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Standard Test Methods for Rubber, Raw—Determination of 5-Ethylidenenorbornene (ENB) or Dicyclopentadiene (DCPD) in Ethylene-Propylene-Diene (EPDM) Terpolymers[1]

This standard is issued under the fixed designation D6047; 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 content of 5-ethylidenenorbornene (ENB) or Dicyclopentadiene (DCPD) in ethylene-propylene-diene (EPDM) terpolymers. They are applicable to diene contents in the 0.1 to 10 mass % range.

1.2 ENB and DCPD are dienes introduced in ethylene/propylene rubbers to generate specific cure properties. Since high precision for diene content determination has become very important, a Fourier Transform Infrared Spectroscopic (FTIR) method was developed. Diene determination was performed in the past by a refractive index technique.

NOTE 1—The procedures for % ENB and % DCPD differ only in the location in the infrared (IR) of the IR peak being quantified.

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]

D297 Test Methods for Rubber Products—Chemical Analysis

D1416 Test Methods for Rubber from Synthetic Sources—Chemical Analysis (Withdrawn 1996)[3]

D3568 Test Methods for Rubber—Evaluation of EPDM (Ethylene Propylene Diene Terpolymers) Including Mixtures With Oil

D3900 Test Methods for Rubber—Determination of Ethylene Units in Ethylene-Propylene Copolymers (EPM) and in Ethylene-Propylene-Diene Terpolymers (EPDM) by Infrared Spectrometry

D4483 Practice for Evaluating Precision for Test Method Standards in the Rubber and Carbon Black Manufacturing Industries

E168 Practices for General Techniques of Infrared Quantitative Analysis (Withdrawn 2015)[3]

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

2.2 *ANCHA Document:*[4]

Specification for Evaluation of Research Quality Analysis of Infrared Spectra

3. Summary of Test Methods

3.1 The test specimen is molded between two PTFE-coated aluminum or Mylar sheets. The ENB content is determined from its infrared absorbance at 1681–1690 cm^{-1}, a measure of ENB's exocyclic double bond. The DCPD content is determined from its infrared absorbance at 1605–1610 cm^{-1}, a measure of DCPD's monocyclic double bond.

3.2 The second derivative of the absorbance is calculated and ratioed to an internal thickness gage. For ENB the resulting second derivative peak near 1690 cm^{-1} is related to ENB mass fraction by calibrating the instrument with known EPDM standards. For DCPD, the resulting second derivative peak near 1610 cm^{-1} is related to DCPD mass fraction by calibrating the instrument with known EPDM standards.

3.3 Two main steps are performed in this procedure: automatic determination of film thickness and quantification of diene.

[1] These test methods are under the jurisdiction of 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.

[3] The last approved version of this historical standard is referenced on www.astm.org.

[4] "Specification for Evaluation of Research Quality Analysis of Infrared Spectra," *Analytical Chemistry*, ANCHA, Vol 47, No. 11, p. 94a.

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3.4 For oil-extended polymers, the oil must be extracted before diene is determined. Test Methods D1416, Sections 67 through 74 and Test Methods D297 can be used for this purpose.

4. Apparatus

4.1 *Press,* Carver-type, capable of pressing films at 150°C and 10 MPa or higher.

4.1.1 *Primary Mold*—A stainless steel (SS) mold, approximately 400 µm thick, with an opening sized appropriately for the specimen film holder described in 4.4 (typically 2 by 2 cm). The mold should have approximately the same dimensions as the press platens.

4.1.2 *Alternate Mold*—A thinner mold may be used; however, precision may be adversely affected at low diene levels. Test precision should be determined when thinner films are utilized. Example: a 127-µm (0.005-in) SS shim with a 15- by 35-mm opening may be used for the simultaneous determination of ethylene (Test Methods D3900) and diene.

4.1.3 *Alternative Mold for Low Molecular Weight (Liquid) EPDM Terpolymers*—For liquid EPDM a ring washer 22 mm OD by 16 mm ID (7/8 in OD by 5/8 inch in ID) 400 µm thick is used as a apacer between salt plates (NaBr, NaCl) to set a fixed path length. The spacer is sized to cover only the outer edge of the salt plate.

4.2 *Sheets for Molding,* either PTFE-coated aluminum sheets or Mylar, Type A, 36 µm thick or less.

4.3 *Specimen Film Holders*—Films may be molded, cut, and transferred to a film holder. Magnetic film holders are ideal. Alternatively, a mold sized to fit in the spectrometer specimen compartment, with an appropriate size opening may be used to support the film without removal after pressing.

4.4 *Infrared Fourier Transform Spectrophotometer*—An instrument capable of measuring absorbances in the range 400 to 6000 cm^{-1} with a transmittance specification (accuracy) of ± 1 % *T* or better. The instrument should be capable of spectral resolution of 2 cm^{-1} (see "Specification for Evaluation of Research Quality Analysis of Infrared Spectra"). A deuterated triglycine sulfate (DTGS) detector should be used. The instrument must be operating in accordance with Practices E168. Practices E932 and E1421 are other important references.

4.4.1 The instrument should be capable of spectral accumulation, averaging, and subtracting capabilities. Water is the primary source of interference in this method. Methods, physical and electronic, that minimize moisture level and variation are required to obtain the highest precision. The preferred method is use of an instrument equipped with a dry gas purge and a specimen shuttle, which permits alternating and repetitive collection of single beam specimen and background spectra (see Section 6). Alternatively, should a specimen shuttle be unavailable, careful purging of the sample compartment with dry nitrogen can yield satisfactory results. High precision of calibration standard data is indicative of adequate purging. When moisture interference is not removed by purging, spectral subtraction of water vapor may be used. A procedure for further method development is described in Appendix X1.

5. Test Specimen Preparation

5.1 *Primary Method*—Place an appropriate amount of the test specimen to fill the mold opening (typically 0.2 to 0.5 g) between two PTFE-coated aluminum or Mylar sheets in the mold. Place the mold between the press platens heated to 125 ± 5°C and apply approximately 10 MPa or higher pressure for 60 ± 10 s.

NOTE 2—High molecular weight polymers may require higher temperatures and pressures to obtain a good test specimen.

5.1.1 Cool the specimen to ambient temperature. Cut, if necessary, a piece of film to the appropriate size to cover the specimen holder window. Detach the specimen film from the aluminum or Mylar and position it on the spectrophotometer sample holder window.

5.2 *Alternate Method*—When using the thinner mold described in 4.1.2, place a small piece (0.04–0.06 g) of test specimen in the mold opening between two Mylar sheets and press as in 5.1. Remove the mold from the press, turn it over and press it again, then remove the mold from the press and cool it to ambient temperature. When cool, carefully remove the Mylar sheets, allowing the specimen film to remain attached to the mold.

5.3 *Alternate Method for Liquid Sample Film Preparation*—Place a washer (described in 4.1.3) on top of a salt plate. Place a small amount (about 0.3 g) of liquid EPDM polymer in the center of the washer filling the hole completely. Place a second salt plate on top of the filled washer. Gently place a 1 kg weight on top of the salt plate/washer assembly and allow the weighted assembly to sit for 2 to 3 min. (For viscous samples it may be necessary to warm the sample prior to pressing.) Remove the weight and allow to cool, if necessary. Wipe off any excess material that may have been pressed out of the assembly. Hold the assembly up to the light and inspect for bubbles or voids, or both. Should there be imperfections, repeat the sample preparation with a larger amount of sample.

6. Spectral Acquisition

6.1 *With a specimen shuttle:*

6.1.1 *Data acquisition parameters:*

6.1.1.1 Resolution: 2 cm^{-1}.

6.1.1.2 Scans/Scan time: Total scan time required, split between specimen and background, is about 90 s.

6.1.2 Place the test specimen in the specimen compartment, allow purge to reestablish, and in alternating fashion, collect single beam specimen (*P*) and "empty specimen compartment" (P_0) spectra. Eight passes of the shuttle should be sufficient (eight specimen and eight empty compartment collections), collecting four scans at each position.

6.1.3 Calculate the specimen absorbance spectrum as minus the $\log_{10}$ of the ratio of the accumulated single beam specimen spectrum to the single beam empty specimen compartment spectrum:

$$A = -\log_{10}(P/P_0) \quad (1)$$

6.2 *Without a specimen shuttle:*

6.2.1 *Data acquisition parameters:*

6.2.1.1 Resolution: 2 cm^{-1}

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6.2.1.2 Scans/Scan Time: Background scan: 32 scans, 20 s total; specimen scan: 32 scans, 20 s total.

6.2.2 Establish dry atmosphere inside empty specimen compartment and collect "empty specimen compartment" (P_0) spectra.

6.2.3 Place test specimen in the specimen compartment and re-establish a dry atmosphere inside the specimen compartment. Collect single beam specimen spectra (P) and calculate the specimen absorption spectra (A) as described in 6.1.3.

7. Calibration of the Spectrophotometer

7.1 Obtain a series of known standards covering the 0–10 mass % diene range. Calibration may be based on secondary standards qualified by other laboratories using this method or, more generally, by primary standards whose diene content is well known. Primary standards may be established via use of ^{1}H Nuclear Magnetic Resonance (NMR), in conjunction with other techniques. The calibration standards employed in the development of this method were determined by a combination of refractive index and ^{1}H NMR (utilizing samples dissolved in deuterated o-dichlorobenzene at 120°C; the ENB assignment was based exclusively on the exocyclic olefinic protons of ENB). The use of four standards at the 0 (copolymer), 2, 5, and 10 mass % levels are the minimum recommended.[5]

7.2 Using the procedures in Section 6, acquire a minimum of five absorbance spectra for each of the calibration standards described in 7.1. Several repetitions on separate specimens of each standard may be averaged to improve the accuracy of the calibration.

7.3 Using the procedures in Section 8, calculate the ratio of the second derivative diene peak height to the internal thickness gage for each of the spectra acquired.

7.4 Calculate a linear calibration line (diene peak ratio versus assigned values of the standards in mass % diene) by computing a slope and intercept using standard least squares linear regression techniques.

8. Diene Determination

8.1 Prepare the specimen film as described in Section 5.

8.2 Collect a single absorbance spectrum based on the procedure in Section 6.

8.3 *Determination of Film Thickness:*

8.3.1 Correct the offset of the spectrum by bringing the lowest point of the spectrum to zero (that is, determine the minimum absorbance in the spectrum and offset the spectrum to bring the absorbance to zero).

8.3.2 To determine the film thickness automatically, calculate the difference of the absorbance at the basepoint near 2703 cm^{-1} minus the absorbance at the basepoint near 2750 cm^{-1}. If the net difference is positive, the sample belongs to Group 1. Otherwise, it belongs to Group 2 (see Fig. 1).

8.3.2.1 Group 1: Thickness gage is the net absorbance difference between 2708 cm^{-1} (isooptic point) and 2450 cm^{-1} (anchor point) (see Fig. 2).

8.3.2.2 Group 2: Thickness gage is the net absorbance difference between 2668 cm^{-1} (isooptic point) and 2450 cm^{-1} (anchor point) (see Fig. 3).

8.4 *Diene Quantitation:*

8.4.1 Normalize the total spectrum to one optical density (OD) by multiplying the total spectrum by $1/A$, where A is the net absorbance at thickness gage.

8.4.2 *ENB Calculation*—Calculate the peak height (in OD) of the second derivative (the second derivative algorithm should use at least nine point smoothing) between 1681 and 1690 cm^{-1} by applying the following formula:

$$\text{Peak Ht} = A_{1681} - (0.75\,A_{1688} + 0.25\,A_{1689}) \quad (2)$$

This will be called the ENB peak height throughout this procedure. Fig. 4 gives a visual impression of a typical second derivative spectrum of EPDM.

8.4.3 Use the calibration developed in Section 8.4.2 to compute a mass % ENB for the sample, employing the principle that only interpolation (and not extrapolation) is used. If the ENB peak height determined in 8.4.5 is lower than the ENB peak height of the lowest, or higher than the ENB peak height of the highest calibration standard, then the ENB mass % should be reported as "out of range for the calibration employed."

8.4.4 *DCPD Calculation*—Calculate the peak height (in OD) of the second derivative (the second derivative algorithm should use nine point smoothing) between 1601 and 1620 cm^{-1} by applying the following formula:

$$Peak\ Ht = (A_{1601} - A_{1610}) \quad (3)$$

This will be called the DCPD peak height throughout this procedure.

8.4.5 Use the calibration developed in Section 8.4.4 to compute a mass % DCPD for the sample, employing the principle that only interpolation (and not extrapolation) is used. If the DCPD peak height determined in 8.4.5 is lower than the DCPD peak height of the lowest, or higher than the DCPD peak height of the highest calibration standard, then the DCPD mass % should be reported as "out of range for the calibration employed."

9. Report

9.1 Report the following information:

9.1.1 ENB content to two decimal places:

ENB = xx.xx mass %

DCPD = xx.xx mass %

9.1.2 Type of mold utilized,

9.1.3 Whether spectra were acquired with or without a specimen shuttle.

[5] The sole source of supply for the ENB standards known to the committee at this time is ExxonMobil Chemical Polymer Laboratories, P.O. Box 5200, Baytown, TX 77520. The sole source of supply for the DCPD standards known to the committee at this time is UniRoyal Chemical Company, Chemical Characterization Lab, Benson Road, Middlebury, CT 06749. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

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