Designation: D5594 − 98 (Reapproved 2012)

Standard Test Method for Determination of the Vinyl Acetate Content of Ethylene-Vinyl Acetate (EVA) Copolymers by Fourier Transform Infrared Spectroscopy (FT-IR)[1]

This standard is issued under the fixed designation D5594; 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 infrared procedures for determining the vinyl acetate content of EVA copolymers using pressed films (Procedure A) or molded plaques (Procedure B) and internal corrections for sample thickness.

1.2 This test method is applicable to the analysis of EVA copolymers containing 0.5 to 55 % vinyl acetate except as specified in 1.3.

1.3 Talc interferes with the 1020 cm^{-1} vinyl acetate band. Resins containing <5 % vinyl acetate and talc are excluded from the scope of this test method.

1.4 The values stated in SI units are to be regarded as the standard. The values given in brackets are provided for information purposes only.

1.5 *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.* Specific precautionary statements are given in Section 8.

NOTE 1—This test method is not equivalent to ISO 8985.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

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

IEEE/ASTM SI-10 Use of the International System of Units (SI): The Modem Metric System

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

2.2 *ISO Standard:*

ISO 8985 Plastics—Ethylene/Vinyl Acetate Copolymer Thermoplastics—Determination of Vinyl Acetate[3,4]

3. Terminology

3.1 *Definitions:*

3.1.1 Units, symbols, and abbreviations used in this test method appear in Terminology E131 or IEEE/ASTM SI-10.

3.2 *Abbreviations:*

3.2.1 *EVA*—ethylene-vinyl acetate copolymer.

3.2.2 *PTFE*—tetrafluorethylene polymer.

3.2.3 *FT-IR*—Fourier transform infrared.

4. Summary of Test Method

4.1 The vinyl acetate content is measured using infrared absorption band at 1020 cm^{-1} (0.5 to 5 % vinyl acetate) or 609 cm^{-1} (5 to 55 % vinyl acetate).

4.2 Sample thickness is measured internally using an ethylene infrared absorption band at 720 cm^{-1} (28 to 55 % vinyl acetate), 2020 cm^{-1} (0.5 to 28 % vinyl acetate), or 4250 cm^{-1} (5 to 28 % vinyl acetate).

4.3 Regression analysis is performed on vinyl acetate/ethylene ratios versus known vinyl acetate contents for EVA copolymer standards. The resulting equation is used to calculate the vinyl acetate content for subsequent EVA copolymer samples.

5. Significance and Use

5.1 Properties of EVA copolymers are affected by the amount of vinyl acetate incorporated in the copolymer: This

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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] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

[4] Nicolet 20 S × B, available from Nicolet Instrument Corp., Analytical Division, 5225 Verona Rd., Madison, WI 53711-4495, and Perkin Elmer 1760, a registered trademark of Perkin-Elmer Corp., 761 Main Ave., Norwalk, CT 06859-0156, or equivalents, have been found suitable for this purpose.

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

test method provides a means to determine the vinyl acetate level in copolymer samples.

5.2 Before proceeding with this test method, reference should be made to the specification of the material being tested. Any test specimen preparation, conditioning, dimensions, or testing parameters, or a combination thereof, covered in the materials specification shall take precedence over those mentioned in this test method. If there are no material specifications, then the default conditions apply.

6. Apparatus

6.1 *Fourier Transform Infrared (FT-IR) Spectrophotometer,* equipped with a detector, which gives a linear response over the desired concentration range, is capable of 4-cm^2 resolution (nominal), and is able to scan from 4400 to 450 cm^{-1}.

NOTE 2—A DTGS detector has been found suitable for this application.

6.2 *Hot Plate,* (Sample Preparation Procedure A only).

6.3 *Microscope Slides,* (Sample Preparation Procedure A only).

6.4 *Laboratory Press,* capable of at least 9 000 kg [20 000 lb] 150°C [300°F], (Sample Preparation Procedure B only).

6.5 *Backing Plates,* steel or aluminum (Sample Preparation Procedure B only).

6.6 *Brass Shim Stock (Roll),* 50 to 150 µm [2 to 6 mil] thick and 150 mm [6 in.] wide (Sample Preparation Procedure B only).

6.7 *Polyester Sheet,* or fiberglass impregnated PTFE cloth (Sample Preparation Procedure B only).

6.8 *PTFE Film* (Sample Preparation Procedure B, resins containing ≥40 % vinyl acetate only).

6.9 *Templates,* (mold) with 150 × 150 mm [6 × 6 in.] pieces of paper or brass shim stock (item 6.6) containing cavities of a size and shape appropriate for the sample holders used, and, if applicable, sheets of items 6.7 and 6.8 (Sample Preparation Procedure B only).

6.10 *Cooling Block,* steel or aluminum, at least 150 × 150 mm [6 × 6 in.], approximately 25 mm [1 in.] thick, channeled for cooling water (Sample Preparation Procedure B only).

7. Materials

7.1 EVA copolymer standards containing nominal vinyl acetate concentrations of 0.5 to 55 %, by weight.

7.2 Dry ice (Sample Preparation B Procedure A only).

8. Hazards

8.1 Care should be taken to avoid burns when handling microscope slides on the hot-plate (Sample Preparation Procedure A), and gloves should be worn when plaques are prepared using a heated press (Sample Preparation Procedure B).

8.2 Care also should be taken to avoid breaking the microscope slides while removing the pressed polymer film.

8.3 Care should be taken to avoid burns when handling dry ice.

9. Specimen Preparation

9.1 *Procedure A:*

9.1.1 Control the hot-plate temperature at 250 ± 10°C.

9.1.2 Place a microscope slide, containing a fraction of the sample pellet, on the hot-plate.

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

9.1.4 Remove the microscope slide from the hot-plate and quench the pressed polymer film by dipping the two slides into a beaker of cold water. Remove the film and blot dry with an absorbent towel.

9.1.5 Absorption maxima, measured on film produced by this procedure, shall not exceed 1.5 absorbance units for either of the analytical bands used.

9.2 *Procedure B:*

NOTE 3—Omit 9.2.1 to 9.2.11 for analysis of blown film.

9.2.1 Select a brass or paper mold with a thickness appropriate to the vinyl acetate content of the sample. The absorption maxima of the vinyl acetate and ethylene bands measured on the plaque are not to exceed 1.5 absorbance units.

NOTE 4—To meet the absorbance requirement specified in 9.2.1 it will be necessary to vary the mold thickness as the vinyl acetate content changes. The mold thickness required typically will be between 50 and 150 µm [2 to 6 mil].

9.2.2 Place a polyester sheet (or fiberglass impregnated PTFE cloth) followed by a brass or paper mold on a backing plate. For resins with vinyl acetate content ≥40 %, a PTFE film should be placed on top of the brass mold, or, if using a paper mold, under the paper.

9.2.3 Place a quantity of sample, appropriate to the thickness of the mold used, in the center of each opening in the mold. Do not overfill the mold openings. If flashing occurs, the brass mold and backing plates can be cleaned with a nylon scrubbing pad.

9.2.4 Place another piece of polyester sheet (or fiberglass impregnated PTFE cloth) and a backing plate on top of the sample. For resins with vinyl acetate content ≥40 %, a PTFE film should be placed over the sample before the polyester sheet (or fiberglass impregnated PTFE cloth).

9.2.5 Place the resulting "sandwich" in the press with the platens heated at 150 to 175°C.

9.2.6 Close the press until the top platen barely touches the top plate and leave for sufficient time to permit the sample to soften and outgas.

NOTE 5—Acceptable plaques, free of gas bubbles, have been obtained when the sample is allowed to soften for 3 min.

9.2.7 Close the press completely and apply at least 9 000 kg [20 000 lb] force for approximately 1 min.

9.2.8 Cool the "sandwich" to room temperature, release the pressure, and remove the "sandwich" from the press.

9.2.9 In cases where the press does not have cooling capability or where sample throughput needs to be increased, the following alternative to 9.2.8 may be used. The "sandwich" is removed from the press hot and placed on a metal cooling block through which cold water is circulated. A mass of at least 4 kg [9 lb] is placed on top to the "sandwich" while it cools to room temperature.

9.2.10 For resins with vinyl acetate content <40 %, separate the backing plates and remove the plaques from the mold.

9.2.11 For resins with vinyl acetate content ≥40 %, place the "sandwich" on dry ice for at least 15 s before separating the backing plate, polyester sheet (or fiberglass impregnated PTFE cloth), and the PTFE film from the plaque.

9.2.12 Select plaques that are clear and of uniform thickness for the FT-IR analysis.

10. Calibration

10.1 Record the open beam background spectrum from 4400 to 450 cm^{-1} at a nominal resolution of 4 cm^{-1}.

10.2 Place a standard EVA copolymer film (plaque), prepared as described in 9.1 or 9.2, in the sample beam of the FT-IR spectrometer.

10.3 Record the infrared spectrum from 4400 to 450 cm^{-1} at a nominal resolution of 4 cm^{-1} . The signal-to-noise ratio, S/N, should be acceptable for the desired precision. A typical EVA copolymer spectrum (9.0 % vinyl acetate) is shown in Fig. 1.

10.4 Ratio the sample spectrum to the background spectrum and convert the results to absorbance.

10.5 Measure the area of one vinyl acetate band and one ethylene band selected from the choices given in Table 1. Absorbance maxima for the analytical bands chosen are not to exceed 1.5 absorbance units.

10.6 Draw a baseline tangent to the absorption minima on either side of each peak. Determine the area of each peak above the baseline.

10.7 Calculate the vinyl acetate/ethylene area ratio for the appropriate data reduction procedure defined in 12.1.

10.7.1 For linear regression analysis:

$$r = A_{va}/A_{et} \tag{1}$$

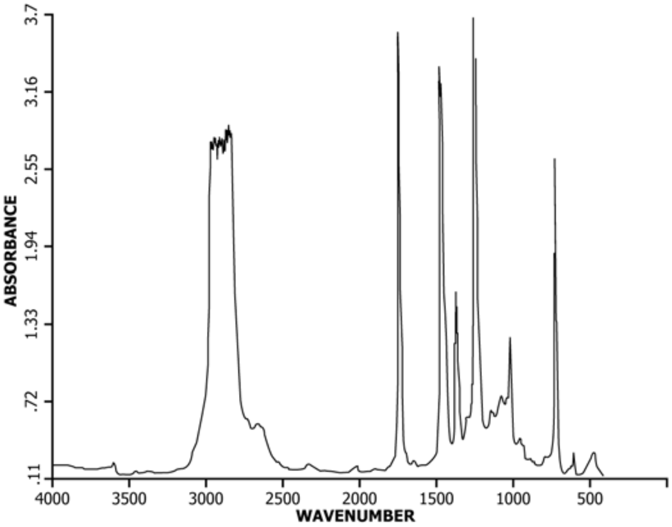

FIG. 1 FT-IR Spectrum of EVA Copolymer Standard (4.8 % Vinyl Acetate) Analyzed by Procedure B

10.7.2 For nonlinear regression analysis:[5]

$$R = A_{va}/(A_{va}+A_{et}) \tag{2}$$

where:

A_{va} = Area of vinyl acetate band, and
A_{et} = Area of ethylene band.

10.8 Repeat 10.2 through 10.7.2 for each standard EVA copolymer film (plaque).

10.9 A minimum of five standards shall be used for the linear regression of the 0.5 to 5.0 % vinyl acetate range. The number of standards used for the nonlinear regression of either the 5.0 to 28 % or 28 to 55 % vinyl acetate ranges shall not be less than six.

10.10 The standards must cover the full range of vinyl acetates to be analyzed. Extrapolation is not permitted.

11. Procedure

11.1 Prepare samples as described in 9.1 for films or 9.2 for plaques.

11.2 Record the open beam background spectrum from 4400 to 450 cm^{-1} at a nominal resolution of 4 cm^{-1}.

11.3 Place a sample film (plaque) in the sample beam of the FT-IR spectrometer.

11.4 Record the infrared spectrum from 4400 to 450 cm^{-1} at a nominal resolution of 4 cm^{-1} . The signal-to-noise ratio, S/N, should be acceptable for the desired precision.

11.5 Ratio the sample spectrum to the background spectrum and convert the result to absorbance.

11.6 Measure the area of one vinyl acetate and one ethylene band selected from the options given in Table 1. Absorbance maxima for the analytical bands chosen are not to exceed 1.5 absorbance units.

11.7 Draw a baseline tangent to the absorption minima on either side of each peak. Determine the area of each peak above the baseline.

11.8 Calculate the vinyl acetate to ethylene area ratio as specified in 10.7.

12. Calculation

12.1 *Regression Analysis:*

12.1.1 For vinyl acetate standards between 0.5 and 5.0 %, use linear regression analysis to determine the calibration equation of the data obtained in 10.7 and 10.8.

12.1.2 For vinyl acetate standards covering the range 5.0 to 28 % or 28 to 55 %, use nonlinear regression analysis, of the data obtained in 10.7 and 10.8, to determine an equation of the form:

$$VA, wt\,\% = a + \frac{(b \times R)}{1+(c \times R)} \tag{3}$$

where:
a, b, and *c* are regression coefficients.

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[5] Cole, K. C., Pellerius, T. E., D•••, M. M., and Paroli, R. M., "New Approach to Quantitative Analysis of Two-Component Polymer Systems by Infrared Spectroscopy," *Applied Spectroscopy*, Vol 50, No. 6, June 1996, pp. 774–780.

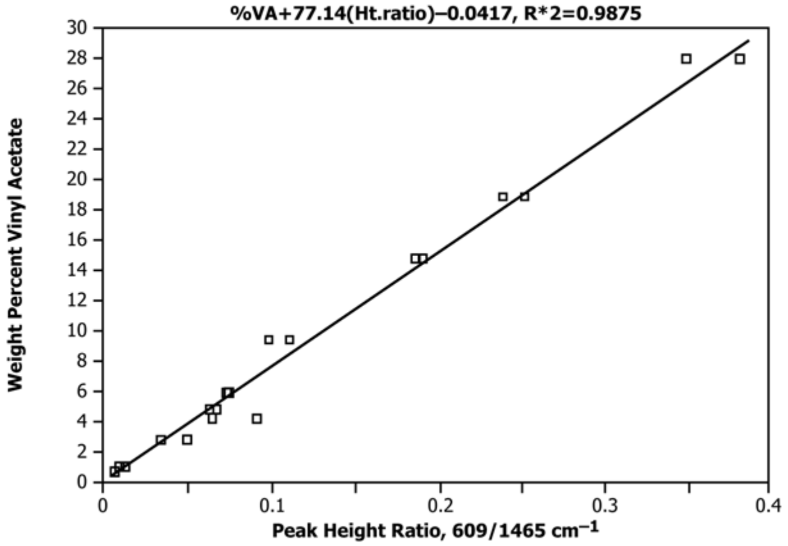

FIG. 2 Vinyl Acetate Correlation Curve (609 cm^{-1}/1465 cm^{-1} Height Ratio) Prepared Using Procedure B

TABLE 1 Vinyl Acetate Content (Weight %) Using 609 cm^{-1} and 2019 cm^{-1} Bands

Sample	Peak Height Measurements					Peak Area Measurements				
	Average	S_r	S_R	r	R	Average	S_r	S_R	r	R
A	2.38	0.12	0.44	0.35	1.23	2.39	0.15	0.38	0.42	1.06
B	4.80	0.19	0.23	0.53	0.64	5.03	0.42	0.59	1.18	1.65
D	5.76	0.41	0.54	1.16	1.51	5.65	0.78	0.84	2.19	2.34
E	8.37	1.02	1.20	2.85	3.36	8.77	1.99	2.05	5.57	5.73
C	15.46	0.77	1.15	2.15	3.21	16.55	7.55	7.55	21.15	21.15
G	20.38	0.80	6.48	2.23	18.14	21.07	21.12	21.12	59.15	59.15
F	30.14	2.35	2.92	6.58	8.19	29.04	2.72	4.42	7.62	12.39

12.2 Enter the sample area ratio from 11.8 into the appropriate regression equation from 12.1 to calculate the weight percent vinyl acetate.

13. Report

13.1 Report the following information:
13.1.1 Complete identification of sample,
13.1.2 Analytical bands used, and
13.1.3 Percent vinyl acetate.

14. Precision and Bias

14.1 The precision and bias of this test method are under investigation by a task group of Section 20.70.08.

14.2 *Repeatability*—The repeatability standard deviation has been determined on the three resin samples shown in Table 2 and Table 3.

15. Keywords

15.1 ethylene-vinyl acetate copolymer; EVA; FT-IR; infrared spectroscopy; vinyl acetate

TABLE 2 Vinyl Acetate Content (Weight %) Using 1029 cm^{-1} and 2019 cm^{-1} Bands

Sample	Peak Height Measurements					Peak Area Measurements				
	Average	S_r	S_R	r	R	Average	S_r	S_R	r	R
A	2.10	0.04	0.36	0.12	1.02	2.24	0.25	0.44	0.70	1.22
B	4.74	0.11	0.18	0.31	0.50	4.76	0.28	0.41	0.78	1.15
D	5.78	0.12	0.27	0.35	0.76	6.05	0.66	0.70	1.86	1.96
E	8.77	1.16	1.44	3.25	4.03	9.47	2.33	2.33	6.63	6.53
C	16.60	1.89	3.04	5.30	8.52	17.80	7.80	7.80	21.85	21.85
G	18.49	1.51	3.29	4.24	9.21	. . .	. . .	. . .	. . .	. . .
F	27.50	6.50	8.60	18.20	24.08	17.56	2.34	2.92	6.56	8.17

TABLE 3 Vinyl Acetate Content (Weight %) Using 609 cm^{-1} and 1465 cm^{-1} Bands

Sample	Peak Height Measurements				
	Average	S_r	S_R	r	R
A	2.05	0.48	0.92	1.36	2.58
B	4.88	0.50	0.72	1.42	2.00
D	5.60	0.85	1.01	2.38	2.83
E	8.92	1.10	1.27	3.10	3.55
C	15.40	1.27	2.54	3.55	7.10
G	18.62	0.121	2.12	3.39	5.93
F	27.12	2.82	3.58	7.89	10.02

ANNEXES

(Mandatory Information)

A1. MACROS FOR CALCULATING VINYL ACETATE CONTENT OF EVA COPOLYMERS FROM FT-IR SPECTRA USING MOLDED PLAQUES

EVA COPOLYMERS CONTAINING 1.5–6 % VINYL ACETATE:

```
HVA
 NSS=32
 NSB=32
 VEL=30
 NDP=8000
 NTP=8000
 AFN=HG
 TEM=100
 NPR
 SET
 PAU...CLEAR BEAM TO TAKE BACKGROUND...PRESS>< RETURN>
 SCB
 for iii=1 TIL3
 XSP=620
 XEP=560
PAU...PRESS < RETURN>...THEN ENTER THICKNESS (MILS)... PREES < RETURN> AGAIN
 VF0
 VF1=YEP–YSP
 VF1=VF1/VF0
 VFW=VF1 * SLOPE VALUE
 VF2=VF2 + Y-INTERCEPT VALUE
 PRN VF2
 VF3=VF2+VF2
 DSS
 NXT III
 VF3=VF3/3
 OMD
 THE AVERAGE PERCENT VA IS...
 PRN VF3 END
```

EVA Copolymers Containing 0.5–6 Vinyl Acetate

```
 CRT LVA
     CR “% VINYL ACETATE RANGE: 0–6 %”
     cr “CLEAN BEAM TO TAKE BACKGROUND”
     PAU
     SCB
     FOR III<1 TIL 100>
     CR “INSERT SAMPLE”
     PAU
     SCS RAS ABS DSS
     SXP=2100 XEP=1910
     ASS VF0=YEP–YSP
     XSP=1040 XEP=970
     ASS VF1=YEP–YSP
     VF2=VF1/VF0
     VF3=VF2 * 0.3648
     VF3=VF3+0.048
     CR “PEAKHEIGHT 1020/PEAK HEIGHT 2019”
     VF2=
     CR “PERCENT (%) VINYL ACETATE=”
     VF3=
     NXT III
     END
```

FIG. A1.1 Macros for Calculating Vinyl Acetate Content of EVA Copolymers from FT-IR Spectra Using Molded Plaques

A2. SUMMARY OF PYROLYSIS TITRATION AND SAPONIFICATION DATA FOR EVA COPOLYMER REFERENCE MATERIALS

TABLE A2.1 Summary of Pyrolysis Titration and Saponification Data for EVA Copolymer Reference Materials

		I	II	III	IV	V	VI	VII	VIII	IX	X
Lab 1	$\bar{x}$	0.68	1.11	2.80	4.15	4.78	5.84	9.34	14.54	18.46	27.62
Pyrolysis	S	0.038	0.018	0.045	0.115	0.078	0.111	0.140	0.201	0.071	0.088
(DuPont)	CV	5.59	1.62	1.61	2.77	1.63	1.90	1.50	1.38	0.38	0.32
		–	+	+	+	+	0	–	–	–	–
Lab 2	$\bar{x}$	0.61	0.87	2.72	4.07	4.70	5	9.33	14.86	18.90	28.05
Pyrolysis	s	0.003	0.022	0.014	0.022	0.042	0	0.024	0.073	0.468	0.060
(Toyo Soda)	CV	0.49	2.53	0.51	0.54	0.89	1	0.26	0.49	0.25	0.21
		–	–	–	–	–	–	+	–	–	
Lab 3	$\bar{x}$	0.71	0.97	2.77	4.10	4.73	5.81	9.33	14.91	18.78	28.18
Pyrolysis	s	0.030	0.133	0.053	0.080	0.127	0.040	0.074	0.233	0.100	0.269
(DuPont)	CV	4.22	13.71	1.91	1.95	2.68	0.69	0.79	1.56	0.53	0.95
		+	–	–	–	–	–	–	+	0	+
Lab 4	$\bar{x}$	0.80	1.02	2.82	4.19	4.81	5.92	9.46	14.98	19.00	28.27
Saponification	S	0.042	0.046	0.052	0.059	0.049	0.067	0.059	0.061	0.072	0.089
	CV	5.25	4.51	1.84	1.41	1.02	1.13	0.62	0.41	0.38	0.31
		+	+	+	+	+	+	+	+	+	+
	$\bar{x}$	0.70	0.99	2.78	4.13	4.76	5.84	9.36	14.82	18.78	28.03
	$s_{\bar{x}}$	0.079	0.100	0.043	0.053	0.049	0.052	0.064	0.195	0.235	0.288
	$CV_{\bar{x}}$	11.29	10.10	1.55	1.28	1.03	0.89	0.68	1.32	1.25	1.03

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