Designation: D 6814 – 02ε1

Standard Test Method for Determination of Percent Devulcanization of Crumb Rubber Based on Crosslink Density[1]

This standard is issued under the fixed designation D 6814; 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.

ε[1] NOTE—Sections 4, 8 and 10 were editorially updated in December 2002.

1. Scope

1.1 This classification describes the procedure for determining percent devulcanization from crosslink density measurements of devulcanized rubber and control crumb rubber in the laboratory. Percent devulcanization is a quantitative determination.

1.2 The values stated in SI units are the standard.

1.3 *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:*

D 297 Test Methods for Rubber Products—Chemical Analysis[2]

3. Terminology

3.1 *Definitions:*

3.1.1 *rubber, n*—natural or synthetic elastomer that has been chemically crosslinked/vulcanized to enhance its useful properties.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *devulcanization, n*—a process of breaking down chemical crosslinks in cured rubber.

4. Summary of Test Method

4.1 The crumb rubber sample is extracted in hot acetone per Test Methods D 297 and dried at 70 ± 2°C in a forced-ventilating air oven for 16 ± 1 h. The dried crumb rubber is swollen in a solvent (for examples of polymer-solvent pairing, see Appendix X1) with reagent grade purity, selection based on rubber type, for 24 h at room temperature. The solvent is replaced with fresh solvent three times during the swelling process. After swelling, the solvent is wiped quickly from the surface of the swollen crumb rubber using a clean paper towel. Measure the weight of the swollen sample in a preweighted and tared weighing bottle with closure. Dry it at 70 ± 2°C in a forced-ventilating air oven for 16 ± 1 h. Cool to room temperature in a desiccator and weigh. The density of the dried crumb rubber sample is measured using methanol instead of distilled water as an immersion liquid because of good wettability of methanol to rubber. Using the swelling ratio, polymer density, polymer-solvent interaction parameter, and the Flory-Rehner equation,[3] the crosslink density of the sample is calculated. Percent devulcanization is calculated using crosslinking density data of devulcanized crumb rubber and the control.

5. Significance and Use

5.1 It is important for rubber compounders to know the extent of devulcanization a rubber might have undergone during recycling. It allows the compounder to determine if more curing agents are needed during mixing of devulcanized rubber when used either as partial replacement or stand alone.

6. Apparatus

6.1 *Analytical Balance*, precision 0.0001 g.

6.2 *Extraction Apparatus*, glass conical flask, extraction cup, and condenser.

6.3 *Beaker*, 50 mL.

6.4 *Oven*, temperature controlled within ±2°C.

6.5 *Paper Towel*.

6.6 *Weighing Bottles with Caps*.

7. Reagents and Materials

7.1 The following reagents are used:

7.1.1 *Acetone*, USP grade,

7.1.2 *Toluene*, ACS grade, and

7.1.3 *Methanol*, ACS grade.

7.2 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that

[1] This test method is under the jurisdiction of ASTM Committee D11 on Rubber and is the direct responsibility of Subcommittee D11.26 on Rubber Recycling.

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[2] *Annual Book of ASTM Standards*, Vol 09.01.

[3] Flory, P. J., *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953, Chap. 13 (Equation 38), p. 578.

all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[4] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8. Procedure

8.1 Weigh 10 ± 0.5 g of crumb rubber.

8.2 Extract the sample with hot acetone for 16 h using the extraction apparatus per Test Methods D 297 to eliminate the acetone-solubles.

8.3 Dry the solids in an oven for 16 ± 1 h at 70 ± 2°C in a forced-ventilating air oven. Discard the acetone.

8.4 Cool the sample to 23 ± 2°C.

8.5 Pour 200 ± 10 cm^3 of toluene onto the dried sample (different rubber based crumb rubber may need different solvent). See Appendix X1. Let the sample swell at room temperature for 72 h. Do not stir during the swelling process. Replace the solvent with fresh solvent every 24 h during the swelling period.

8.6 Remove liquid from the swollen sample and "pat dry" quickly with a soft paper towel to remove excess liquid.

8.7 Weigh the sample in a closed, tared, weighing bottle and record the weight of the swollen sample.

8.8 Remove the cap from the weighing bottle and put both the cap and the swollen rubber into a 70 ± 2°C forced-ventilating air oven overnight.

8.9 Remove the dried sample bottle and cap from the oven, immediately recap the bottle and allow to cool at room temperature. Weigh the closed bottle and calculate the weight of dried sample.

8.10 For density measurement, weigh 0.5 ± 0.1 g of the dried crumb rubber sample up to 0.0001 g on a tared aluminum foil for easy handling of sample. Record the weight. The difference between this weight and tared weight of aluminum foil is the weight of dry sample.

8.11 Take out the sample from the balance with aluminum foil. Wet the sample with several drops of methanol. Transfer the wet sample to the weighing pan of the balance that is tared and immersed in methanol. Record the weight of the sample in methanol.

8.12 Calculate the density of dry crumb rubber using the equation that is given below.

$$\text{Density at } 23 \pm 2°C \text{ in g/cm}^3 = 0.7913 \times A/(A - B) \quad (1)$$

where:

A = weight of specimen measured in air, g,
B = weight of specimen measured in methanol, g, and
0.7913 = density of methanol at 23 ± 2°C in g/cm^3.

9. Calculation of Crosslink Density (ν_e)

9.1 The Flory-Rehner[3] equation is used for calculation of crosslinking density.

$$\nu_e = \frac{-[ln(1 - V_r) + V_r + \chi_1 V_r^2]}{[V_1(V_r^{1/3} - V_r)/2]} \quad (2)$$

where:

ν_e = effective number of chains in a real network per unit volume,
V_r = volume fraction of polymer in a swollen network in equilibrium with pure solvent and is calculated as:

$$V_r = \frac{\text{Weight of dry rubber / density of dry rubber}}{\frac{\text{Weight of dry rubber}}{\text{Density of dry rubber}} + \frac{\text{Weight of solvent absorbed by sample}}{\text{Density of solvent}}} \quad (3)$$

NOTE 1—The difference between the weights of swollen and dried sample are calculated from Procedures 7 and 9.

where:

χ_1 = polymer-solvent interaction parameter, see Appendix X1, and
V_1 = molecular volume of solvent.

10. Calculation of Percent Devulcanization

10.1 See Eq 4.

$$\% \text{ Devulcanization} = \left[1 - \left(\frac{\text{Crosslink density of devulcanized rubber}}{\text{Crosslink density of control crumb rubber}}\right)\right] \times 100 \quad (4)$$

where the control crumb rubber is the compound before duvulcanization.

11. Precision and Bias

11.1 Round-robin testing will be conducted and precision and bias statements will be balloted for inclusion when testing is completed.

12. Keywords

12.1 devulcanization; rubber

[4] Reagent Chemicals, American Chemical Society Specifications, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see Analar Standards for Laboratory Chemicals, BDH Ltd., Poole, Dorset, U.S., and the United States Pharmacopeia and National Formulary, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

APPENDIX

(Nonmandatory Information)

X1. EXAMPLE OF SOLVENT FOR SWELLING CRUMB RUBBER

X1.1 Solvents for swelling crumb rubber are listed in Table X1.1.

TABLE X1.1 Example of Solvents for Swelling Crumb Rubber[A]

Polymer	Solvent	Interaction Parameter[B]
Cis-polyisoprene	Toluene	0.391 (at 25°C)
	Benzene	0.437 (at 25°C)
Polyisobutylene	Toluene	0.557 (at 25°C)
	Cyclohexane	0.436 (at 25°C)
Butadiene-styrene	Benzene	0.442 (at 25°C)
(7.15:28.5)	Cyclohexane	0.489 (at 25°C)
Butadiene-acrylonitrile		
82:18	Benzene	0.390 (at 25°C)
70:30	Benzene	0.486 (at 25°C)
61:39	Benzene	0.564 (at 25°C)

[A] Rodriguez, F., *Principle of Polymer Systems*, 2nd Ed., McGraw-Hill, New York, 1982, Ch. 2.

[B] For calculation of other interaction parameters, refer to the same reference as Footnote A.