



Standard Test Method for Copolymerized Ethyl Acrylate In Ethylene-Ethyl Acrylate Copolymers¹

This standard is issued under the fixed designation D 3594; 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 ethylene-ethyl acrylate copolymers containing from 1 to 25 % ethyl acrylate comonomer.

1.2 The values stated in SI units are to be regarded as the standard. (See Practice E 380.)

1.3 *This standard does not purport to address all of the safety problems, 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 similar or equivalent ISO standard.

2. Referenced Documents

2.1 ASTM Standards:

B 883 Terminology Relating to Plastics²

D 1898 Practice for Sampling of Plastics³

E 131 Terminology Relating to Molecular Spectroscopy⁴

E 168 Practices for General Techniques of Infrared Quantitative Analysis⁴

E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods⁵

E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near Infrared Spectrophotometers⁴

E 380 Practice for Use of the International System of Units (SI)⁵

3. Terminology

3.1 See Terminology D 883.

4. Summary of Test Method

4.1 The infrared absorption band at 11.60 μm responds to increases in comonomer content. There is no absorption at this

wavelength when there is no comonomer present. It apparently is unique and characteristic of the copolymer. There is no interference from the monomer at this wavelength.

4.2 The infrared absorption band at 11.60 μm is of medium intensity; consequently, fairly thick films are employed. This is an advantage in that errors in measurements of the thicknesses of films have minimal influence on the analytical result. Film thickness is selected so that not more than 80 % of the infrared energy is absorbed at the analytical wavelength. The approximate thicknesses found to be satisfactory for different concentrations of comonomer are as follows: (1) less than 5 weight % ethyl acrylate = 0.5 mm, (2) 5 to 15 weight % ethyl acrylate = 0.25 mm, and (3) 15 to 25 weight % ethyl acrylate = 0.18 mm. It is necessary first to press a film approximately 0.25 mm in thickness and scan it to observe the absorption intensity unless the approximate ethyl acrylate content is known.

4.3 For the highest precision, the test method requires that the thickness of the sample film be determined accurately.

4.4 The general procedure is to scan the absorption band from 10.50 to 12.50 μm, although a single-point measurement may also be used. This test method describes the use of a scan and employs the base-line method as outlined in 7.2 and the figure illustrating the Base-Line Method for Measuring Absorbance of Practices E 168. A calibration curve is prepared by plotting absorbance per millimetre values versus weight percent ethyl acrylate for several copolymers which have had ethyl acrylate contents established by a fast neutron activation analysis of oxygen content. The ethyl acrylate content of an unknown sample is then obtained by referring the absorbance per millimetre value to the calibration curve.

5. Significance and Use

5.1 Ethyl acrylate is copolymerized with ethylene to produce film, molding, and wire coating resins with improved physical properties. Ethyl acrylate comonomer increases flexibility, stress cracking resistance, toughness, and clarity. A rapid quantitative technique is needed for the evaluation of the amount of ethyl acrylate in a resin for specification purposes because physical properties change rapidly with increasing comonomer content.

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 (Section D20.70.08).

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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 14.01.

⁵ Annual Book of ASTM Standards, Vol 14.02.

5.2 Infrared spectrophotometric analysis, when suitably calibrated, can be used for the measurement of the concentration of comonomer present. Calibration is performed with samples that have been analyzed for oxygen content by fast neutron activation analysis. Oxygen content is converted to ethyl acrylate comonomer content by a simple calculation.

5.3 A purpose of the infrared method of analysis is to provide a procedure for use in quality control analysis. It is a rapid, secondary method of analysis as contrasted with the more expensive and time-consuming fast neutron activation analysis which is the primary, calibrating method.

6. Apparatus

6.1 *Infrared Spectrophotometer*,⁶ capable of spectral resolution⁶ equivalent to that defined by Practice E 275 and exhibited in Fig. 7 of that practice. The instrument should be capable of scale expansion along the wavelength (or wave number) axis.

6.1.1 *Fourier Transform Infrared Spectrophotometer (FT-IR)*, with nominal 4 cm^{-1} resolution.

6.2 *Compression-Molding Press*, small, with platens capable of being heated to 150°C .

6.3 *Metal Plates*, two, 150 by 150 mm or larger, of 0.5-mm thickness with smooth surfaces, chromium plated preferably.

6.4 *Brass Shims*, three, approximately 75 by 75 mm and thicknesses of 0.50 mm, 0.25 mm, and 0.18 mm, with an aperture in the center at least 25 by 38 mm.

6.5 *Micrometer Calipers*, with thimble graduations of 0.001 mm.

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

7. Material

7.1 *Polyethylene Terephthalate or Aluminum Sheets*, 80 by 80-mm, or slightly larger, to cover brass shims.

8. Hazards

8.1 Use gloves when plaques are prepared using a heated press. Take care to avoid burns when handling microscopic slides with the hot plate.

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

9. Sampling

9.1 The copolymer shall be sampled in accordance with Practice D 1898.

10. Calibration

10.1 It is necessary to establish the ethyl acrylate comonomer content of at least eight calibration samples by an independent method. The samples should vary in ethyl acrylate content over the range from near zero to about 25 %. A method that has been found to give high precision and accuracy for

oxygen content is fast neutron activation analysis.⁷ The ethyl acrylate comonomer content, E , is calculated from the oxygen analysis, assuming that all oxygen present is due to ethyl acrylate, as follows:

$$E, \text{ wt } \% = \frac{100 \times X}{31.5} \quad (1)$$

where:

X = oxygen content of unknown copolymers, weight %.

10.2 Set the controls of the infrared spectrometer for quantitative conditions with a good signal-to-noise ratio and satisfactory reproducibility. Use a sufficiently expanded chart scale such that line width can be measured accurately. Use a scanning speed sufficiently slow to give good reproducibility of band shape. Set the slit width narrow enough that there is little distortion of the true band shape. Record the instrument conditions used.

NOTE 2—For the Perkin-Elmer Model 221 Spectrophotometer the following settings are satisfactory: Prism NaCl, slits 2X, slit program 927, attenuator speed 600, amplifier gain adjusted to give good response, chart scale $0.01\text{ }\mu\text{m/mm}$, chart speed $0.5\text{ }\mu\text{m/min}$, electrical balance and suppression adjusted to specifications in instrument manual. Comparable operating conditions should be used when other instruments are employed.

10.3 Scan the films from 10.50 to $12.50\text{ }\mu\text{m}$.

NOTE 3—Films having high gloss may exhibit interference fringes in the infrared spectrum. These fringes make it difficult to establish a base line. In such cases, the film should be abraded slightly to reduce the gloss. This can be performed by lightly rubbing with a clean pencil eraser.

10.4 Measure the baseline absorbance (see Terminology E 131) of each film using a procedure similar to that shown in Fig. 1 of this test method and outlined in 7.2 and the figure illustrating the Base-Line Method for Measuring Absorbance of Practices E 168.

10.5 Measure the thickness of the scanned portion of the films with the micrometer to the nearest 0.005 mm by averaging at least five readings over the area.

10.5.1 Care should be taken in making the micrometer readings not to indent the surfaces of the film by over-tightening the micrometer. The films of high ethyl acrylate are softer and more prone to indentation.

10.6 Calculate the absorbance per millimetre, A , as follows:

$$A = A_b/t \quad (2)$$

where:

A_b = baseline absorbance, and

t = thickness, mm.

10.7 Prepare a calibration graph similar to that shown in Fig. 2 from the values of absorbance per millimetre and weight percent ethyl acrylate comonomer.

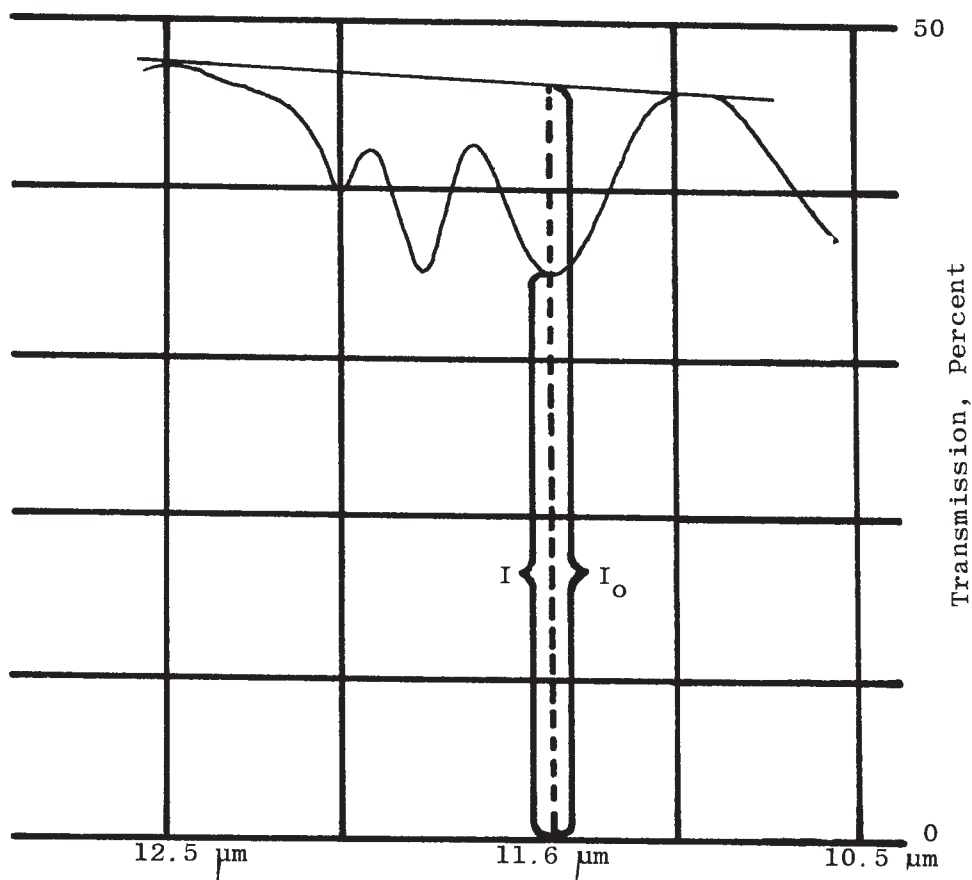
11. Procedure

11.1 *Sample Preparation:*

11.1.1 Preheat the press to 140 to 150°C .

⁶ The Perkin-Elmer Model 221 Spectrophotometer, or equivalent, has been found satisfactory for this purpose.

⁷ Neutron activation analyses are available from Gulf Science and Technology Co., Product Evaluation Dept., P. O. Drawer 2038, Pittsburgh, PA 15230, and Union Carbide Corp., Nuclear Products and Services, P. O. Box 324, Tuxedo, NY 10987.



NOTE 1—Example illustrates baseline location, baseline wavelengths, and calculation absorbance per millimetre.

NOTE 2—The absorbance per millimetre value, A , is applied to the calibration curve to obtain the concentration of ethyl acrylate comonomer.

$$A = \frac{\log_{10} T_0/I}{t}$$

where:

t = thickness, mm.

FIG. 1 Typical Spectrophotometer Scan of Ethylene-Ethyl Acrylate Copolymer

11.1.2 Place a brass shim on a polyethylene terephthalate or cleaned aluminum sheet, which in turn covers a metal plate.

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

11.1.4 Cover with another sheet of polyethylene terephthalate or aluminum and another metal plate.

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

11.1.6 Allow the sample to preheat for 30 s. Apply the full press pressure at 140 to 150°C for 1 min or until all exudation ceases.

11.1.7 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).

11.1.8 Release the pressure and remove the sample.

11.1.9 Using the micrometer, measure the thickness of the sample to ± 0.01 mm at three or more places within the sample beam area. Calculate an average of the three measurements and record in millimetres.

11.2 Spectral Measurements:

11.2.1 Mount the films on the film mounts so that the thickness measured portion is centered in the infrared beam.

11.2.2 Scan the samples slowly from 10.50 to 12.50 μm .

11.2.3 Draw a base line in the manner shown in Fig. 1.

11.2.4 Measure the absorbance at maximum intensity.

12. Calculation

12.1 Calculate the absorbance per millimetre, A , as follows:

$$A = (\log_{10} I_o/I)/t \quad (3)$$

where:

t = thickness, mm.

12.2 Refer the absorbance per millimetre of each sample to the calibration curve to find the value of weight percent ethyl acrylate comonomer.

13. Report

13.1 Report the following information:

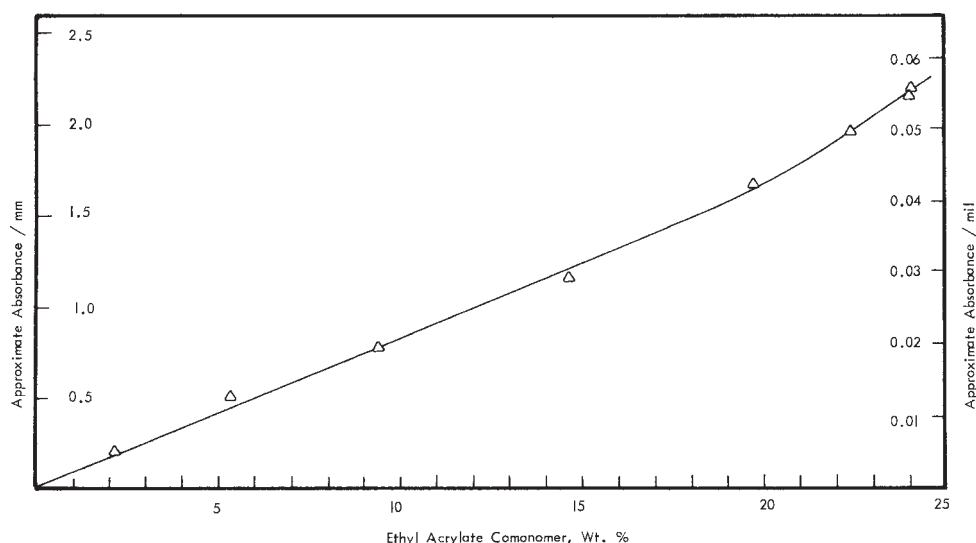


FIG. 2 Example of Typical Calibration Curve for Ethyl Acrylate Comonomer in Ethylene-Ethyl Acrylate Copolymer at 11.6 μm

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

13.1.2 Date of test,

13.1.3 Weight percent ethyl acrylate comonomer,

13.1.4 Any sample or spectral anomalies observed during the measurements, and

13.1.5 Any deviation in procedure from this test method.

14. Precision and Bias (See Practice E 177)⁸

14.1 The following values were determined for the coefficient of variation of this test method, on the basis of an interlaboratory test program involving five laboratories and three materials and assuming duplicate analyses to report an

average value. Based on these interlaboratory tests, the data appear to be linear between 1 and 25 %:

Interlaboratory Coefficient of Variation:

1.70 % of mean value

Interlaboratory Coefficient of Variation:

Sample A (19.2 % ethyl acrylate by neutron activation analysis): 3.3 % of mean value

Samples B and C (6.8 % and 3.2 % ethyl acrylate by neutron activation analysis): 2.3 % of mean value

14.2 Precision and Mean Bias (versus neutron activation analysis):

Sample A + 13.0 % of reference value.

Sample B + 8.8 % of reference value.

Sample C + 3.1 % of reference value.

15. Keywords

15.1 ethyl acrylate; ethylene copolymer; infrared absorption

⁸ Supporting data are available from ASTM Headquarters. Request RR: D20-1063.

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