Designation: D8154 – 24

Standard Test Methods for ^{1}H-NMR Determination of Ketone-Ethylene-Ester and Polyvinyl Chloride Contents in KEE-PVC Roofing Fabrics[1]

This standard is issued under the fixed designation D8154; 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 pertains to the determination of the relative contents of ketone-ethylene-ester (KEE) and polyvinyl chloride (PVC) after their extraction from reinforced roofing membranes or fabrics. Based on proton nuclear magnetic resonance spectroscopy (^{1}H-NMR), the method allows for the quantification of PVC with respect to an internal standard. The KEE content is then obtained by difference. The test method is not applicable to membranes or blends that contain high molecular weight polymers other than PVC and KEE.

1.2 *Units*—The values stated in SI units are to be regarded as standard. No other units of measurement are included in this 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.4 *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]

D1079 Terminology Relating to Roofing and Waterproofing

D6754/D6754M Specification for Ketone Ethylene Ester Based Sheet Roofing

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*—Terminology D1079 and Specification D6754/D6754M shall apply to this test method.

4. Summary of Test Method

4.1 *Test Methods*—There are two related test methods to quantify PVC and KEE in roofing fabrics. In both methods, the polymer blend is extracted from the fabric and purified by a series of dissolution, centrifugation, and precipitation. After drying, the blend is dissolved in deuterated tetrahydrofuran along with a ^{1}H-NMR internal standard. In Method A, PVC content is quantified by comparing its ^{1}H-NMR signal with that of the internal standard, and KEE is obtained by difference. Method B adds to Method A a calibration curve the slope of which providing for a correction factor. This correction factor is applied to the polymer content obtained by Method A to provide for greater precision on the PVC and KEE contents.

5. Significance and Use

5.1 Determination of the percentage of KEE compound in sheet roofing is of concern to many specifiers and building owners. Method A, the faster method, is best used for quality control. Method B may apply better to research and development or investigative work.

6. Interferences

6.1 The NMR analysis of the polymer blend extracted from the sheet roofing is sensitive to impurities, including plasticizer, filler, reinforcement, and trace solvent (other than the NMR solvent). The procedure here is meant to purify the blend for proper analysis.

7. Equipment and Apparatus

7.1 *Glassware.* Erlenmeyer flask and stopper, 125 mL. Weighing bottle, 25 mL.

7.2 *Porcelain ware.* Büchner funnel, 10 cm in diameter.

7.3 *Platform shaker.* Must accept 125 mL Erlenmeyer, and allow for swirling at 120 to 150 rpm.

[1] This test method is under the jurisdiction of ASTM Committee D08 on Roofing and Waterproofing and is the direct responsibility of Subcommittee D08.18 on Nonbituminous Organic Roof Coverings.

Current edition approved Jan. 1, 2024. Published January 2024. Originally approved in 2017. Last previous edition approved in 2017 as D8154 – 17. DOI: 10.1520/D8154-24.

[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.

7.4 *Metal spatula.* To stir the suspension during the precipitation step.

7.5 *Pasteur pipettes.* To transfer solubilized polymer and solvent from one flask to another.

7.6 *Centrifuge.* Capable of 10 000 RPM.

7.7 *Centrifuge tubes.* 50 mL. Must be resistant to THF, for example, fluorinated ethylene propylene.

7.8 *Watch glass.* To dry polymer in the oven.

7.9 *Vacuum oven.* Adjustable to 65 ± 2 °C.

7.10 *Vacuum pump.* To provide for 100 kPa of vacuum in the oven.

7.11 *Balance.* Sensitive to 0.000001 g (1 microgram).

7.12 *NMR sample tubes.* 5 mm in diameter.

7.13 *NMR Fourier Transform Spectrometer.* Equipped with a proton probe. 400 MHz field strength or higher is recommended.

8. Reagents and Materials

8.1 *Water.* 500 mL, and crushed ice, 1 kg, for an ice bath.

8.2 *Whatman filter paper No. 2.* For the Bückner funnel.

8.3 *Lint-free paper towel.* To blot sample dry of solvent.

8.4 *Hexane.* Technical grade, 60 mL.

8.5 *Tetrahydrofuran (THF).* Technical grade, 150 mL.

8.6 *Methanol.* Technical grade, 450 mL. Maintained near 5 °C in an ice bath.

8.7 *Deuterated tetrahydrofuran (THF-d8).* 99.5 % pure or better.

8.8 *1,2,4,5-Tetrachloro-3-nitro-benzene.* Certified reference material, TCNB, 99.7 % pure or better.

8.9 *Polyvinyl chloride (PVC) powder.* For calibration in Method B. It is ideally obtained from the membrane producer. If this fails, PVC could be obtained from a primary source, that is, a raw material producer, ascertaining that the product source and grade are the same as those used in actual sheet roofing production. PVC could be obtained for instance from oxyvinyls. For best precision in polymer quantification, the raw materials for calibration samples should be those used in the membrane fabrication.

8.10 *Ketone ethylene ester (KEE) pellets.* For calibration in Method B. It is ideally obtained from the membrane producer. If this fails, KEE could be obtained from a primary source, that is, DuPont™ (Elvaloy® polymer), ascertaining that the product grade is that used in the sheet roofing fabrication.

9. Hazards

9.1 *Chemical Hazards*—Several solvents are used in this test method, including methanol, THF, hexane, along with TCNB. Check their material safety data sheet to identify specific hazards. Follow local regulations for proper disposal of spent chemicals.

9.2 *Centrifugation*—Centrifugation of dissolved sheet roofing involves high speeds and it must be balanced with counter weights for safe operation. Refer to the operator's manual for details. Centrifugation flasks must be resistant to the fluid being used and must not swell.

9.3 *Magnetic Fields*—NMR spectroscopy involves strong magnetic fields. Analysis by NMR requires safety and equipment training. Follow local laboratory guidelines.

10. Sampling

10.1 Samples are obtained from sheet roofing or from pre-production runs. Cut two pieces of 4 cm^2 taken 1 m apart along the length of the same roll. Each piece will be analyzed for polymer content to provide for duplicate analysis.

11. Sample Preparation

11.1 *Polymer Extraction and Purification Procedure:*

11.1.1 From each 4 cm^2 piece of sheet, cut about 0.5 g into small pieces, approximately 3 mm by 3 mm. Place cut pieces into a 125 mL Erlenmeyer flask and add 60 mL of hexane. Stopper the flask and place it on a platform shaker to swirl at 120 rpm for 24 h.

NOTE 1—Hexane is used to clean the sheet and extract low molecular weight plasticizer that would affect the PVC and KEE contents measured by NMR.

11.1.2 Filter off the hexane into a Büchner funnel with cellulose Whatman filter paper No. 2. Place the pieces of sample onto a lint-free paper towel and blot them dry.

11.1.3 Place sample pieces into a 125 mL Erlenmeyer flask, add 45 mL of tetrahydrofuran (THF), and close the flask with its stopper. Place the flask on a platform shaker and stir its content at 150 rpm until sample polymer has completely dissolved and there is no evidence of gel.

NOTE 2—Dissolution time depends on composition. It may take up to 5 h for the sample to dissolve.

11.1.4 Transfer dissolved sample to a 50 mL centrifugation tube. Rinse the Erlenmeyer flask with 5 mL of THF and use this rinse solvent to completely fill the centrifugation tube. Cap the tube and centrifuge its content for 30 min at 10 000 rpm. After centrifugation, carefully transfer the supernatant liquid with a Pasteur pipette to a 125 mL Erlenmeyer flask (for transport and storage, if necessary), leaving the precipitated solid at the bottom of the centrifugation tube.

11.1.5 Precipitate the dissolved polymer by pouring the supernatant THF into 150 mL of cold methanol (5 °C) in a 400 mL beaker and stir with a metal spatula for 5 min. Allow the mixture to stand for another 5 min at 5 °C (for example, in an ice bath) to allow for the polymer to precipitate out of solution.

11.1.6 Filter the polymer precipitate through a vacuum funnel over No. 2 Whatman filter paper. Remove the polymer from the filter paper while it is still damp, and place the polymer onto a watch glass to dry the excess of THF in an oven at 65 °C for 15 min.

11.1.7 Repeat 11.1.3 – 11.1.6 twice for a total of three iterations to retain a polymer sample free of interference as defined in Section 6.