ASTM INTERNATIONAL

Designation: D6645 – 18

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

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

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

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

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, or 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 an ethyl branch (that is, butene copolymer), a butyl branch (that is, hexene copolymer), and a hexyl branch (that is, octene copolymer), respectively.[3]

4.2 This test method determines the methyl group (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

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[3] 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).

A Summary of Changes section appears at the end of this standard.

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 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 IR calibration curves.

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

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 can 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[4] 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 can interfere with a conclusive identification of a hexene copolymer from its 895 cm^{-1} resonance, depending on the relative intensities of the two peaks.

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[4] Trademark of the Ciba Specialty Chemicals Co.

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 must 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 must 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:*