Designation: D5576 – 00 (Reapproved 2013)

Standard Practice for Determination of Structural Features in Polyolefins and Polyolefin Copolymers by Infrared Spectrophotometry (FT-IR)[1]

This standard is issued under the fixed designation D5576; 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 practice covers infrared procedures for determining the molecular structural features in polyolefins and polyolefin copolymers. The structural features of primary concern are the types and numbers of branches. Although this practice centers its attention on polyolefins and polyolefin copolymers, the techniques, with proper modification, can be used for some other polymers as well.

NOTE 1—Quantitative determinations require either an internal or an external evaluation of sample thickness. ASTM test methods available for specific features are listed in Tables 1 and 2.

1.2 *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 to determine the applicability of the regulatory limitations prior to use.*

NOTE 2—There is no known ISO equivalent to this standard.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D883 Terminology Relating to Plastics

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

D1600 Terminology for Abbreviated Terms Relating to Plastics

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

D3594 Test Method for Copolymerized Ethyl Acrylate In Ethylene-Ethyl Acrylate Copolymers

D5594 Test Method for Determination of the Vinyl Acetate Content of Ethylene-Vinyl Acetate (EVA) Copolymers by Fourier Transform Infrared Spectroscopy (FT-IR)

D6248 Test Method for Vinyl and Trans Unsaturation in Polyethylene by Infrared Spectrophotometry

E131 Terminology Relating to Molecular Spectroscopy

E168 Practices for General Techniques of Infrared Quantitative Analysis

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 *Definitions*—For definitions of plastics terms used in this practice see Terminology D883 and D1600.

3.2 Units, symbols and abbreviations used in this practice appear in Terminology E131 or IEEE/ASTM SI-10.

4. Summary of Practice

4.1 Infrared absorption bands suitable for quantitative analysis by FT-IR are listed in Tables 1 and 2. These are only typical bands and are not to be construed as exhaustive.

4.2 For quantitative determinations, sample specimen thickness is measured internally at some band representing the basic chain structure, such as 2019 cm^{-1} for polyethylene, or externally using a micrometer (see Tables 1 and 2 for ASTM test methods).

NOTE 3—**Warning:** Molding can cause carbonyl formation due to oxidation. This should be checked in the 1700 to 1750 cm^{-1} range.

5. Significance and Use

5.1 The structural features expressed by these determinations affect the ultimate polymeric properties and are useful in showing correlations with many performance properties.

6. Apparatus

6.1 *Infrared Spectrophotometer,* either double beam or a Fourier transform (FT-IR).

[1] This practice 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.

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

TABLE 1 Polyolefin Structural Features Determined by FT-IR

Structure	Absorption Band, cm^{-1}	ASTM Test Method
Methyl group (polyethylene)	1378	D2238
Methyl group (eth-prop copol)	1380	
Pendant methyl	935	
Terminal vinyl	908	D6248
Trans-vinylene	965	D6248
Vinylidene	888	D3124

TABLE 2 Structural Features in Polyolefin Copolymer Determined by FT-IR

Structure	Absorption Band, cm^{-1}	ASTM Test Method
Vinyl acetate	609	D5594
	1020	D5594
	3270	D5594
Styrene	770–700	
	1600–1500	
Ethyl acrylate	1640–1730	
	862	D3594
Ethylene acrylate	1280–1200	
	1640–1625	

6.1.1 Double-beam infrared spectrophotometer capable of a 4 cm^{-1} spectral resolution as defined in Practice E932. The instrument should be capable of scale expansion along the wavelength axis.

6.1.2 *Fourier Transform Infrared Spectrometer,* capable of 4 cm^{-1} resolution. The instrument should be capable of scale expansion along the wavelength axis. Also, see Practice E1421 for testing procedures.

6.2 *Hot Plate.*

6.3 *Microscope Slides.*

6.4 *Compression-Molding Press,* capable of 200°C.

6.5 *Metal Plates,* two, 150 by 150 mm or larger, of 0.5–mm thickness with smooth surfaces.

6.6 *Brass Shims,* approximately 75 by 75 mm, of 0.5-mm thickness with an aperture in the center at least 25 by 38 mm.

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

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

7. Materials

7.1 *Polyethylene Terephthalate, Aluminum or Matte Finished Teflon-Fiberglass Sheets.*

8. Hazards

8.1 Wear gloves when plaques are prepared using a heated press.

8.2 The optical bench of the FT-IR spectrometer contains a laser. To avoid eye injury, do not look directly into the laser beam.

9. Procedure

9.1 *Sample Preparation:*

9.1.1 *Procedure A:*

9.1.1.1 Control the hot plate temperature at 100 ± 10°C above the melting temperature of the polymer.

9.1.1.2 Place a portion of the sample on a microscope slide on the hot plate.

9.1.1.3 Cover the sample with another slide and press with a wooden pestle. Use firm circular motions to press a uniform film.

9.1.1.4 To quench the pressed polymer film, dip the two slides carefully into a beaker of cold water. Remove the film and blot dry.

9.1.2 *Procedure B:*

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

9.1.2.2 Place a brass shim on the sheet material chosen (see 7.1) that, in turn, covers a metal plate.

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

9.1.2.4 Cover with another piece of sheet (see 7.1) and another metal plate.

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

9.1.2.6 Allow the sample 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.

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

9.1.2.8 Release the pressure and remove the sample.

9.1.2.9 Select plaques that are clear and of uniform thickness for the FT-IR analysis. To avoid interference fringes in the spectrum, the plaque/film surfaces must be slightly dimpled.

9.2 *Spectral Measurements:*

9.2.1 Place the sample in the infrared spectrophotometer.

9.2.2 Set the controls of the infrared spectrophotometer for quantitative conditions with a good signal to noise ratio and satisfactory repeatability. For a FT-IR, a spectral resolution of 4 cm^{-1} and an apodization function (Beer-Norton medium and Happ-Genzel have been found to be appropriate) that gives good quantitation should be used.

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

9.2.4 Determine which structural feature(s) are present and select the appropriate ASTM method for quantitative determination.

10. Calculation

10.1 If no standard method is available and an estimate of the concentration of the feature of interest is sought, the approach in 10.1.1-10.1.3 is suggested.

10.1.1 Determine the thickness of the plaque or, preferably, its spectral cross-section, b, in cm^2/g, by measuring the thickness and density or alternatively the mass and surface area of a uniformly thick portion of the plaque

10.1.2 Measure the absorbance of the peak of interest. Choose a baseline between valleys on either side of the peak in a manner to produce the most accurate and repeatable representation of the actual background absorbance

10.1.3 Calculate the concentration, c, of the feature using either the Beer-Lambert Law ($A = a \cdot b \cdot c$) with the appropriate molar absorptivity, a, or an appropriate calibration curve. If a calibration curve is used, it should have a minimum of 5 data points, and the unknown should be within the high and low limits of the standards.

11. Report

11.1 Report the following information:

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

11.1.2 Date of test, and

11.1.3 Any sample or spectral anomalies observed during the measurement.

12. Keywords

12.1 copolymers; FT-IR; infrared spectrophotometry; polyethylene; structural features

SUMMARY OF CHANGES

Committee D20 has identified the location of selected changes to this standard since the last issue (D5576 - 00(2006)) that may impact the use of this standard. (April 1, 2013)

(1) Reapproved without change.