Designation: D832 – 07 (Reapproved 2012)

Standard Practice for Rubber Conditioning For Low Temperature Testing[1]

This standard is issued under the fixed designation D832; 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.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 This practice covers the characteristic mechanical behavior of rubbers at low temperatures, and outlines the conditioning procedure necessary for testing at these temperatures.

1.2 One of the first stages in establishing a satisfactory technique for low temperature testing is the specification of the time and temperature of exposure of the test specimen. It has been demonstrated that any one or more of the following distinct changes, which are detailed in Table 1, may take place on lowering the test temperature:

1.2.1 Simple temperature effects,

1.2.2 Glass transitions, and

1.2.3 First order transitions (crystallization), and solubility and other effects associated with plasticizers.

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:*[2]

D471 Test Method for Rubber Property—Effect of Liquids

D1053 Test Methods for Rubber Property—Stiffening at Low Temperatures: Flexible Polymers and Coated Fabrics

D1329 Test Method for Evaluating Rubber Property—Retraction at Lower Temperatures (TR Test)

D1566 Terminology Relating to Rubber

D2136 Test Method for Coated Fabrics—Low-Temperature Bend Test

D5964 Practice for Rubber IRM 901, IRM 902, and IRM 903 Replacement Oils forASTM No. 1, ASTM No. 2, and ASTM No. 3 Oils

3. Significance and Use

3.1 Low temperature testing of rubber can yield repeatable results only if the preconditioning of the samples is consistent. Properties such as brittleness and modulus are greatly affected by variations in time/temperature exposures. This practice is intended to provide uniform conditioning for the various low temperature tests conducted on rubbers.

4. General Conditioning

4.1 At least 16 h should elapse between vulcanization and testing of a sample.

4.1.1 If the time between vulcanization and testing is less than 16 h, it shall be agreed upon between customer and supplier and noted in the report section of the test method employed.

5. Simple Temperature Effects (Viscoelasticity)

5.1 Most elastic properties of rubber change as the temperature is changed. As the temperature is reduced toward the glass transition temperature, T_g, the specimen becomes increasingly stiff, loses resilience, and increases in modulus and hardness. At some point, still above T_g, the resilience reaches a minimum. As the temperature is lowered beyond this point, the resilience then increases until a temperature just above T_g is reached.

5.2 Viscoelastic changes are usually complete as soon as the specimen has reached thermal equilibrium. Longer exposure time should be avoided to minimize crystallization or plasticizer-time effects that might influence the test results. The magnitude of these changes depends on the composition of the material and the test temperature.

6. Glass Transition

6.1 Glass transition is a reversible physical change in a material from a viscous or rubbery state to a brittle glassy state (refer to Terminology D1566: transition, glass; transition second order). It does not involve a change in phase and is not a thermodynamic change. It generally occurs over a small temperature range. It is designated as T_g. The T_g of polymers, obtained from measurements of change of modulus with change in temperature, depend upon both the rate of specimen deformation and the rate of temperature change. Primary

---

[1] This practice is under the jurisdiction of ASTM Committee D11 on Rubber and is the direct responsibility of Subcommittee D11.10 on Physical Testing.

Current edition approved Dec. 1, 2012. Published February 2013. Originally approved in 1945. Last previous edition approved in 2007 as D832 – 07. DOI: 10.1520/D0832-07R12.

[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.

TABLE 1 Differentiation Between Crystallization and Glass Transition

Property	Crystallization	Glass Transition
Physical effects **(1, 2, 4, 6, 7)**[A]	Becomes stiff (hard) but not necessarily brittle	Becomes stiff and brittle
Temperature-volume relation **(1, 2, 3, 4, 5, 8)**	Significant decrease in volume	No change in volume, but definite change in coefficient of thermal expansion
Latent heat effect **(4, 5, 8)**	Heat evolved on crystallization	Usually no heat effect, but definite change in specific heat
Rate **(2, 4, 6, 7, 8)**	Minutes, hours, days, or even months may be required. In general, as temperature is lowered, rate increases to a maximum and then decreases with increase in deformation. Rate also varies with composition, state of cure, and nuclei remaining from previous crystallizations, or from compounding materials such as carbon black.	Usually rapid; takes place within a definite narrow temperature range regardless of thermal history of specimen. May be limited rate effect **(2)**
Temperature of occurrence **(4, 5, 7, 8**	Optimum temperature is specific to the polymer involved.	Very wide limits, depending on composition
Effect on molecular structure **(1, 2, 5, 6, 8)**	Orientation of molecular segments; random if unstrained, approaching parrallelism under strain	Change in type of motion of segments of molecule
Materials exhibiting properties **(5, 7, 8)**	Unstretched polymers including natural rubber (low sulfur vulcanizates), chloroprene, Thiokol A polysulfide rubber, butadiene copolymers with high butadiene content, most silicones, some polyurethanes. Butyl rubbers crystallize when strained. Straining increases rate of crystallization of all of the above materials.	All

[A] The numbers in parentheses refer to the following references:

(1) Juve, A. E., Whitby, G. S., Davis, C. C., and Dunbrook, R. F., *Synthetic Rubber*, John Wiley& Sons, New York, NY, 1954, pp. 471–484.

(2) Boyer, R. F., and Spencer, R. S., *Advances in Colloid Sciences*, Vol II, edited by H. Mark and G. S. Whitby, Interscience Publishers, Inc., New York, NY, 1946, pp. 1–55.

(3) Boyer, R. F., and Spencer, R. S., High Polymer Physics, *A Symposium*, edited by Howard A. Robinson, Chemical Publishing Co., Inc., Brooklyn, NY, 1948, pp. 170–184.

(4) Wood, L. A., and Bekkedahl, Norman, *High Polymer Physics*, *loc cit*, 1948, pp. 258–293.

(5) Schmidt, A. X., and Marlies, C. A., *Principles of High Polymer Theory and Practice*, McGraw-Hill Book Co., New York, NY, 1948, pp. 175–193.

(6) Treloar, L. R. G., *The Physics of Rubber Elasticity*, Oxford University Press, London, 1949, pp. 152–191.

(7) Liska, J. W., "Low Temperature Properties of Elastomers," *Symposium on Effects of Low Temperature on the Properties of Materials*, STP 78, ASTM, 1946, pp. 27–45.

(8) Turner, Alfrey, Jr., "Mechanical Behavior of High Polymers," Vol VI of *High Polymer Series*, Interscience Publishers, Inc., New York, NY, 1948, pp. 80–83 and 340–374.

properties, such as hardness and ultimate elongation, and temperature coefficients of properties such as volume and enthalpy, change rapidly near T_g. Thus, thermal expansivity and specific heat appear discontinuous at T_g.

6.2 Some rubbers such as copolymers or polymer blends may show more than a single T_g because of separate contributions by their polymeric components. There may also be damping peaks not directly attributable to glass transitions. A glass transition occurs at a temperature below which the thermal energies of molecular segments are insufficient to free them from the force field of their immediate neighbors within the experimental time scale.

6.3 Values determined for T_g are higher for test methods that require high frequency distortions of the specimen than for those that require low frequency distortions. The latter seem to have the greater resolving power for multiple peaks. For those methods in which the test temperature is changed at a controlled rate, T_g depends upon the rate that is chosen. Therefore, T_g is not a true material property since it depends upon the test method used to obtain it. The method used should always be stated.

7. First Order Transitions (Crystallization)

7.1 A first order transition is a reversible change in phase of a material; in the case of polymers, it is usually crystallization or melting of crystals (refer to Terminology D1566: transition, first order). When a specimen is equilibrated at a temperature at which crystallization is possible, changes in properties resulting from the crystallization may begin immediately or after an induction period of up to several weeks. The time to reach an equilibrium state of crystallization is likewise widely variable. Both times are dependent on the material being tested and the temperature. Crystallization increases the hardness and modulus. A specimen that has crystallized once may crystallize much more rapidly on subsequent tests, unless, in the meantime, it has been heated sufficiently to destroy the crystal nuclei.

7.2 Examples of materials that crystallize relatively rapidly in certain temperature ranges include Thiokol A[3] polysulfide rubber, chloroprenes (excepting the RT types), natural rubber, and some butadiene copolymers cured without sulfur or with low sulfur. Materials that may require much longer times for crystallization effects to become evident include butyl rubber, high sulfur cures of natural rubber, most silicone rubbers, some polyurethane rubbers, RT types of chloroprene, and rubbers containing fluorine.

7.3 The temperature at which crystallization proceeds most rapidly is specific to the polymer involved. For natural rubber, this is near −25°C; for chloroprenes, −10°C; for butadiene copolymers, −45°C; for dimethyl silicones, −55°C; for polyester-type polyurethanes, −10°C; and for butyl rubber, −35°C. Both above and below these temperatures, crystallization is slower. Accordingly, any attempt to compare materials (particularly those subject to change in properties resulting from crystallization or plasticizer time effects) on a basis of exposure at a given temperature for a specified time is almost

---

[3] The sole source of supply of this material known to the committee at this time is Thiokol Chemical Corp, Newtown-Yardly Rd., Newtown, PA 18940. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

certain to be misleading. Such specific temperature may be near the optimum rate of crystallization of one of the materials and many degrees above or below the optimum of another.

7.4 The only rubbers that may be expected to crystallize spontaneously are those that also develop crystallinity on stretching. Application of stress usually increases the crystallization rate, apparently by forming effective nuclei. Stress application may be used to accelerate tests of crystal growth, but may give misleading results regarding induction periods.

7.5 Specimens to be tested for crystallization should be decrystallized immediately before testing by heating them in an oven for 30 min at 70°C. They should then be conditioned at standard laboratory temperature for 45 min and no more than 60 min before testing.

8. Effects Associated with Plasticizers

8.1 When the test material contains certain plasticizers, time effects not necessarily associated with crystallization may be observed. These effects occur over a wide range of time, temperature, and composition. Some may be due to limited low temperature solubility of such plasticizers in the compound. If the original plasticizer concentration is less than the amount corresponding to saturation at the test temperature, no time effects will be observed.

8.1.1 The effects consist of delayed stiffening that occurs over a wide temperature range and, in some instances, an elevation of the brittle temperature that occurs over a narrow temperature range. In the case of elevation of the brittle temperature, plasticized compositions may become brittle after an extended exposure to temperatures slightly higher than their normal brittle temperatures.

8.2 Low temperature serviceability of a plasticized rubber product may depend on whether or not the plasticizer remains in the rubber.

8.2.1 For example, the temperature at which a rubber oil seal retracts 10 % (TR10, Test Method D1329) may be −45°C originally but only −35°C after exposure to IRM 903 (the replacement for ASTM Oil No. 3; refer to Test Method D471 and Practice D5964) for 70 h at 100°C. Part of the liquid plasticizer has been extracted and replaced by the oil, which is a relatively poor plasticizer; hence the change in TR10.

CONDITIONING PROCEDURES FOR MECHANICAL TESTS

9. Tests for Simple Temperature Effects (Viscoelastic Effects) Only

9.1 Make tests at −70, −55, −40, −25, −10, 0, and +23°C, respectively. Hold the test specimen at each test temperature until it reaches thermal equilibrium. Calculated times required for thermal equilibrium are given in Table 2.

9.2 In a flat sheet specimen, the time required for thermal equilibrium may be taken as being directly proportional to the sheet thickness. Thus, for a 25-mm thick slab, the times given in Table 2 for a 2.5 mm thick sheet should be multiplied by 10.

9.2.1 If the air temperature is changed 100°C, the temperature differentials would be 10, 5, 2, and 1°C, respectively, for the respective time periods. For any temperature change, *T*, the temperature differential in Table 2 should be multiplied by *T*/10.

TABLE 2 Calculated Conditioning Time Required for Center of Rubber Specimen to Reach Approximate Temperature of Surrounding Still Air for Temperature Change of 10°C

Temperature Differential Between Air and Center of Specimen, °C	Time Required, s		
	Test Methods D1053 Specimen	2.5-mm Thick Sheet	Cylinder 12.7 mm Thick, 19 mm in Diameter
1.0	255	522	1740
0.5	332	682	2250
0.2	433	888	2940
0.1	510	980	3420

9.2.2 For example, if the test specimen described in Test Methods D1053, at a room temperature of 20°C is placed in air at −70°C, the temperature change would be 90°C; and at the end of 510 s, the temperature differential between the center of the specimen and air would be 0.9°C, making the temperature of the center of the test specimen −69.1°C.

9.2.3 The above times can be reduced at least 50 % by providing air circulation with velocities of 4.5 m/s past the specimen, and by about 85 % by using a circulating liquid bath.

9.2.4 The required measurements of modulus, hardness, or brittleness should be made as soon as the specimen has reached equilibrium temperature except for any conditioning time required by the method, while maintaining the specimen at the same temperature.

10. Tests for Effects of First Order Transition (Crystallization) Only

10.1 Test each material at the temperature at which it crystallizes most rapidly, when this is known.

10.1.1 For unstressed specimens, this temperature is near:

10.1.1.1 −25°C for natural rubber,
10.1.1.2 −10°C for chloroprenes,
10.1.1.3 −45°C for butadiene copolymers,
10.1.1.4 −55°C for silicones,
10.1.1.5 −56°C for *cis*-1,4 butadiene, and
10.1.1.6 10°C for polyurethanes.

10.2 When the temperature of maximum rate of crystallization is unknown, make tests at a series of temperatures including, but not necessarily limited to, −70, −55, −40, −25, −10, 0, and +10°C.

10.3 Allow the temperature of the specimen to come to equilibrium as described in Section 9; then make one set of the required measurements immediately and another after 72 h. Increased stiffness is an indication of crystallization or of a plasticizer effect.

10.3.1 Test in a gaseous medium unless otherwise specified.

11. Tests for Effects Associated with Plasticizers

11.1 It is suggested that tests for maximum effects associated with plasticizers be made at 5°C above the brittle point temperature.

11.2 Follow the procedure in Section 10 except for studies of effects on brittle point temperatures, where tests should be made after 15 min, 60 min, and as many other intervals as desired up to 7 days.

11.3 For tests longer than 60 min, a gaseous medium should be used.

12. Keywords

12.1 brittleness; brittle point; crystallization; enthalpy; first order transition; glass transition; low temperature test; modulus; plasticizer effects; resilience; second order transition; simple temperature effects; solubility; stiffening; subnormal temperature; thermodynamic change; viscoelasticity

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org). Permission rights to photocopy the standard may also be secured from the ASTM website (www.astm.org/COPYRIGHT/).