% GMS in polypropylene sample

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