

**SEMATECH Provisional Test Method  
for Evaluating Bulk Polymer Samples  
of UPW Distribution System  
Components (DSC and TGA Methods)**

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# SEMATECH Provisional Test Method for Evaluating Bulk Polymer Samples of UPW Distribution System Components (DSC and TGA

**Methods)**

Technology Transfer # **92010939B-STD**

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**Abstract:** This test method uses thermal analysis techniques to examine polymeric samples used in ultrapure water distribution system components. Comparison of the sample to a reference standard provides indications of performance characteristics of the resin (chemical inertness, thermal stability) and physical properties of the polymer resin (crystallinity, molecular weight, morphology). The procedure uses differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). This document is in development as an industry standard by Semiconductor Equipment and Materials International (SEMI). When available, adherence to the SEMI standard is recommended.

**Keywords:** Ultrapure Water Distribution Systems, Testing, Polymers, Thermal Properties, Differential Scanning, Calorimetry, Thermal Gravimetric Analysis

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## SEMASPEC #92010939B–STD

### SEMATECH Provisional Test Method for Evaluating Bulk Polymer Samples of UPW Distribution System Components (DSC and TGA)

#### 1. Introduction

- 1.1 *Purpose*—This method is intended as a means of determining the thermal properties of the polymeric materials used in ultrapure water components with respect to known polymer standards. Use this document in conjunction with the other chemical test methods described in SEMASPEC #92010934B–STD.
- 1.2 *Scope*—This test method covers the examination of polymeric samples using thermal analysis techniques, namely differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). The materials that can be examined using this method include all polymers commonly used in UPW components.

#### 2. Referenced documents

##### 2.1 *ASTM Standards*<sup>1</sup>

ASTM D883	Standard Definitions of Terms Relating to Plastics
ASTM D3417	Standard Test Method for Heats of Fusion and Crystallization of Polymers by Thermal Analysis
ASTM D3418	Standard Test Method for Transition Temperatures of Polymers by Thermal Analysis
ASTM D4591	Standard Test Method for Determining Temperatures and Heats of Transitions of Fluoropolymers by Differential Scanning Calorimetry
ASTM E473	Standard Definitions of Terms Relating to Thermal Analysis
ASTM E967	Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers, Practice for
ASTM E968	Heat Flow Calibration of Differential Scanning Calorimeters, Practice for

##### 2.2 *SEMATECH*<sup>2</sup>

SEMASPEC #92010933B–STD	SEMATECH Guide to Test Methods for UPW Distribution System Components
SEMASPEC #92010934B–STD	SEMATECH Provisional Test Method for Sample Preparation for Chemical Testing of UPW Distribution System Components

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<sup>1</sup>American Society for Testing and Materials. 1916 Race St. Philadelphia, PA 19103.

<sup>2</sup>SEMATECH. 2706 Montopolis Dr. Austin, TX 78741.

### **3. Terminology**

#### 3.1 *Acronyms and Abbreviations*

3.1.1 *DMA*—dynamic mechanical analysis

3.1.2 *DSC*—differential scanning calorimetry

3.1.3 *TGA*—thermal gravimetric analysis

3.1.4 *TMA*—thermal mechanical analysis

#### 3.2 *Definitions*

3.2.1 *glass transition temperature ( $T_g$ )*—the temperature at which an amorphous polymer changes from the glassy state to the rubbery state.

3.2.2 *melting temperature*—*In semi-crystalline polymers*, the temperature at which the crystalline phase becomes amorphous.

### **4. Summary of Test Methods**

4.1 *DSC*—Several configurations are available for a differential scanning calorimeter. This method uses a calorimeter that has a single or dual furnace with two thermally separate compartments (although the method is not limited to this configuration). The pan with the sample is placed in one of the compartments, and a blank pan is placed in the other compartment as a reference. The two compartments are heated at the same rate and then maintained at the same temperature. Both compartments are continuously purged. The heat influx to the sample compartment (required to maintain equal temperatures) is recorded as a function of time or temperature. Thermal transitions or phase changes in the sample are observed either as offsets in the baseline or as peaks.

4.2 *TGA*—After the sample has been placed on the pan and suspended inside a temperature programmable furnace, it is heated through a predetermined temperature profile and continuously purged to remove volatilized products. Its weight is continuously monitored and eventually plotted as a function of time or temperature. The thermal gravimetric analysis (TGA) method can be used to detect any thermally induced changes in the sample that produce significant amounts of gaseous components.

### **5. Significance and Use**

5.1 Examination of the thermal properties of a polymer resin, in comparison to a known polymer standard, can be used to detect differences in morphology (i.e., crystallinity or glass transition temperature.) Differences in morphology can result from changes in manufacturing conditions or resin purity, and can affect the overall performance characteristics of the resin (i.e., chemical inertness, thermal stability, or durability).

5.2 Major differences between the melting point ( $T_m$ ), glass transition temperature ( $T_g$ ), weight loss, or decomposition temperature ( $T_d$ ) between a test sample and the control sample may indicate quality control problems of such properties as crystallinity, molecular weight, extent of polymerization, and thermal stability in the sample being tested for usability and thermal stability.

5.3 Internal stresses can be revealed by DSC and volatile additives can be easily detected by TGA.

## 6. Apparatus

6.1 *Furnaces*—Typically, DSC and TGA instruments are part of an integrated, computer controlled, thermal-analysis system that may also include modules for thermal mechanical analysis (TMA) and dynamic mechanical analysis (DMA). Basic requirements of a DSC furnace are outlined below:

### 6.1.1 DSC Furnace Requirements:

Temperature accuracy of at least 0.1°C  
Sensitivity of at least 10  $\mu\text{W}/\text{cm}$   
Dynamic range of 8–28  $\text{mW}/\text{cm}$   
Calorimetric accuracy of better than 0.1%  
Temperature range of at least 0–600°C in increments of 0.1°C.  
Provisions for gas purging

### 6.1.2 TGA Furnace Requirements

Temperature range of at least 0–1000°C  
Temperature precision of at least 2°C  
TGA weighing accuracy of at least 0.1% with a sensitivity of 0.1  $\mu\text{g}$

6.2 *Analytical Balance*, accurate to  $\pm 0.1$  mg.

## 7. Materials

*Nitrogen* and *Dry Air*, 99.99% pure—routed through a drying tube before entering the instruments.

## 8. Precautions

8.1 *Safety Precautions*—This test method may involve hazardous materials, operations, and equipment. This test method does not purport to address the safety considerations associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to determine the applicability of regulatory limitations before using this method.

### 8.2 *Technical Precautions*

8.2.1 The analyst should understand the effect of the thermal history of a polymer on its thermal behavior. The use of thermal conditioning should be included in all DSC analyses to allow comparisons between samples with common thermal histories (see Section 14.1.2).

8.2.2 All polymer standards should be thermally conditioned using the same parameters as those used in the sample analyses.

8.3 *Interferences*—TGA measurements can be hampered by vibrations of the instrument that can lead to noise in the thermogram. Therefore, the TGA apparatus should be supported by a solid, level bench and should be seated on a rubber, lead, or granite isolation slab.

## **9. Sampling, Test Specimens, and Test Units**

### *9.1 Sample Preparation*

9.1.1 Both TGA and DSC samples can be prepared by cutting small pieces of the bulk sample with clean scissors or with a sharp-blade utility knife. Sample pans are typically 5–6 mm in diameter and 1 mm in depth.

[Note: Shearing or tearing polymer samples can introduce internal stresses that may produce additional features in the DSC thermogram.]

9.1.1.1 DSC sample weights should be in the range of 5–15 mg. Place the sample in the pan, place an aluminum sample cover on top of the sample, and crimp the edges of the pan over the edge of the cover. The pan should be properly sealed.

[Note: This is usually accomplished by using a DSC sample press, or "crimper."]

9.1.1.2 TGA sample weights should be in the range of 5–15 mg. Place the sample, uncovered, directly into the sample pan (usually made of platinum). Before each use of the sample pan, clean it of organic residue by heating it for 10–20 seconds in a propane flame.

## **10. Preparation of Apparatus**

Prior to an analysis, purge the DSC and TGA furnaces with N<sub>2</sub> or dry air for at least 10 minutes to remove moisture from the system.

## **11. Calibration and Reference Standards**

### *11.1 Calibration of Equipment*

11.1.1 DSC—The DSC should be calibrated using melting point standards covering the range of temperatures to be used in the analysis.

11.1.1.1 Details of the calibration may differ from one system to another, but the general approach is to match the onset of melting temperatures indicated by the furnace thermocouple readouts to the known melting points of standards analyzed in the DSC.

11.1.1.2 Perform the calibrations according to the manufacturer's specifications. Monthly calibration checks are recommended.

11.1.2 TGA—The instrument must be calibrated to ensure accurate weight and temperature measurement. Perform this procedure according to the manufacturer's specifications. Monthly calibration checks are recommended.

## **12. Conditioning**

### *12.1 Sampling Conditions*

#### *12.1.1 Differential Scanning Calorimetry*

12.1.1.1 For amorphous polymers, the temperature range of a DSC thermogram should extend from room temperature to approximately 20°C above the reported glass transition temperature.

12.1.1.2 For crystalline polymers, the upper temperature should be approximately 20°C above the reported melting point. A heating rate of 20°C/min is recommended.

12.1.1.3 The furnace requires 10 to 20 minutes to stabilize. Once it has stabilized, wait at least an additional five minutes before proceeding with the temperature ramp.

#### 12.1.2 Thermal Gravimetric Analysis

12.1.2.1 The temperature range of a thermal gravimetric analysis should extend from room temperature to approximately 50°C above the reported decomposition temperature of the resin. Usually, an upper temperature of 500°C is sufficient. A heating rate of 20°C/min is recommended.

### 13. Test Procedure

#### 13.1 *Procedure for DSC (Differential Scanning Calorimetry)*

13.1.1 Using blank sample pans and covers in both the sample and reference compartments, run a furnace baseline using a temperature range from  $\pm 10^\circ$  of the desired range of the sample run. Use a heating rate of 10°C/min.

13.1.2 Set the air or nitrogen purge rate according to instrument specifications (typically around 30 cm<sup>3</sup>/min). Both compartments should be continuously purged to remove any volatilized products of heating.

13.1.3 The baseline should be relatively flat. Most instruments are equipped with adjusters to eliminate baseline curvature and slope if the baseline is not flat.

13.1.4 Place the sample pan in the sample compartment and leave an empty pan in the reference compartment.

13.1.5 After initial temperature stabilization, conduct the sample run using the desired temperature range and the same flow rate as that used for the baseline. The sample scan should be normalized to the baseline scan.

#### 13.2 *Procedure for TGA (Thermal Gravimetric Analysis)*

13.2.1 Thoroughly clean the sample pan, place the empty pan on the balance. Set the purge gas (nitrogen or dry air) flow rates in accordance with the manufacturer's instructions. The sample must be continuously purged to remove any volatilized products.

13.2.2 After the balance stabilizes, zero the sample weight readout.

13.2.3 Carefully place the sample in the pan and position the pan in the furnace.

13.2.4 Allow the weight readout to stabilize.

13.2.5 Initiate the temperature ramp. (Typically, a constant temperature ramp of 20°C/min is used.) Variations may include one or more isothermal holding times.

### 14. Data Analysis

#### 14.1 *Differential Scanning Calorimetry*

14.1.1 Calculate the glass transition temperature and melting point from the baseline offset and peak that are associated with these phenomena, respectively. This can be done manually, but it is usually accomplished by using thermal analysis software routines. For as-received samples, differences greater than 5°C should be considered significant.

Note any shoulders, split peaks, peak broadening, or other artifacts in the DSC thermogram.

[Note: For some polymers, the glass transition temperature occurs below room temperature and will, therefore, be outside the temperature range of this method. Some high-performance materials decompose prior to the glass transition; therefore, the  $T_g$  of those materials will not be observed in the DSC data.]

- 14.1.2 Thermal Conditioning—The DSC thermograms of polymers can reflect subtle differences in the thermal history of different samples.
- 14.1.2.1 These differences may appear in the form of split peaks, shoulders, or peak broadening. They may be due to differences in processing, internal stresses, or prior heat exposure. To separate these effects from true morphological differences, a common thermal history between samples must be introduced. This practice is often referred to as annealing or thermal conditioning, and is commonly accomplished by recording the thermogram of an as-received sample and a second thermogram on the same sample.
- 14.2 *Thermal Gravimetric Analysis*—Note any weight losses greater than 0.1%. Below this level, it is difficult to separate significant weight losses from thermal desorption of adsorbed moisture or instrument noise and vibrations. Significant weight losses may be an indication of outgassing due to volatilization of additives or low molecular weight polymer chains.

## **15. Data Presentation**

- 15.1 The report should contain the following information:
  - 15.1.1 DSC and TGA Thermograms, of the as-received and thermally conditioned test sample, along with the thermally conditioned thermograms of the control sample.
  - 15.1.2 Complete Identification of the Test Sample, including resin type, tradename, source (pipe, fitting, valve, etc.), manufacturer's code or lot number, and previous history.
  - 15.1.3 Description of Sample Preparation, including sample weight and details of sample collection.
  - 15.1.4 DSC and TGA Descriptions, including manufacturer, model number, and TGA balance configuration.
  - 15.1.5 Thermal Analysis Parameters, including heating rate, holding times, purge gases used, and purge gas flow rates.
  - 15.1.6 Atmospheric Conditions in Test Room.
  - 15.1.7 Tabulation of Glass Transition, Melting Point, and Significant Weight Losses of the Test Sample, along with the corresponding data for the control sample.
  - 15.1.8 Analyst Identification.
  - 15.1.9 Date of Test.

## **16. Precision and Bias**

- 16.1 A typical DSC or TGA furnace should give repeatable temperatures of  $\pm 0.5^\circ\text{C}$  over the entire range of the experiments considered in this method.

- 16.2 Determination of the onset of thermal transitions may depend on the manual or computerized method used in the calculation.
- 16.3 Sample to sample variability is discussed in Section 14.1.2.1.
- 16.4 Although DSC is the most common method used to determine the glass transition and melting temperatures of a polymer, other methods such as thermal mechanical analysis (TMA) and dynamic mechanical analysis (DMA) may be used. These methods may yield slightly different values for  $T_g$  and  $T_m$ , depending upon the experimental parameters and the polymer in question. Comparisons between polymer samples and known standards should only be made using data derived from identical thermal techniques.

#### **Additional References**

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