Designation: D 5576 – 00

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 D 5576; 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 similar or equivalent ISO standard.

2. Referenced Documents

2.1 *ASTM Standards:*

D 883 Terminology Relating to Plastics[2]

D 1505 Test Method for Density of Plastics by the Density-Gradient Technique[2]

D 1600 Terminology of Abbreviated Terms Relating to Plastics[2]

D 2238 Test Methods for Absorbance of Polyethylene Due to Methyl Groups at 1378 cm^{-1} [2]

D 3124 Test Method for Vinylidene Unsaturation in Polyethylene by Infrared Spectrophotometry[3]

D 3594 Test Method for Copolymerized Ethyl Acrylate in Ethylene-Ethyl Acrylate[3]

D 5594 Test Method for Determination of Vinyl Acetate Content of Ethylene-Vinyl Acetate (EVA) Copolymers by Fourier Transform Infrared Spectroscopy (FT-IR)[4]

D 6248 Test Method for Vinyl and Trans Unsaturation in Polyethylene by Infrared Spectrophotometry[4]

E 131 Terminology Relating to Molecular Spectroscopy[5]

E 168 Practices for General Techniques of Infrared Quantitative Analysis[5]

E 932 Practice for Describing and Measuring Performance of Dispersive Infrared Spectrophotometers[5]

E 1421 Practice for Describing and Measuring Performance of Fourier Transform Infrared (FT-IR) Spectrometers: Level Zero and Level One Tests[5]

IEEE/ASTM SI–10 Standard for Use of the International System of Units (SI): The Modern System[6]

3. Terminology

3.1 *Definitions*— For definitions of plastics terms used in this practice see Terminology D 883 and D 1600.

3.2 Units, symbols and abbreviations used in this practice appear in Terminology E 131 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.

[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] *Annual Book of ASTM Standards,* Vol 08.01.

[3] *Annual Book of ASTM Standards,* Vol 08.02.

[4] *Annual Book of ASTM Standards,* Vol 08.03.

[5] *Annual Book of ASTM Standards,* Vol 03.06.

[6] *Annual Book of ASTM Standards,* Vol 14.02.

***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	D 2238
Methyl group (eth-prop copol)	1380	
Pendant methyl	935	
Terminal vinyl	908	D 6248
Trans-vinylene	965	D 6248
Vinylidene	888	D 3124

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

Structure	Absorption Band, cm^{-1}	ASTM Test Method
Vinyl acetate	609	D 5994
	1020	D 5994
	3270	D 5994
Styrene	770–700	
	1600–1500	
Ethyl acrylate	1640–1730	
	862	D 3594
Ethylene acrylate	1280–1200	
	1640–1625	

6. Apparatus

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

6.1.1 Double-beam infrared spectrophotometer capable of a 4 cm^{-1} spectral resolution as defined in Practice E 932. 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 E 1421 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

This section identifies the location of selected changes to this practice. For the convenience of the user, Committee D-20 has highlighted those changes that may impact the use of this practice. This section may include descriptions of the changes or the reasons for the changes, or both.

D 5576-00:

(*1*) Changed title.

(*2*) Added ASTM test methods for the determination of referenced features added to Section 2.

(*3*) Rewrote procedures section to make it consistent with the equivalent sections in the newly referenced test methods.