Designation: D6645 – 01 (Reapproved 2010)

Standard Test Method for Methyl (Comonomer) Content in Polyethylene by Infrared Spectrophotometry[1]

This standard is issued under the fixed designation D6645; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of methyl groups (that is, comonomer content) in polyethylenes by infrared spectrophotometry. The test method is applicable to copolymers of ethylene with 1-butene, 1-hexene, or 1-octene having densities above 900 kg/m^3. High-pressure low-density polyethylenes (LDPE) and terpolymers are excluded.

1.2 The values stated in SI units, based on IEEE/ASTM SI-10, are to be regarded as the standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

NOTE 1—There is no known ISO equivalent to this standard.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D792 Test Methods for Density and Specific Gravity (Relative Density) of Plastics by Displacement

D1505 Test Method for Density of Plastics by the Density-Gradient Technique

D1898 Practice for Sampling of Plastics (Withdrawn 1998)[3]

D2238 Test Methods for Absorbance of Polyethylene Due to Methyl Groups at 1378 cm^{-1}

D3124 Test Method for Vinylidene Unsaturation in Polyethylene by Infrared Spectrophotometry

D5576 Practice for Determination of Structural Features in Polyolefins and Polyolefin Copolymers by Infrared Spectrophotometry (FT-IR)

E131 Terminology Relating to Molecular Spectroscopy

E168 Practices for General Techniques of Infrared Quantitative Analysis

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E932 Practice for Describing and Measuring Performance of Dispersive Infrared Spectrometers

E1421 Practice for Describing and Measuring Performance of Fourier Transform Mid-Infrared (FT-MIR) Spectrometers: Level Zero and Level One Tests

IEEE/ASTM SI-10 Standard for Use of the International System of Units (SI): The Modern System

3. Terminology

3.1 *Terminology*—The units, symbols, and abbreviations used in this test method appear in Terminology E131 or IEEE/ASTM SI-10.

3.2 *comonomer*—α-olefin monomer. In this test method, comonomer refers to 1-butene, 1-hexene, and 1-octene only.

4. Summary of Test Method

4.1 The band located between 1377 cm^{-1} and 1379 cm^{-1} is due to a deformation vibration of the $-CH_3$ group. Bands at approximately 772 cm^{-1} (branch methylene rocking mode), 895 cm^{-1} (methyl rocking mode), and 785 cm^{-1} (branch methylene rocking mode) are characteristic of ethyl (that is, butene copolymer), butyl (that is, hexene copolymer), and hexyl (that is, octene copolymer) branches, respectively.[4]

4.2 This test method determines the methyl (that is, comonomer) content of a polyethylene copolymer based on the IR absorbance at 1378 cm^{-1} from a pressed plaque. The comonomer type has to be known and a calibration curve has to be available prior to the analysis. If the comonomer is not known a priori, the presence of bands at 772 cm^{-1}, 895 cm^{-1}, and 785 cm^{-1} can be used to identify ethyl (minimum of 1 branch per 1000 carbons), butyl (minimum of about 5 branches per 1000 carbons), and hexyl (minimum of about 5 branches per 1000 carbons) branches, respectively. A more sensitive and

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[1] This test method is under the jurisdiction of ASTM Committee D20 on Plastics and is the direct responsibility of Subcommittee D20.70 on Analytical Methods.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] The last approved version of this historical standard is referenced on www.astm.org.

[4] Blitz, J. P., and McFadden, D. C., "The Characterization of Short Chain Branching in Polyethylene Using Fourier Transform Infrared Spectroscopy," *J. Appl. Pol. Sci.*, 51, 13 (1994).

less ambiguous identification is obtained by C13 NMR spectroscopy. The latter technique is also used as a reference technique to provide polymer standards for the generation of calibration curves.

NOTE 2—For comonomer identification, it is recommended, for maximum sensitivity, to view the second derivative of the IR spectrum.

4.3 The method is calibrated by plotting absorbance at 1378 cm^{-1} per unit area of the methylene combination band at 2019 cm^{-1} (that is, internal thickness correction approach) or per unit of spectral cross-section (that is, the reciprocal of the product of plaque thickness and density) versus number of branches per 1000 carbons as determined by C13 NMR spectroscopy. Although both approaches give equivalent results, the one using internal thickness correction is recommended in this test method since it is considerably simpler to execute.

5. Significance and Use

5.1 This method determines the number of branches (that is, comonomer content) in copolymers of ethylene with 1-butene, 1-hexene or 1-octene. This information can be correlated with physical properties such as melting point, density, and stiffness, all of which depend on the degree of crystallinity of the polymer. Differences in the comonomer content thus may have a significant effect on the final properties of products made from these resins.

6. Interferences

6.1 A conformational CH_2 wagging absorbance at 1368 cm^{-1} overlaps the methyl absorbance at 1378 cm^{-1}, but does not cause significant interference in this test method since its intensity is not significantly affected by the comonomer content, but rather by the plaque thickness. The result of not correcting for this overlap is a positive ordinate intercept for the calibration curve (see 10.4). Another conformational CH_2 wagging absorbance at 1352 cm^{-1} does not significantly overlap the 1378 cm^{-1} absorbance.

6.2 The presence of most pigments will interfere with this method.

6.3 The presence of low molecular weight hydrocarbons will produce high results in this method due to absorbance by their end methyl groups at 1378 cm^{-1}.

6.4 The secondary antioxidant Irgafos 168[5] shows an absorbance at 768 cm^{-1} which interferes with the identification of low levels (that is, typically less than 5 branches per 1000 carbons or less) of ethyl branches.

6.5 Vinylidene groups absorb at 888 cm^{-1} and thus may interfere with a conclusive identification of a hexene copolymer from its 895 cm^{-1} resonance, depending on the relative intensities of the two peaks.

7. Apparatus

7.1 *Infrared Spectrophotometer,* either double beam or a Fourier transform (FTIR).

7.1.1 *Dispersive Infrared Spectrophotometer,* capable of achieving a spectral bandwidth of 4 cm^{-1} (see Practice E932). The instrument should be capable of scale expansion along the wavenumber axis.

7.1.2 *Fourier Transform Infrared Spectrometer,* capable of 4 cm^{-1} resolution (see Practice E1421). The instrument should be capable of scale expansion along the wavenumber axis.

7.2 *Compression Molding Press,* with platens capable of being heated to 180°C.

7.3 *Two Metal Plates,* 150 by 150 mm or larger, of 0.5-mm thickness with smooth surfaces.

7.4 *Brass Shims,* approximately 75 by 75 mm, of 0.3 mm thickness with an aperture in the center at least 25 by 38 mm.

7.5 *Micrometer (optional),* with thimble graduations of 0.001 mm.

7.6 *Film Mounts,* with apertures at least 6 by 27 mm, to hold the specimens in the infrared spectrophotometer.

8. Materials

8.1 *Polyethylene Terephthalate, Aluminum Foil or Matte Finished Teflon-Fibreglass Sheets.*

9. Hazards

9.1 Caution must be used during plaque preparation to handle the hot platens with appropriate gloves for hand protection.

10. Procedure

10.1 *Preparation of Polymer Plaque:*

10.1.1 Preheat the press to about 50°C above the melting point of the polymer.

10.1.2 Place a 0.3-mm thick brass shim on the sheet material chosen (see 8.1) which in turn covers a metal plate.

NOTE 3—When using aluminum foil, place the dull side next to the polymer to give the sample film some texture, thereby reducing fringe effects in the infrared spectrum.

10.1.3 Add polymer in sufficient quantity to completely fill the shim aperture during pressing.

10.1.4 Insert the mold assembly between the press platens and apply a slight pressure.

10.1.5 Allow the polymer to preheat for about 30 s. Apply the full press pressure at a temperature approximately 50°C above the melting point of the polymer for 1 min or until all exudation ceases.

10.1.6 Turn off the heat, turn on the cooling water, and allow the polymer to press quench at full pressure until the temperature drops below 50°C (or cool enough to remove the mold assembly by hand).

10.1.7 Select plaques that are clear for the FTIR analysis. To avoid interference fringes in the spectrum, the plaque surfaces must be slightly dimpled.

10.2 *Spectral Acquisition:*

10.2.1 Place the polymer plaque in the infrared spectrophotometer.

10.2.2 Set the controls of the infrared spectrophotometer for quantitative conditions with a good signal to noise ratio and a

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[5] Trademark of the Ciba Specialty Chemicals Co.

spectral resolution (bandwidth) of 4 cm^{-1}. For an FTIR, an apodization function (Beer-Norton medium and Happ-Genzel have been found to be appropriate) that gives good quantitation should be used.

10.2.3 Record the infrared spectrum from 4000 cm^{-1} to 500 cm^{-1}.

10.3 *Spectral Data Reduction:*

10.3.1 Determine the absorbance at a fixed wavenumber (not necessarily at the apex of the 1378 cm^{-1} peak) between 1378 and 1379 cm^{-1}. A linear baseline is to be set between the valleys present at 1400 cm^{-1} and 1330 cm^{-1} (see Fig. X1.1 in Appendix X1).

10.3.2 Determine the area of the combination band at 2019 cm^{-1} (see Fig. X1.1 in Appendix X1). The baseline and integration limits are to be set between the valleys on each side of the peak (that is, typically between 1980 and 2100 cm^{-1}).

NOTE 4—Several software packages are available with which macros can be written to perform the data reduction automatically and consistently.

10.4 *Calibration:*

10.4.1 For a minimum of five (preferably about ten) polymer standards containing known levels of the comonomer of interest, calculate the ratio of the absorbance (A) at 1378 cm^{-1} (see 10.3.1) and the area of the combination band at 2019 cm^{-1} (see 10.3.2) and plot:

A (1378 cm^{-1}) / Area (2019 cm^{-1}) vs. Number of branches (N) per 1000 carbons.

A linear regression fit should give a positive ordinate intercept (representing the contribution from the CH_2 wagging absorbance at 1368 cm^{-1} and the $–CH_3$ main chain end groups) and an R^2 value of 0.98 or better. According to the Lambert-Beer Law:

$$A\left(1378\ cm^{-1}\right)/Area\left(2019\ cm^{-1}\right) = a \cdot N + b \qquad (1)$$

where:

a = slope of the regression line, and
b = ordinate intercept.

Depending somewhat on the exact wavenumber at which the absorbance of the 1378 cm^{-1} peak is measured, the slopes of the regression lines should be close to the following:

a_b (butene copolymers) = 0.009
a_h (hexene copolymers) = 0.008
a_o (octene copolymers) = 0.007

NOTE 5—The above recommended "internal thickness correction" approach has been found to yield equivalent results to the more labor intensive approach of measuring thickness (b) to the nearest 0.01 mm and density (d) of the plaque and graphing A (1378 cm^{-1}) ⁄ (b · d) vs. N.

NOTE 6—A wedge compensation or spectral subtraction using a homopolyethylene sample as described in Method D2238 is not required.

10.5 *Calculations:*

10.5.1 Having determined the thickness corrected absorbance, use the equation for the appropriate regression line fitted to the calibration points to calculate the number of branches (N) per 1000 carbons (see 10.4). Ensure that the value obtained is within the high and low limits of the standards. To convert to comonomer content, use the following expressions:

$$Wt\% = 100 \cdot \frac{N \cdot M_{com}}{N \cdot M_{com} + \frac{(1000 - 2N)}{2} \cdot 28} \qquad (2)$$

$$Mol\% = 100 \cdot \frac{\frac{Wt\%}{M_{com}}}{\frac{Wt\%}{M_{com}} + \frac{100 - Wt\%}{28}}$$

where:

M_{com} = the molecular weight of the α-olefin comonomer.

11. Report

11.1 Complete identification of material tested including name, manufacturer, lot number and physical form when sampled,

11.2 Date of test,

11.3 Number of methyl groups per 1000 carbons and/or comonomer content in wt % or mole % for each sample, and

11.4 Any sample or spectral anomalies observed during the measurement.

12. Precision and Bias

12.1 The repeatability relative standard deviation for a butene LLDPE with a comonomer content of 4.1 mol % based on 12 analyses over a period of two weeks is 0.9 %.

12.2 The reproducibility of this test method is being determined and will be available on or before January 1, 2005.

13. Keywords

13.1 branching; comonomer; FTIR; infrared spectrophotometry; polyethylene

APPENDIX

(Nonmandatory Information)

X1.

X1.1 See Fig. X1.1.

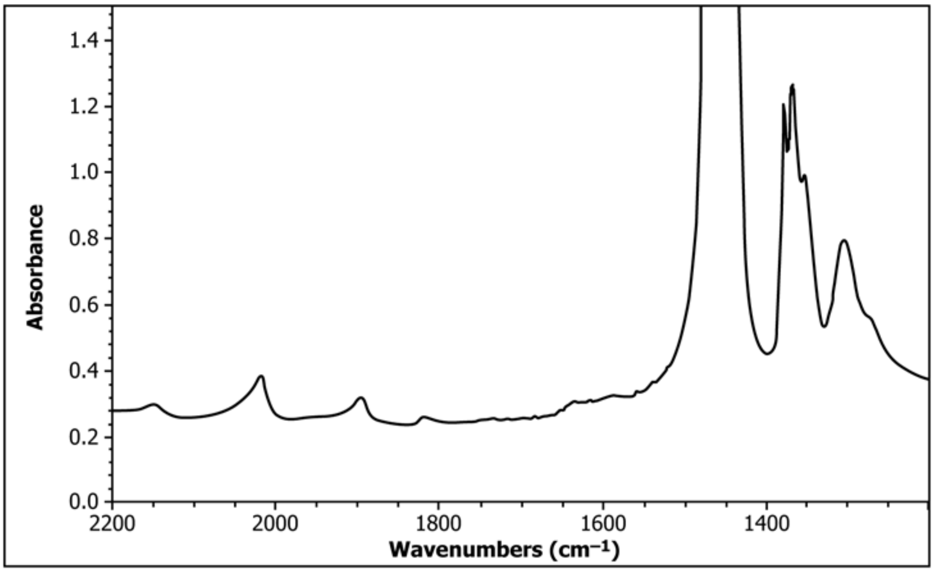

FIG. X1.1 FTIR Spectrum (2200 cm^{-1} to 1200 cm^{-1}) of a Butene Copolymer Containing 17 Branches per 1000 Carbons

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