Designation: D 3900 – 05a

Standard Test Methods for Rubber—Determination of Ethylene Units in Ethylene-Propylene Copolymers (EPM) and in Ethylene-Propylene-Diene Terpolymers (EPDM) by Infrared Spectrometry[1]

This standard is issued under the fixed designation D 3900; 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 These test methods cover the determination of the proportion of ethylene and propylene units in ethylene-propylene copolymers (EPM) and ethylene-propylenediene terpolymers (EPDM) over the range from 35 to 85 mass % ethylene. Four test methods are needed to encompass the variety of commercial polymers that contain additives or polymerized diene units that interfere with the various infrared peaks. Except when interferences are present, all four test methods should give similar results. The test methods appear in the following order:

1.1.1 *Pressed Film Test Methods*:

	Sections
Test Method A—For EPM and EPDM between 35 and 70 mass % ethylene	9-14
Test Method B—For EPM and EPDM between 60 and 85 mass % ethylene, except for ethylene/propylene/1,4-hexadiene terpolymers	15-19
Test Method C—For all EPM and EPDM polymers between 35 and 85 mass % ethylene, using near infrared	20-24

1.1.2 *Cast Film Test Methods*:

Test Method D—For all EPM and EPDM polymers between 35 and 85 mass % ethylene, except for ethylene/propylene/1,4-hexadiene terpolymers	25-32

1.2 These test methods are not applicable to oil-extended EPDM unless the oil is first removed in accordance with Test Method D.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *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.*

2. Referenced Documents

2.1 *ASTM Standards:* [2]

D 297 Test Methods for Rubber Products—Chemical Analysis

D 3568 Test Methods for Rubber—Evaluation of EPDM (Ethylene Propylene Diene Terpolymers) Including Mixtures With Oil

D 4483 Practice for Evaluating Precision for Test Method Standards in the Rubber and Carbon Black Manufacturing Industries

E 168 Practices for General Techniques of Infrared Quantitative Analysis

3. Summary of Test Methods

3.1 *Test Method A*—Pressed films are measured for their infrared absorbance ratios at 8.65/13.85 μm (1156/722 cm^{-1}), and mass percent ethylene is read from a calibration obtained from standard polymers.

3.2 *Test Method B*—Thin pressed films are measured for their infrared absorbance ratios at 7.25/13.85 μm (1379/722 cm^{-1}), and mass percent ethylene is read from a calibration obtained from standard polymers.

3.3 *Test Method C*—Pressed films are measured for their infrared absorbance ratios at 8.65/2.35 μm (1156/4255 cm^{-1}) using near infrared, and mass percent ethylene is read from a calibration obtained from standard polymers.

3.4 *Test Method D*—Ultra-thin cast films on a salt plate are measured for their infrared absorbance ratios at 7.25/6.85 μm (1379/1460 cm^{-1}), and mass percent ethylene is read from a calibration obtained from standard polymers.

4. Significance and Use

4.1 These test methods can be used for determining which EPDM polymers are evaluated in the different compounds in Test Methods D 3568.

[1] These test methods are under the jurisdiction of ASTM Committee D11 on Rubber and are the direct responsibility of Subcommittee D11.11 on Chemical Analysis.

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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.

TABLE 1 Type 1 Precision

NOTE—The midpoint of the range was used to calculate (*r*) and (*R*).

Test Method	Ethylene Range, %	Within Laboratories[A]			Between Laboratories[A]		
		S_r	*r*	(*r*)	S_R	*R*	(*R*)
A	40 to 60	0.569	1.61	3.22	0.857	2.43	4.86
A	65 to 76	0.471	1.33	1.90	1.74	4.92	7.0
B	60 to 66	0.433	1.23	1.95	0.540	1.53	2.43
D (Non OE)	40 to 70	0.856	2.42	4.40	2.11	5.97	10.9
D (OE)	72	2.12	6.00	8.3	3.55	10.0	13.9

[A] S_r = repeatability, standard deviation, in measurement units.
r = repeatability, in measurement units.
(r) = repeatability, (relative) percent.
S_R = reproducibility, standard deviation, in measurement units.
R = reproducibility, in measurement units.
(R) = reproducibility, (relative) percent.

4.2 Differences in ethylene sequence distribution cause differences in crystallinity and green strength at the same ethylene content. Since these are important variables in EPM and EPDM processability and end-use properties, the ethylene content of the rubber should not be used as the sole measurement to determine the suitability of a particular rubber for an intended purpose.

5. Interferences

5.1 Ethylene/propylene/1,4-hexadiene EPDM has an interference at the 7.25-µm (1379-cm^{-1}) peak and should be measured by Test Method A or C.

5.2 Various commercial polymers have interferences due to additives and stabilizers that prevent or hinder the use of the 8.65-µm (1156-cm^{-1}) peak. Test Methods A and C should be applied carefully, or Test Methods B and D should be used as described in the procedure.

5.3 Extender oil, when present, will interfere with all determinations and must be removed before infrared analysis.

6. Apparatus

6.1 *Hydraulic Press*, capable of 200 MPa (29 000 psi) and 150°C.

6.2 *Infrared Spectrophotometer*, double-beam, having a percent transmission specification of ±1 %, or better, at full scale, capable of recording a spectrum over the 2.5 to 15-µm (4000 to 667-cm^{-1} or 400 000 to 66 700-m^{-1}) region for Test Methods A, B, and D. Test Method C requires an instrument capable of recording a spectrum over the 2.0 to 15-µm (2000 to 667-cm^{-1} or 200 000 to 66 700-m^{-1}) region. Any spectrophotometer complying with these requirements may be used. The equipment shall be operated by an experienced analyst according to the manufacturer's directions for optimum performance. Recommended practices for general techniques of infrared quantitative analysis are given in Practices E 168.

6.3 For routine testing, Fourier Transform Infrared (FT-IR) may be used in place of double beam instruments provided the baseline calculation procedures in the Procedures and Calculation Sections of each method are followed. Sample film temperature is lower with FT-IR than double beam instruments, and some partly crystalline polymers may respond differently. Calibration equations (Section 33) may have different mathematical forms with FT-IR.

7. Sampling

7.1 Take precautions to ensure as representative a sample as possible for spectral analysis, since infrared absorption is additive in nature and will be influenced by extraneous materials.

7.2 Where possible, take the sample from a freshly cut surface to avoid testing of a partially oxidized polymer.

8. Precision and Bias [3]

8.1 This precision and bias section has been prepared in accordance with Practice D 4483. Refer to Practice D 4483 for terminology and other statistical calculation details.

8.2 The precision results in this precision and bias section give an estimate of the precision of these test methods with the materials (rubbers) used in the particular interlaboratory program as described below. The precision parameters should not be used for acceptance or rejection testing of any group of materials without documentation that they are applicable to those particular materials and the specific testing protocols that include these test methods.

8.3 A Type 1 (interlaboratory) precision was evaluated. Both repeatability and reproducibility are short term; a period of a few days separates replicate test results.

8.4 The precision of these test methods was determined from an interlaboratory study of several materials by several laboratories on two days as explained below:

Test Method	Ethylene Range, %	No. of Laboratories	No. of Materials
A	40–60	6	3
A	65–76	5	2
B	60–66	4	2
D (Nonoil—Extended Polymer)	40–70	4	4
D (Oil-Extended Polymer)	72	3	1

A test result is a single determination of percent ethylene.

8.5 The results of the precision calculations for repeatability and reproducibility are given in Table 1 for Test Methods A, B, and D.

NOTE 1—Insufficient data were generated for Test Method C to calculate a precision statement. However, extensive use of Test Method C

[3] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D11–1021.

TABLE 2 Type 1 Precision Test Method A[A]

Material	Mean Level, %	Within Laboratories			Between Laboratories		
		S_r	r	(r)	S_R	R	(R)
EPDM–1237	52.4	0.259	0.724	1.38	0.557	1.56	2.98
EPDM–865	56.9	0.225	0.629	1.11	0.688	1.93	3.39
EPDM–2154	58.1	0.197	0.550	0.947	0.766	2.15	3.70
EPDM–306	67.9	0.400	1.12	1.65	0.814	2.28	3.36
EPDM–227	74.4	0.711	1.99	2.67	1.12	3.14	4.22

[A] $p = 9$, $q = 5$, and $m = 2$.

within one laboratory suggests precision levels similar to the other test methods.

8.6 The precision of these test methods may be expressed in the format of the following statements, which use an *appropriate value* of r, R, (r), or (R), to be used in decisions about test results. The appropriate value is that value of r or R associated with a mean level in Table 1 closest to the mean level under consideration at any given time, for any given material, in routine testing operations.

8.7 *Repeatability*—The repeatability, r, of these test methods has been established as the appropriate value tabulated in Table 1. Two single test results, obtained under normal test method procedures, that differ by more than this tabulated r (for any given level) must be considered as derived from different or nonidentical sample populations.

8.8 *Reproducibility*—The reproducibility, R, of these test methods has been established as the appropriate value tabulated in Table 1. Two single test results obtained in two different laboratories, under normal test method procedures, that differ by more than the tabulated R (for any given level) must be considered to have come from different or nonidentical sample populations.

8.9 Repeatability and reproducibility expressed as a percent of the mean level, (r) and (R), have equivalent application statements as above for r and R. For the (r) and (R) statements, the difference in the two single test results is expressed as a percent of the arithmetic mean of the two test results.

8.10 *Bias*:

8.10.1 Bias was established with a round-robin test conducted on six EPM standard polymers by the five U.S. EPM/EPDM manufacturers. Each manufacturer made eight determinations on each of the six standards, using his own infrared method and absorbance/ethylene calibration chart. Each individual calibration chart had been established with infrared tests of C_{14}-tagged pilot plant polymers or equivalent, with confirming tests such as NMR used where necessary.[4]

8.10.2 Ethylene contents of the following ten EPM standards were established via 13C NMR by a consortium of European and North American laboratories.

Standard No.	Mass Percent Ethylene[5]
1	40.1
2	52.4
3	58.6
4	66.8
5	70.8
6	78.6
7	44.8
8	52.6
9	69.5
10	77.5

8.10.3 The standards were each produced in a commercial plant and sizable quantities have been set aside for calibration purposes (see 13.2).

8.11 The precision of Test Method A was determined utilizing FTIR spectrometers from an interlaboratory study of five materials by nine laboratories on two days. The results of the precision calculations for repeatability and reproducibility are given in Table 2. The FTIR spectrometers utilized were calibrated using the percent ethylene values established by 13C NMR.

TEST METHOD A—PRESSED FILM METHOD USING THE 8.65/13.85-μm PEAK RATIO

9. Scope

9.1 This test method covers the determination of percent ethylene in EPM and EPDM between approximately 35 and 70 mass %.

9.2 This test method may be used with caution between approximately 60 and 80 mass % ethylene, but is inferior to Test Method B in precision with many instruments.

9.3 Additives in some commercial polymers will cause an additional absorbance on the shoulder of the 8.65-μm (1156-cm^{-1}) peak at approximately 8.93 μm (1120 cm^{-1}), giving difficulty in drawing the baseline. Where this occurs, Test Method B or D must be used.

9.4 This test method is not intended for oil-extended polymers unless the oil is first removed by extraction.

10. Summary of Test Method

10.1 This test method makes use of the ratio of the absorbance of methyl groups from propylene units at 8.65 μm (1156 cm^{-1}) versus the absorbance of methylene sequences from ethylene units at 13.85 μm (722 cm^{-1}). A series of known EPM polymers is used to prepare a calibration of $A_{8.65}/A_{13.85}$ versus mass percent ethylene.

11. Reagents and Materials

11.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society,

[4] Gardner, I. J., Cozewith, C., Ver Strate, G., "Infrared Determination of Composition of Ethylene-Propylene Copolymers," *Rubber Chemistry and Technology*, Vol 44, September 1971, pp. 1015–1024.

[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D11–1065.