



Standard Test Method for Rubber—Evaluation of Residual Unsaturation in Hydrogenated Nitrile Rubber (HNBR) by Curemeter Testing¹

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1. Scope

1.1 This test method covers a technique for evaluating a parameter, derived from curemeter testing of a standard hydrogenated nitrile rubber (HNBR) formulation, that is related to the percent residual unsaturation of the HNBR. The standard materials, test formulation, and mixing procedure are fully described. This test method is applicable to all grades of HNBR in the raw unvulcanized state.

1.2 The evaluation of the unsaturation parameter, designated by UP, is based on special regression equations developed from the measured values for two curemeter parameters versus the percent unsaturation measured by infrared spectrophotometry as defined by Test Method D 5670. The data used for this are contained in Appendix X1.

1.2.1 The use of a curemeter and a standard formulation to evaluate the residual unsaturation in HNBR has the advantage of being a relatively simple test, available to most rubber testing laboratories. The disadvantage lies in the nonlinear relationship between HNBR unsaturation and the measured curemeter parameters of scorch time, tS1 and maximum curemeter torque, MH.

1.2.2 The use of UP, which is calculated from a scorch time parameter and a maximum torque parameter, both of which are obtained from Table A1.1 permits the development of a more realistic relationship of the unsaturation levels among a group of HNBR samples than the less definitive technique of simple ranking. The ranking technique is not definitive because the relationship between the curemeter parameters and the unsaturation is highly nonlinear. Curemeter ranking of a series of HNBR samples at low true unsaturation compared to the ranking of a series of samples at high true unsaturation, may give misleading indications of unsaturation differences among the group of rubbers.

1.2.3 If, U, the unsaturation in percent of a tested HNBR sample is known, it can be used to calculate the approximate unsaturation (in percent) of unknown HNBR samples.

1.3 Mixing and curemeter testing variations, both within and between laboratories, may influence the results as obtained by this test method. These variations will be smaller for within-laboratory testing.

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.*

2. Referenced Documents

2.1 ASTM Standards:

D 2084 Test Method for Rubber Property—Vulcanization Using Oscillating Disk Cure Meter²

D 3182 Practice for Rubber—Materials, Equipment and Procedures for Mixing Standard Compounds and Preparing Standard Vulcanized Sheets²

D 5289 Test Method for Rubber Property—Vulcanization Using Rotorless Cure Meters²

D 5670 Test Method for Rubber—Determination of Residual Unsaturation in Hydrogenated Nitrile Rubber (HNBR) by Infrared Spectrophotometry²

3. Summary of Test Method

3.1 Separate compounds using different samples of HNBR are prepared in a Miniature Internal Mixer (MIM). One or more compound(s) contain(s) the experimental or candidate HNBR sample(s) to be evaluated and the other compound(s) contain(s) HNBR sample(s) of known residual unsaturation.

3.2 The maximum torque and scorch times of the formulations are used to evaluate the UP of HNBR samples with unknown unsaturation. If samples of HNBR with known unsaturation are also evaluated, the measured UP of these samples may be used to obtain the approximate unsaturation in percent, of the unknown samples.

3.3 Lower maximum torque and longer scorch and cure times indicate lower residual unsaturation.

4. Significance and Use

4.1 Hydrogenated nitrile rubbers are available at different levels of unsaturation and different acrylonitrile content. Highly saturated grades offer optimum resistance to aging, such as exposure to heat, ozone, and chemicals, and can only be vulcanized effectively with peroxides or high energy radiation.

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² Annual Book of ASTM Standards, Vol 09.01.

4.2 Partially unsaturated grades can be cured by sulfur systems in addition to peroxides and high energy radiation.

4.3 This test method allows for an evaluation of an unsaturation parameter, UP, with or without the testing of a control or known percent unsaturation sample of HNBR, from the measured values for two curemeter parameters; scorch time, tS1, in minutes and maximum torque, MH, in dNm.

4.4 Values of t'90 are also correlated with the unsaturation, but tS1 and MH are measured properties more responsive to changes in unsaturation level.

4.5 The residual unsaturation can be determined more accurately and quantitatively by infrared spectrophotometry (see Test Method D 5670).

4.6 This test method may be used for quality control, research and development, and comparison of different HNBR samples.

5. Standard Test Formula

5.1 The standard test formula is shown in Table 1.

5.2 For meaningful results it is necessary to use the same lot of raw materials within each test series.

6. Mixing Procedure

6.1 Weighing of materials and mixing in a Miniature Internal Mixer (MIM) is carried out in accordance with Practice D 3182.

6.2 It is recommended to pre-blend the compounding materials other than rubber as described in Practice D 3182.

6.3 Mix with the head temperature of the MIM at $60 \pm 3^\circ\text{C}$ ($140 \pm 5^\circ\text{F}$) and a rotor speed of 6.3 to 6.6 rad/s (60 to 63 rpm). A fill factor of about 82 % (70 cm^3) is recommended for effective mixing.

6.4 Mixing Cycle:

	Duration (min)
6.4.1 Charge the mixing chamber with the rubber, lower the ram, and start the timer.	0
6.4.2 Masticate the rubber.	0.5
6.4.3 Raise the ram and add pre-blended powders, taking care to avoid losses. Sweep the orifice and lower the ram.	2.5
6.4.4 Raise the ram, sweep, lower the ram, and allow batch to mix.	1.0
Total time	4.0

6.4.5 Turn off the rotors, raise the ram, remove the mixing chamber, and discharge the batch. Record maximum batch temperature, if desired.

6.4.6 Pass the batch five times through a laboratory mill with the rolls at a tight setting and a roll temperature of $50 \pm$

5°C ($122 \pm 9^\circ\text{F}$), folding the mill sheet in half and maintaining the grain on each pass.

6.4.7 Check and record the batch mass. If it differs from the theoretical value by more than 0.3 %, discard the batch.

7. Testing

7.1 Individual formulations containing one or more rubber samples of unknown or known residual unsaturation, or both, are mixed and the maximum torque and scorch time are measured as MH and tS1 in accordance with Test Method D 2084, using a temperature of 160°C (320°F), 1° amplitude, and a recorder range of 0–50.

7.2 Maximum torque (MH) and scorch time (tS1) also can be determined in accordance with Test Method D 5289.

7.3 If only tS1 is measured, a 15-min recorder time can be used, while for MH and t'90 a 60-min recorder time is recommended.

7.4 The MH and tS1 values of the formulations containing HNBR of unknown residual unsaturation are measured as well as the known HNBR unsaturation standard(s).

8. Limitation

8.1 This test method provides the highest sensitivity for HNBR samples with a residual unsaturation of below approximately 6 %. It is less discriminating for higher unsaturation levels.

9. Evaluating the Unsaturation Parameter (UP)

9.1 The value for UP is evaluated from two special curemeter parameters: the scorch parameter, SP, obtained from the measured scorch time, tS1, in minutes, and the torque parameter, TP, obtained from the measured maximum torque, MH, in dNm. The values for SP and TP are obtained from Table A1.1 of Annex A1.

9.2 *Calculating UP*—Using the measured values of tS1 in minutes, locate the corresponding value of the scorch parameter, SP, in Table A1.1 of Annex A1. Using the measured value of MH in dNm, locate the corresponding value of the torque parameter, TP, in Table A1.1 of Annex A1. Calculate the unsaturation parameter, UP, for each HNBR tested, by means of Eq 1.

$$UP = [SP + TP]/2 \quad (1)$$

where:

UP = Unsaturation Parameter for any HNBR (sample),

SP = Table A1.1 curemeter parameter for scorch time measurement, tS1, and

TP = Table A1.1 curemeter parameter for maximum torque measurement, MH.

9.3 *Calculating U*—If the unsaturation in percent of a tested HNBR sample is known, it can be used as a reference to calculate the approximate unsaturation in percent of sample with unknown unsaturation, by means of Eq 2.

$$U = [U(\text{ref})/UP(\text{ref})]UP \quad (2)$$

where:

U = approximate unsaturation in % for any HNBR,

TABLE 1 Standard Test Formula^a

Materials	Parts by Mass
Hydrogenated nitrile rubber	100.0
Zinc oxide (IRM 91)	5.0
Stearic acid (SRM 392)	1.0
Spider sulfur	0.8
Tetramethyl thiuramdisulfide (TMTD) (IRM 1)	2.0
2-mercaptobenzothiazole (MBT)	0.2
Total	109.0

^aNote—Weigh the rubber and ingredient blend to the nearest 0.01 g and individual ingredients, if used, to the nearest 0.001 g.