INTERNATIONAL

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Standard Test Method for *In Situ* Determination of Network Parameters of Crosslinked Ultra High Molecular Weight Polyethylene (UHMWPE)[1]

This standard is issued under the fixed designation F2214; 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 describes how the crosslink density, molecular weight between crosslinks, and number of repeat units between crosslinks in ultra high molecular weight polyethylene (UHMWPE) crosslinked by ionizing radiation or by chemical means can be determined by measuring the swelling ratio of samples immersed in o-xylene. Examples of experimental techniques used to make these measurements are discussed herein.

1.2 The test method reported here measures the change in height of a sample specimen while it is immersed in the solvent. Volumetric swell ratios assume that the sample is crosslinked isotropically, and that the change in dimension will be uniform in all directions. This technique avoids uncertainty induced by solvent evaporation or temperature change.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

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

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *crosslink density, v_d*—the theoretical average number of crosslinks per unit volume [mol/dm^3].

3.1.2 *molecular weight between crosslinks, M_c*—the theoretical average molecular weight between crosslinks [g/mol].

3.1.3 *swell ratio, q_s*—the ratio of the volume of the sample in an equilibrium swollen state to its volume in the unswollen state.

4. Summary of Test Method

4.1 The height of a cubic specimen is measured, and the specimen is placed in a dry chamber. A selected solvent is chosen according to the Flory network theory and is introduced into the chamber. The chamber is heated to the reference temperature. The sample height is monitored as a function of time until steady state (equilibrium) is achieved. The swell ratio is calculated from the final steady state (equilibrium) height and the initial height.

5. Significance and Use

5.1 This test method is designed to produce data indicative of the degree of crosslinking in ultra high molecular weight polyethylene that has been crosslinked chemically or by ionizing radiation.

5.2 The results are sensitive to the test temperature, solvent, and method used. For the comparison of data between institutions, care must be taken to have the same test conditions and reagents.

5.3 The data can be used for dose uniformity analysis, fundamental research, and quality assurance testing.

6. Apparatus

6.1 The apparatus shall include any device that allows a non-invasive measurement of the change in one dimension of the sample as it swells in the solvent. This measurement could include, but is not limited to:

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[1] This test method is under the jurisdiction of ASTM Committee F04 on Medical and Surgical Materials and Devices and is the direct responsibility of Subcommittee F04.15 on Material Test 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.

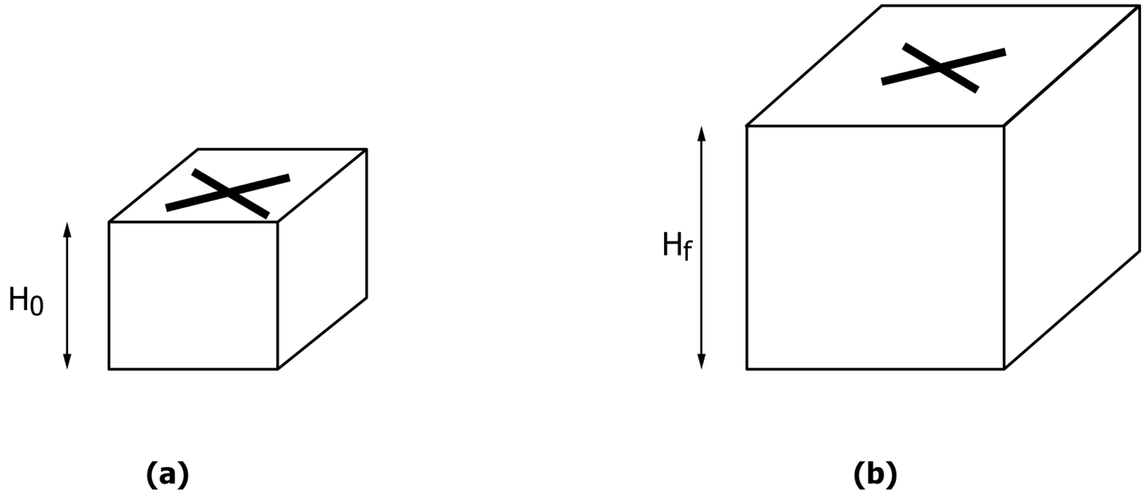

FIG. 1 Marked Measurement Direction Before (a) and After (b) Swelling

6.1.1 Mechanical measurements, such as linear variable displacement transducers (LVDTs).

6.1.1.1 If a mechanical probe is used, it must be constructed of a material that exhibits little thermal expansion, such as quartz or ceramic.

6.1.2 Optical measurements, such as cameras or laser micrometers.

6.1.2.1 Optical measurements should be insensitive to any refractive index changes in the UHMWPE sample, given the changing temperature of the system.

6.1.3 Inductive measurements, such as proximity sensors. Inductive measurements must be insensitive to temperature or solvent composition.

6.2 The sensitivity of the measurement shall be 1 % of the initial height of the sample, H_0. An uncertainty analysis has demonstrated that this sensitivity will produce a relative error in crosslink density less than 10 % for samples swollen to a fraction 50 % beyond their initial height. Thicker samples will allow a less sensitive measurement.

6.3 The solvent in the temperature chamber shall be able to reach a temperature of at least 150 °C, with an expanded uncertainty of ±1 °C. Gradients shall not exceed 0.2 °C/cm (NB o-xylene boils at 144 °C).

6.4 The smallest chamber dimension shall be at least three times the size of the largest initial sample dimension.

6.5 The volume of the chamber shall be at least ten times that of the sample. The chamber should be sufficiently sealed as to prevent gross solvent evaporation during the course of the experiment (typically 3 to 8 h, depending on the crosslink density).

NOTE 1—The data acquisition software should collect both sample dimension and temperature at a rate of at least 0.1 Hz.

7. Reagents

7.1 *Ortho-Xylene (o-xylene),* ≥98 %, boiling point 144 °C.

7.2 *Anti-oxidant,* 2,2'-methylene-bis (4-methyl-6-tertiary butyl phenol).[3]

8. Safety Precautions

8.1 O-xylene is toxic and flammable, and should be handled only with heat and chemically protective laboratory gloves. The swelling apparatus should ideally be placed inside a vented fume hood, or vented with an elephant trunk should space considerations be an issue. Do not inhale the o-xylene vapors, as dizziness or a headache could result.

8.2 Irganox 1010, the antioxidant, is identified by the manufacturer as an irritant and an inhalation hazard.

9. Test Specimens

9.1 At least three specimens with a minimum sample height of 500 µm should be machined. The top and bottom surfaces should be parallel and smooth. The width and length (or diameter, in the case of cylindrical samples) should be less than one third the size of the sample chamber (see 6.4). The height-to-width aspect ratio should be at least 1:2 to minimize buckling, with 1:1 preferred. The machining should be performed so as to minimize thermal degradation of the samples.

9.2 *Orientation of Samples*—Given that the swelling behavior can depend on molecular alignment induced by processing conditions, the test specimens should be machined so that the relevant processing direction can be easily identified. The samples can then be oriented in the swelling apparatus relative to the molding direction (that is, perpendicular to the extrusion of compression molding direction). The specimens can be marked as shown in Fig. 1 to aid in sample alignment.

9.3 If the radiation dose can differ from the surface to the center of the sample, the location in the part where the

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[3] Trade name: Irganox 1010 has been found satisfactory for this purpose. Available from Ciba-Geigy, 540 White Plains Rd., P.O. Box 2005, Tarrytown, NY 10591-9005.

specimen is taken should be noted, as the swell ratio will depend on the radiation dose.

10. Procedure

10.1 Add approximately 0.5 to 1 % (mass fraction) of the antioxidant to the o-xylene to make a stock solution.

10.2 The initial sample height should be measured with a resolution of 1 % of the sample height using a micrometer. This value should be recorded. The measurement direction on the sample can be indicated with a permanent marker. An example is shown in Fig. 1.

10.3 The sample should be pre-wet with o-xylene, then quickly placed in the dry chamber with the sample correctly oriented as marked in 10.2.

10.4 The initial sample dimension, as determined with the measurement system of the instrument described in 6.1, should be recorded.

10.5 Start recording the sample dimension at a minimum rate of one point every 10 s.

10.6 Introduce the o-xylene stock solution into the chamber at a slow rate to prevent disturbing the sample.

10.7 Raise the temperature of the solvent in the chamber to 130 ± 1 °C.

10.8 Continue to monitor the temperature and sample dimension until equilibrium is achieved (within ±10 µm) over a period of 15 min.

10.9 Decrease the temperature to below 50 °C. Discard the o-xylene in an environmentally responsible manner, and clean the sample cell thoroughly.

10.10 Examine the sample after the test is complete. If it has shown signs of cracking, or is yellowed, thermal degradation is likely to have occurred. This data will be suspect and should be discarded.

11. Calculation of Swell Ratio

11.1 The swell ratio, q_s, is computed as indicated from the height measurement:

$$q_s = (V_f/V_0) = (H_f/H_0)^3 \quad (1)$$

where:

V_f = final volume,
V_0 = initial volume,
H_f = final height, and
H_0 = initial height.

NOTE 2—This calculation assumes that the sample is isotropic.

12. Calculation of Crosslink Density and Molecular Weight Between Crosslinks

12.1 Given the steady state swell ratio, q_s, of a polymer immersed in a specific solvent at a particular temperature, the crosslink density, molecular weight between crosslinks, and number of crosslinks/chain can be computed if one knows the Flory interaction parameter, χ_1, for the polymer-solvent system.

12.2 From Flory's network theory, which explains the swell ratio of a polymer-solvent system as a competition between elastic forces and forces derived from the free energy of mixing, the following expression is derived for the crosslink density, ν_d, as a function of the steady state swelling ratio, the Flory interaction parameter, and φ_1, the molar volume of the solvent.[4,5]

$$\nu_x = -\frac{ln\,(1 - q_s^{-1}) + q_s^{-1} + \chi_1 q_s^{-2}}{\varphi_1\,(q_s^{-1/3} - 0.5q_s^{-1})} \quad (2)$$

12.2.1 The expression in Eq 2 assumes a three-dimensional network composed primarily of "H-bonding," or the formation of crosslinks along the main chain rather than at the chain ends. Additionally, network entanglements may partially contribute to the refractive forces. Thus the calculated crosslink density will account for these contributions as well. The expression in Eq 2 has been shown to be valid for swelling ratios up to q = 10, or M_c >10 000 g/mol.

12.3 The expression in Eq 2 can be reduced to calculate the molecular weight between crosslinks, M_c, where $\bar{\nu}$ is the specific volume of the polymer.

$$M_c = (\bar{\nu}\nu_d)^{-1} \quad (3)$$

12.4 For polyethylene in o-xylene at 130 °C, the following approximate parameters shall be used:

Parameter	Value
χ_1 (o-xylene-PE, 130 °C)	$0.33 + 0.55/q_s$
φ_1 (o-xylene) [cm^3/mol]	136
$\bar{\nu}^{-1}$ [g/dm^3]	920

13. Report

13.1 Report the following information:

13.1.1 Complete identification of the sample,

13.1.2 Solvent and temperature used,

13.1.3 Initial heights of the samples,

13.1.4 Final heights of the samples,

13.1.5 Calculated swell ratio, crosslink density, and molecular weight between crosslinks for all the specimens, and

13.1.6 The orientation of the specimens relative to the principle processing direction (that is, ram extrusion direction, or compression molding direction).

14. Precision and Bias

14.1 *Precision*—The precision of this test method is based on an interlaboratory study of ASTM F2214, Standard Test Method for In Situ Determination of Network Parameters of Crosslinked Ultra High Molecular Weight Polyethylene (UHMWPE), conducted in 2022. Six volunteer laboratories were asked to test four different materials. Every "test result" represents an individual determination, and all participants were instructed to report three replicate test results for each material. Practice E691 was followed for the design of study

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[4] Flory, P. J., *Principles of Polymer Chemistry*, Ithaca and London, Cornell University Press, 1953.

[5] Flory, P. J., and Rehner, J., "Statistical mechanics of cross-linked polymer networks. II. Swelling," *J. Chem. Phys.*, Vol 11, No. 11, 1943, pp. 521–526.