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Standard Practice for Polyurethane Raw Materials: Gel Tests for Polyurethane Non-Foam Formulations[1]

This standard is issued under the fixed designation D7997; 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 practice covers procedures for determining the gel times of polyurethane non-foam formulations using commercially available gel test equipment.

1.2 Definitions, terms, and techniques are described along with procedures for calculating sample weights.

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.*

NOTE 1—There is no known ISO equivalent to this standard.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D883 Terminology Relating to Plastics

3. Terminology

3.1 *Definitions*—For general definitions of terms used in this practice see Terminology D883.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *gel point*—the extent of polymerization at which the upper limit, as defined by the procedure being run, is reached.

3.2.2 *gel time*—the time from the initiation of the reaction to the gel point.

3.2.3 *resin blend (formulated polyol)*—complete ingredient formulation without the isocyanate component.

3.2.4 *index*—the ratio of the equivalents of the isocyanate component to the equivalents of the resin blend of a polyurethane formulation.

4. Summary of Practice

4.1 The gel time of a polyurethane non-foam formulation is determined by measuring the time required for the viscosity of the polymerizing system to increase to a set level using a gel meter. It is recommended that the torque of the gel meter be verified with a gauge certified to NIST standards.

5. Significance and Use

5.1 *General Utility:*

5.1.1 This practice is suitable for research, quality control, specification testing and process control.

5.1.2 It is useful to define and verify the reactivity of non-foam polyurethane formulations.

5.2 *Limitations:*

5.2.1 Operator-to-operator variability and lab-to-lab variability can be significant.

5.2.2 The variability of this practice is dependent on the equipment used to measure the gel time. It is recommended that the testing laboratory and the client agree on the equipment and the conditions to be used that include the following:

5.2.2.1 Gel Tester and gel point criteria,

5.2.2.2 Speed/rpm of the mixer,

5.2.2.3 Type and shape of the mix blades,

5.2.2.4 Size and type (for example, shape, lined or unlined) of container for mixing the components and for measuring the gel time, and

5.2.2.5 The volume (or height) of material to be placed in the container for measuring the gel time and the depth of the measuring wire or spindle of the gel tester from the bottom of the container.

5.2.3 The estimation of precision in this practice is very limited. Users of this practice shall develop their own precision data to determine if these procedures meet their requirements.

5.2.4 It is possible that low-levels (ppm, ppb) of contaminants will not be detected using this practice.

6. Sampling

6.1 Since organic isocyanates react with atmospheric moisture, take special precautions in sampling. Usual sampling

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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.

methods, even when conducted rapidly, can cause contamination of the sample with insoluble urea. Therefore, blanket the sample with dry air or nitrogen at all times. (**Warning—** Diisocyanates are eye, skin and respiratory irritants at concentrations above the occupational exposure limit (TLV or PEL). Diisocyanates can cause skin and respiratory sensitization (asthma) in some people. Once sensitized, it is essential to limit further exposure to diisocyanates. Use a combination of engineering controls and personal protective equipment, including respiratory, skin and eye protection, to prevent overexposure to diisocyanates. Consult the product suppliers' Safety Data Sheet (SDS) for more detailed information about potential health effects and other specific safety and handling instructions for the product.)

7. Test Conditions

7.1 Isocyanate samples shall remain sealed against moisture until immediately before testing.

8. Equipment and Reagents

8.1 *Commercial gel meter* or other equipment capable of determining a large increase in viscosity that occurs in a polymerizing urethane system at or near the gel point.

8.2 *Balance,* capable of weighing to 0.1 mg.

8.3 *Containers* appropriate for the particular gel test being run.

8.4 *Stopwatch or electronic timer.*

8.5 *Heating device* as described in the specific procedure.

8.6 *Methyl ethyl ketone (MEK)* or other solvent appropriate for cleaning the equipment after use.

8.7 *Motorized mixer with blades* (or spatula for manual mixing).

8.8 *Two component non-foam polyurethane formulation* consisting of a resin blend as needed to obtain the desired gel time and an isocyanate component.

NOTE 2—Additional equipment may be listed in specific procedures in the Appendixes.

9. General Procedure

9.1 A general procedure is outlined below with examples of specific steps provided in the Appendixes.

9.1.1 Charge the container used in the gel test with a carefully weighed amount of the resin blend and the isocyanate being reacted. A 1.05 index is typical for gel tests but can be adjusted for a specific test or formulation.

9.1.2 Immediately start the timer or stopwatch and mix the components thoroughly (the timer is to be started at the beginning of the mix, that is, when the reaction is initiated).

9.1.3 Introduce the container with the reacting system to the gel meter and monitor the reaction. Because some formulations solidify, consider using disposable stirring paddles or probes.

9.1.4 Stop the timer when the reaction reaches the gel point. Many commercial units will shut off automatically at the defined gel point.

9.1.5 Record the gel time.

10. Sample Calculations

10.1 Calculate the equivalent weight, EW_p, of the resin blend as follows:

$$EW_p = \frac{100}{\frac{(OH + Ac)100}{56100} + \frac{\%W}{9}} \quad (1)$$

where:

OH = the hydroxyl number of the resin blend in milligrams of KOH per gram of sample,
Ac = the acid number of the resin blend in milligrams of KOH per gram of sample,
%W = the percent water in the resin blend,
56100 = the equivalent weight of KOH in milligrams of KOH per equivalent, and
9 = the equivalent weight of water in grams per equivalent.

10.2 Calculate the equivalents of the resin blend, EQ_p, as follows:

$$EQ_p = X_p / EW_p \quad (2)$$

where:

X_p = the amount of resin blend to be reacted with the isocyanate component in grams

10.3 Calculate the equivalents, EQ_i, of the isocyanate component needed to prepare the batch at an index of 1.05 as follows:

$$EQ_i = 1.05 \times EQ_p \quad (3)$$

where:

1.05 = the index of the batch

10.4 Calculate the equivalent weight, EW_i, of the isocyanate component as follows:

$$EW_i = \frac{42.02 \times 100}{\%NCO} \quad (4)$$

where:

%NCO = the percent by weight of NCO groups present in the sample and
42.02 = grams NCO per equivalent of NCO.

10.5 Calculate the weight, W_i, of isocyanate in grams needed to prepare the batch as follows:

$$W_i = EW_i \times EQ_i \quad (5)$$

11. Report

11.1 Report the gel time and the procedure used.

12. Keywords

12.1 gel time; isocyanate; polyol; polyurethane; raw material; resin blend

APPENDIXES

X1. EXAMPLES OF GEL TIME TEST PROCEDURES FOR POLYURETHANE NON-FOAM FORMULATIONS

(Nonmandatory Information)

X1.1 The information in these nonmandatory appendices is given to provide the reader with examples of test conditions as defined by individual companies. Other acceptable test conditions are possible.

X1.2 Specific suppliers are provided below as examples. Other suppliers are available and users of this practice are encouraged to identify suppliers and parts that meet their specific needs.

X1.3 Test Procedure A is used to determine the gel time of a polyester polyol with an isocyanate component using a Sunshine Gel Meter.

X1.4 Test Procedure B is used to determine the gel time of an isocyanate component with a resin blend using a Gardco Gel Tester.

X1.5 Test Procedure C is used to determine the gel time of a two component elastomer system using a Shyodu Gel Timer and includes information on verifying the torque of the Shyodu Gel Timer with a desktop IMADA DTX-15B Torque Tester.

X2. TEST PROCEDURE A: GEL TIME OF A POLYESTER POLYOL WITH AN ISOCYANATE COMPONENT USING A SUNSHINE GEL METER

X2.1 Scope

X2.1.1 This procedure determines the reactivity of a polyester polyol by measuring the gel time of a non-foam polyurethane formulation using a Sunshine gel meter.

X2.2 Summary of Practice

X2.2.1 A polyester polyol is reacted with an isocyanate and the reactivity is determined by measuring the time required for the viscosity of the polymerizing system to increase to a set level using a gel meter.

X2.3 Equipment and Chemicals

X2.3.1 *Gel meter,* Sunshine Scientific Instruments.

X2.3.2 *Balance,* analytical, 0.01-g readability,.

X2.3.3 *Oven,* circulating air, 110°C.

X2.3.4 *Baths,* oil, circulating high temperature.

X2.3.5 *Stopwatch.*

X2.3.6 *Methyl ethyl ketone (MEK).*

X2.3.7 *Polymeric MDI reagent.*

X2.3.8 *Oil,* high temperature silicone bath.

X2.3.9 *Test tubes,* 18-mm by 150-mm.

X2.3.10 *Jar,* glass, 237-mL (8-oz).

X2.3.11 *Spatula.*

X2.4 Procedure

X2.4.1 Weigh 50 g of polyester polyol into a 237-mL (8-oz) jar. Cover and place the jar in the 110°C oven for one hour.

X2.4.2 Set the oil bath to the desired temperature (example: For a polyester polyol with hydroxyl number of 35 mgKOH/g, set oil bath temperature to 130°C). Set up the gel meter as described in the operation manual.

X2.4.3 Weigh the appropriate amount of isocyanate to the nearest 0.1 g. (See X2.5.) Remove the jar of polyester polyol from the circulating air oven and rapidly add the isocyanate.

X2.4.4 Start the stopwatch as soon as the isocyanate is added.

X2.4.5 Immediately mix with a spatula for 1.5 min and fill an 18-mm by 150-mm test tube to a height of 9.5 cm from the bottom of the tube.

X2.4.6 Place the tube in the gel meter bath and install the spindle so that it remains 2.5 cm off the bottom of the tube.

X2.4.7 Start the gel meter and stop the stopwatch at the same time. Record the time, *SW*, on the stopwatch to the nearest second.

X2.4.8 When the gel meter stops and the buzzer sounds, record the gel meter time, *G*, to the nearest second.

X2.4.9 Immediately remove the spindle from the unit and clean it with MEK.

X2.5 Calculations

X2.5.1 Calculate the equivalent weight, EW_{PE}, of the polyester polyol as follows (see Note X2.1):

$$EW_{PE} = \frac{56.1 \times 1000}{OH} \quad \text{(X2.1)}$$

where:

EW_{PE} = the equivalent weight of the polyester polyol sample,
56.1 = the equivalent weight of KOH in milligrams per milliequivalents,
1000 = the factor for converting milliequivalents to equivalents, and
OH = the hydroxyl number of the polyester polyol sample in milligrams of KOH per gram of sample as determined by the appropriate specification method.

NOTE X2.1—Equation in X2.5.1 assumes negligible contribution from

the acid number and water content of the polyester polyol. The user of this practice must validate this assumption for their particular system

X2.5.2 Calculate the equivalents, E_{PE}, in 50 g of the polyester polyol as follows:

$$E_{PE} = \frac{50}{EW_{PE}} \quad \text{(X2.2)}$$

where:

50 = the amount of the polyester polyol used in the reactivity test in grams

X2.5.3 Calculate the equivalent weight, EW_I, of the appropriate isocyanate as follows:

$$EW_I = \frac{42.02 \times 100}{\%NCO} \quad \text{(X2.3)}$$

where:

42.02 = the equivalent weight of an NCO group in grams per equivalent,
100 = the factor for converting % NCO to grams of NCO, and
%NCO = the %NCO of the isocyanate as determined by the appropriate specification method.

X2.5.4 Calculate the weight, W_I, of isocyanate to be used in the reactivity test as follows:

$$W_I = E_{PE} \times EW_I \quad \text{(X2.4)}$$

where:

W_I = the weight of the isocyanate in grams

X2.5.5 Calculate the total reaction time, *T*, as follows:

$$T = G + SW \quad \text{(X2.5)}$$

where:

G = the time from the gel meter in seconds and
SW = the time from the stopwatch in seconds.

X2.6 Report

X2.6.1 Report gel time results, *T*, to the nearest one second.

X2.7 Precision

X2.7.1 The precision of this test method is not known at this time because inter-laboratory data is not available.

X3. TEST PROCEDURE B: GEL TIME OF AN ISOCYANATE COMPONENT WITH A RESIN BLEND USING A GARDCO GEL TESTER

X3.1 Scope

X3.1.1 This procedure is used to characterize the reactivity of Isocyanate X with a polyol blend.

X3.2 Summary of Practice

X3.2.1 A sample of Isocyanate X is reacted with a polyol blend that consists of polytetrahydrofuran diol and 1,4- butanediol producing a product that is similar to one that is manufactured by end users of Isocyanate X. Although the final polyurethane product has a moderately low average molecular weight, it can be classified as a thermoplastic. As the reaction proceeds, the viscosity of the reaction mixture increases and this increase is monitored with a gel meter. The time required for the mixture to reach the point where the wire stirrer makes only one revolution in 60 seconds is reported as the gel time.

X3.3 Equipment and Chemicals

X3.3.1 *Gardco Hot Pot Gel Timer,* Fast Cure (Paul N. Gardner, Inc.).

X3.3.2 *Oven, forced air,* temperature control to ±0.2°C.

X3.3.3 *Oven, convection.*

X3.3.4 *Balance, analytical,* 0.1-mg readability.

X3.3.5 *Balance, top pan,* 1-kg capacity.

X3.3.6 *Cup,* aluminum, for Gardco gel timer.

X3.3.7 *Stirrer,* wire.

X3.3.8 *Stopwatch,* 1-s readability.

X3.3.9 *Polytetrahydrofuran diol,* OH No. ca. 112 mgKOH/g.

X3.3.10 *1,4-Butanediol,* anhydrous.

X3.3.11 *Xylene,* raw material grade.

X3.3.12 *Dibutyltin dilaurate catalyst.*

X3.3.13 *Syringe,* glass, 50-µL.

X3.3.14 *Bottle, screw-capped,* 30-mL (1-oz).

X3.3.15 *Bottle, screw-capped,* 120- mL (4-oz)

X3.3.16 *Pail,* 2-L (0.5-gal).

X3.3.17 *Mixer,* for 2-L (0.5-gal) pail.

X3.3.18 *Nitrogen.*

X3.3.19 *Polyol blend* (17.8 to 1.0 weight ratio of polytetrahydrofuran to to 1,4 –butanediol).

X3.3.20 *Catalyst solution* (4.75 w/w % dibutyltin dilaurate catalyst in xylene).

X3.4 Instrument Conditions

X3.4.1 Gel meter conditions, 90°C.

X3.4.2 Oven, forced air, 60°C.

X3.4.3 Oven, convection, 90°C.

X3.5 Procedure

X3.5.1 Prepare the polyol blend. The steps to make a 500-g batch are given below as an example.

X3.5.1.1 Place the polytetrahydrofuran diol in a 40-50°C oven until it is completely melted.

X3.5.1.2 Weigh 473.36 g of the well-mixed polytetrahydrofuran diol into a 2-L (0.5-gal) pail followed by 26.64 g of 1,4-butanediol and record the weight of each to the nearest 0.1 g.

X3.5.1.3 Using a mechanical mixer, thoroughly mix the polyol blend for at least 30 minutes.

X3.5.1.4 Determine the hydroxyl number, acid number, and % water of the polyol blend using the appropriate methods.

X3.5.2 Prepare the catalyst solution.

X3.5.2.1 Weigh ca. 0.5975 g of the dibutyltin dilaurate catalyst into a 30-mL (1-oz) bottle and record the weight of the catalyst to the nearest 0.1 mg.

X3.5.2.2 Calculate the weight, *W*, of xylene in grams to be added to the catalyst in order to prepare a 4.75 % solution as follows:

$$W = 21.0526 \times WT \tag{X3.1}$$

where:

WT = the weight of catalyst T-12 weighed into the bottle in grams and

21.0526 = the factor for determining the xylene needed to prepare a 4.75 % catalyst solution.

X3.5.2.3 Weigh the calculated amount of xylene into the 30-mL (1-oz) bottle containing the catalyst to the nearest 0.01 gram.

X3.5.2.4 Pad the catalyst solution with nitrogen and store in a dark place.

X3.5.3 *Stoichiometry:*

X3.5.3.1 For this system, it is important that the gel test be run at an index of 1.05. This can be done by knowing the equivalent weights of both the Isocyanate X and the polyol blend. The NCO content of Isocyanate X is 31.81 %. An equivalent weight, EW_I, of 132.08 will therefore be used.

X3.5.3.2 The equivalent weight of the polyol blend must be determined each time a new bend is prepared. This value may be determined as shown in X3.6.

X3.5.4 *Batch Size:*

X3.5.4.1 The batch size should be about 100 g with an index of 1.05. A typical batch would consist of ca. 70 g of polyol blend and ca. 31 g of Isocyanate X. To determine the exact weights required, see X3.6.

X3.5.5 *Gel Time Determination:*

X3.5.5.1 Weigh 70 g of the polyol into a 120-mL (4-oz) bottle and record the weight to the nearest 0.01 g.

X3.5.5.2 Place the pre-weighted bottle of polyol blend into a 90°C oven.

X3.5.5.3 Place the Isocyanate X sample into a 60°C oven.

X3.5.5.4 Make sure both liquids are at the appropriate temperature.

X3.5.5.5 Add 20 µL of catalyst solution to the jar of polyol blend.

X3.5.5.6 Weigh the appropriate amount of the Isocyanate X (ca. 30-31 g) into the jar of polyol blend.

X3.5.5.7 Immediately start the stopwatch, cap the bottle and mix by shaking for one minute.

X3.5.5.8 Pour this sample into an aluminum cup and place the cup into the gel meter. Attach the wire stirrer and start the meter.

X3.5.5.9 Record the time, *T*, required for the mixture to reach the point where the wire stirrer makes only one complete revolution in 60 seconds.

X3.6 Calculations

X3.6.1 Calculate the equivalent weight, EW_p, of the polyol blend as follows:

$$EW_p = \frac{100}{\frac{(OH + Ac)100}{56100} + \frac{\%W}{9}} \tag{X3.2}$$

where:

OH = the hydroxyl number of the polyol blend in milligrams of KOH per gram of sample,

Ac = the acid number of the polyol blend in milligrams of KOH per gram of sample,

%W = the percent water in the polyol blend,

56100 = the equivalent weight of KOH in milligrams of KOH per equivalent, and

9 = the equivalent weight of water in grams per equivalent.

X3.6.2 Calculate the equivalents, EQ_p, in 70 g of the polyol blend as follows:

$$EQ_p = \frac{70}{EW_p} \tag{X3.3}$$

where:

70 = the amount of polyol blend to be reacted with the sample in grams

X3.6.3 Calculate the equivalents, EQ_i, of Isocyanate X needed to prepare the batch at an index of 1.05 as follows:

$$EQ_i = 1.05 \times EQ_p \tag{X3.4}$$

where:

1.05 = the index of the batch

X3.6.4 Calculate the equivalents, W_i, of Isocyanate X needed to prepare the batch as follows:

$$W_i = EW_i \times EQ_i \tag{X3.5}$$

where:

EW_i = the equivalent weight of Isocyanate X in grams per equivalent, and

W_i = the weight of Isocyanate X in grams.

X3.7 Report

X3.7.1 Report gel time results, *T*, to the nearest one second.

X3.8 Precision

X3.8.1 The repeatability of this procedure at the 95 % confidence limits has been determined to be ±1.42 min for a sample of Isocyanate X whose mean gel time was 26.6 minutes.

X4. TEST PROCEDURE C: GEL TIME OF A TWO COMPONENT ELASTOMER SYSTEM USING A SHYODU GEL TIMER

X4.1 Scope

X4.1.1 This test procedure covers the determination of gel time for systems with gel times of ≥20 seconds.

X4.2 Summary of Practice

X4.2.1 A container is charged with measured amounts of the isocyanate and resin blend and mixed mechanically for a specified amount of time. The mechanical mixer and the Shyodu Gel Timer are controlled by a single GraLab Timer to ensure that the start times are synced. After the specified mixing time is reached, the mechanical mixer automatically stops. The container is removed from the mechanical mixer and the stirring wire of the Shyodu Gel Timer unit is gently lowered into the reacting components. The time for the drag on the wire to exceed the torque on the motor is automatically recorded by the unit and is reported as the gel time.

X4.3 Equipment and Chemicals

X4.3.1 *Shyodu Model 100 Gel Timer* with stirring wires.

X4.3.2 *Constant temperature water bath.*

X4.3.3 *Digital pyrometer or laboratory thermometer.*

X4.3.4 *Digital balance.*

X4.3.5 *Mechanical Mixer*—Speed drill press mixer capable of 2340 rpm or other variable speed mixer.

X4.3.6 *GraLab Digital Timer,* Model 645 or 655.

X4.3.7 *GraLab Contactor,* Model 700-420 (allows the GraLab Timer to control equipment).

X4.3.8 *Mix blade* (type and size as agreed on between the lab and client).

X4.3.9 *Quart cup* (type and style as agreed on between the lab and client).

X4.3.10 *Plastic lined pint sized straight sided container* (9 cm in height by 9 cm in diameter).

X4.3.11 *Resin blend.*

X4.3.12 *Isocyanate component.*

X4.3.13 *IMADA DTX-15B Torque Tester.*

X4.4 Procedure

X4.4.1 *Torque verification of the Shyodu Gel Timer:*

X4.4.1.1 Mount the gel timer on a stationary stand such that the mixing wire from the motor shaft hangs directly over the middle of the plate of the IMADA Torque Tester when inserted (step X4.4.1.4).

X4.4.1.2 Set the distance between the peg holder tracks to 0.75 ± 0.5 inches. Consistency in this step is critical to reducing variability of the measurements.

X4.4.1.3 Insert the 3-in. pegs into the four innermost holes in the tracks.

X4.4.1.4 Inset the mixing wire into the hole in the shaft on the gel timer.

X4.4.1.5 Lower the gel timer to approximately 1 in. above the peg holder track. Consistency in this step is critical to reducing variability of the measurements.

X4.4.1.6 Rotate the motor shaft clockwise until the wire is resting against the pegs.

X4.4.1.7 Verify that the torque tester is reading 0.00.

X4.4.1.8 Turn on the gel timer.

X4.4.1.9 Follow the manufacturer's instructions to measure the maximum torque value and the sustained torque value of the gel timer using the AMADA torque tester.

X4.4.1.10 Repeat steps X4.4.1.6 to X4.4.1.9 19 times for a total of 20 replicates.

X4.4.1.11 Record the averages and standard deviations.

X4.4.1.12 It is up to the user to determine the appropriate tolerances that meet their requirements.

X4.4.2 Equilibrate the isocyanate and resin components to 77°F.

X4.4.3 Connect the GraLab Digital Timer to the drill press mixer and the gel timer using the GraLab Contactor.

X4.4.4 Set the mixing time for drill press to the ten seconds.

X4.4.5 Set the gel timer to two minutes (this value must be beyond the anticipated gel time to ensure that the test goes to completion).

X4.4.6 Insert the mix blade into the drill press and set the mixing speed to 2340 rpm.

X4.4.7 Insert the stirring wire into the hole in the gel timer motor shaft and press the timer reset.

X4.4.8 Weigh 125 g of the resin into the quart cup.

X4.4.9 Carefully add 185 g of the isocyanate to the cup of resin.

X4.4.10 Raise the container to the mechanical mixer blade and start the mixer and the gel timer simultaneously using the GraLab Timer.

X4.4.11 When the mixer stops, lower the container and place it in front of the unit.

X4.4.12 Lift the unit and gently lower the sitting wire in the container of reacting components.

X4.4.13 When the reaction reaches the point where the drag on the wire exceeds the torque of the motor, the motor and the counter will stop and the time, *T*, will be displayed.

X4.4.14 Record the time, *T*, as the gel time.

X4.5 Report

X4.5.1 Gel time in seconds.

X4.5.2 The procedure used or a reference to the procedure used with any modifications.

X4.6 Precision

X4.6.1 The precision of this test method is not known at this time because inter-laboratory data is not available.