SRM's 370-387

Standard Materials for Rubber Compounding

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When the synthetic rubber plants began operation in 1943, the Government took steps to establish a system of quality control that would assure that the rubber produced in 16 plants had essentially the same properties and could be used interchangeably by the manufacturers of rubber products. The most important characteristic for quality control was the curing behavior of the rubber. The measurement of this behavior required mixing the rubber with compounding ingredients, vulcanizing the mixed compound for several periods of time, and measuring the tensile properties of the vulcanizates.

Early interlaboratory tests led the Government to an extensive standardization program in order to achieve the necessary quality control of production. In this program, it became obvious that the compounding ingredients as well as the methods of mixing, curing, and testing required standardization. Therefore, in 1944, the Rubber Reserve Co. established standard compounding ingredients for testing synthetic rubbers. The first standards were commercial lots set aside and distributed by their suppliers, and consisted of five materials. By 1946 a total of 14 standards had been established.

The Office of Rubber Reserve soon recognized that the establishment of suitable standards was a difficult technical problem and called on the National Bureau of Standards for assistance. Finally, in 1948 this Office requested NBS to assume responsibility for these standards. Shortly thereafter, ASTM Committee D-11 appointed a special subcommittee on standard materials, the forerunner of Subcommittee 29 on Compounding Ingredients. This Subcommittee requested the establishment of about 20 standard compounding materials which included the standards required for the synthetic rubber program. The National Bureau of Standards has now available 17 of these materials, including three standard rubbers.

Criteria for Standards

A satisfactory standard for rubber compounding must fulfill the following requirements: It must be uniform throughout the lot. It must not change appreciably before use. Successive lots of the standard should have the same characteristics for the intended use.

By 1947, it was evident that many of the 14 materials established as standards by the Rubber Reserve Co. did not meet these requirements and that a reappraisal of the test formulations was necessary. After an extensive study, the formulations for testing synthetic rubbers were simplified and six of the 14 materials were eliminated. Experience had shown by this time that it is very difficult to reproduce the lower commercial grades used in the rubber industry because of the many active impurities present. Therefore, many of the standards were replaced when the formulations were changed. The highest purity materials commercially available were selected for these replacements. Even the small amount of impurity in the best commercial grades has given considerable difficulty in reproducing lots of some standards.

The original standards were distributed in the customary commercial containers, which were paper bags in some instances. It was found that some materials packaged in this manner changed irreversibly during storage and could not be used after a short time. Therefore, the decision was made to package the compounding ingredients in air-tight metal containers. However, it is not expedient to package the rubbers in metal containers. They were wrapped in polyethylene and packaged in paper bags.

The stability during storage of the standards and proposed standards is being studied. Surveillance of the established standards is maintained to determine when appreciable change in their characteristics has occurred. Portions of the various materials are being stored under four different temperature conditions ranging from −20° to +40° C. and periodic tests are being made. Among the NBS Standards for Rubber Compounding, the only change noted is a slight increase in Mooney viscosity of one of the styrene-butadiene rubbers, SBR-1500. On the other hand, studies made on materials proposed for use as standards indicate that many

of the materials used in the rubber industry are not sufficiently stable for this purpose.

Procurement of Materials

Replacement lots are purchased on the basis of specifications for composition and performance in rubber compounds. The specifications for composition are given in Appendix A. Tests are made to determine that the material complies with these specifications, but no attempt is made to certify the actual composition. The uniformity of the lot and its suitability for a standard are judged by its performance in a standard rubber compound. In some cases several lots have to be tested before a suitable material is obtained.

Materials for the standards have been procured through the issuance of bid invitations to prospective suppliers in accordance with regular Government practices. Thus, successive lots of a standard have frequently been purchased from different suppliers. Each new supplier had to be educated on the stringent requirements enumerated above for a standard. All the suppliers have been cooperative, and have been able to furnish a satisfactory lot in most instances.

Sampling and Testing

In the case of replacement lots of compounding ingredients, several portions are selected at random from the lot prior to packaging. These portions are compared with the previous standard of the particular material to ascertain their equivalence in a standard rubber compound. Generally, four compounds are prepared from each portion and at least four compounds from the previous standard.

The uniformity of the lot is judged from a sample taken during packaging. Experience indicates that 8 to 13 portions selected at predetermined periodic intervals give a suitable sample. Each portion is tested separately in a standard rubber compound. In order to eliminate small errors attributable to the sequence or day in which the compounds are mixed, a statistical design similar to those given in Appendix B is used.

The rubber compounds are prepared in accordance with the appropriate standard formulation and mixing procedure in ASTM Designation D 15. The compounds are mixed on a mill having rolls specially designed to maintain their surface temperature constant within 2 Celsius degrees (*1*). All operations are conducted in a room conditioned at 23° ±1° C. and between 35 and 40% relative humidity.

The viscometer cure characteristics of the compound are determined at either 125° or 150° C., between 2 and 4 hours after mixing by the procedure described in ASTM Designation D 1077. In addition to the time of incipient cure (t_5), the time required for the viscosity to increase from 5 to 35 ML points above the minimum is recorded as the cure index (Δt). The parameter Δt is inversely related to the rate of cure.

Vulcanizates approximately 15 × 15 × 0.2 cm. are prepared in accordance with ASTM Designation D 15 using a chromium-plated, four-cavity mold machined directly in the hot plates of the press. The press is equipped with a special temperature controller which maintains the temperature of the plates constant within 0.1 Celsius degree. This equipment produces vulcanizates that are uniform in thickness within 0.02 mm.

The following tests are made on the vulcanizates:

Test	ASTM Procedure
Strain under a fixed load	D 1456-57T
Stress at a fixed elongation	D 412-51T
Stress at failure	D 412-51T
Elongation at failure	D 412-51T
Electrical resistivity*	D 991-48T**

* Measured only on compounds containing carbon black.
** Modified as described by McKinney and Roth (*2*).

Analysis of Results

A statistical analysis is made of the results for each property. A typical analysis is given in Appendix B for the viscometer cure results obtained with standard sample 371c of sulfur. The several analyses are examined for trends or other evidence of nonuniformity in the material. The reuslts for most standards for rubber compounding show no evidence of heterogeneity in their effect on vulcanization characteristics. In the few instances in which some heterogeneity has been observed, either the variability is slight—i.e., not significant at the 1% level—the portion of the lot exhibiting the variability is not included in the standard sample, the lot is reblended and retested, or a new lot is prepared.

In the case of the rubbers, no attempt is made to reproduce the previous lot exactly. Instead, the most probable values and their uncertainties based on a confidence coefficient of 95% are determined and issued as a certificate with the standard. In calculating the uncertainty limits, allowance is made for intrinsic error of test and systematic effects associated with both sequence of mixing the compounds and day of mixing. In those instances where there is a slight heterogeneity in the material itself, the uncertainty limits also reflect this

variability. Accordingly, the uncertainties given in the certificates for the rubbers are generally larger than would be indicated by the intrinsic error of test which is used to judge the uniformity of the lot.

Problems Encountered in Establishing Standard Materials

(The NBS Standard Sample No. precedes the name of the following standard materials.)

370 Zinc Oxide. The original standard established by the Rubber Reserve Co. was made by the American process. Attempts to reproduce the material were not successful. In 1948, a high-purity zinc oxide made by the French process was chosen for the standard. No difficulty has been encountered in reproducing this material.

371 Sulfur. A distilled product of high purity has been used for the standard. There has been no difficulty in reproducing it.

372 Stearic Acid. The original material chosen for the standard was the highest quality available at the time. It contained some impurities that had a pronounced influence on the vulcanizates of rubber compounds. It was not possible to reproduce the original standard. A distilled stearic acid of low iodine number which is equivalent in rubber to C. P. stearic acid was therefore chosen for the standard. This high quality material has been reproduced twice without difficulty.

373 Benzothiazyl Disulfide. A commercial material is used for the standard. Although the original standard has been reproduced twice, testing of many lots is required to obtain one satisfactory for the standard.

374 Tetramethylthiuram Disulfide. The standard is a commercial material that has been reproduced once after testing a number of lots.

375 Channel Black. This standard has been reproduced several times, but only after testing many lots. The several lots have had detectable differences among them, but the differences have been small enough so that they could be used for specification testing. Special blending of the lot has been necessary to attain the desired uniformity.

376 Magnesia. The original Rubber Reserve Co. standard has been replaced with a lot having an appreciably different effect in polychloroprene. It has also been difficult to obtain a uniform lot of this material.

377-383-. The original lot established for each of these standards (see Appendix A) is still being furnished. Consequently, the problems involved in replacing them are still unknown.

385 Natural Rubber. Extensive investigations during the past 10 years were conducted to obtain a uniform lot of rubber having the desired properties. Liberian crepe produced under carefully controlled conditions was finally selected for this standard. The rubber was produced on two days. There was a slight difference between the two lots of rubber, but each lot was uniform within itself. Accordingly, the lots have been individually certified.

386 SBR-1500. Replacement lots of styrene-butadiene rubber, type 1500, have been similar even though no attempt was made to reproduce the original exactly. There has been some difficulty in attaining the desired uniformity within the lot. The Mooney viscosity of this material has also changed slightly during storage.

387 SBR-1000. This standard is more stable than SBR-1500, but is comparable in uniformity.

Conclusions

The standards for rubber compounding have been useful in the standardization of testing in the synthetic rubber plants. Their success in this application has resulted in their use by other rubber laboratories. However, the establishment of these standards has been and continues to be a difficult technical problem. The difficulties have been alleviated whenever a high-purity material has been obtained.

Appendix A

Specifications for Compositions of Standards

370 Zinc Oxide. This standard conforms to the requirements of the American Chemical Society for reagent grade zinc oxide and has a surface area of approximately 3 square meters per gram.

371 Sulfur. This standard is a distilled sulfur conforming to the following requirements:

Purity	99.90% minimum
Loss at 100° C.	0.05% maximum
Ash	0.02% maximum
Insolubles in CS_2	0.10% maximum
Insolubles in benzene	0.10% maximum
Organic material	0.05% maximum
Acidity as H_2SO_4	0.005% maximum
Physical state	
Through 100-mesh sieve	100%
Through 200-mesh sieve	90 to 95%

372 Stearic Acid. This standard is a distilled stearic acid conforming to the following requirements:

Titer (solidification point)	65° C. minimum
Iodine number	2 maximum
Loss at 105° C	0.5% maximum
Ash	0.1% maximum
Acid number	195 to 199
Mineral acid	none
Fat, unsaponifiable, and insoluble material	0.5% maximum
Physical state:	Flake or powder

373 Benzothiazyl Disulfide. This standard conforms to the following requirements:

Benzothiazyl disulfide	93.0% minimum
Mercaptobenzothiazol	0.5 to 0.75%
Moisture	0.5% maximum
Ash	0.7% maximum
Mineral oil	2.0%
Zinc soap	2.0% maximum
Melting point	165° C maximum
Physical state	
Through 100-mesh sieve	99.9% minimum

374 Tetramethylthiuram Disulfide. This standard conforms to the following requirements:

Moisture	0.05% maximum
Ash	0.10% maximum
Insolubles in $CHCl_3$	0.15% maximum
Melting point	163° C minimum
Physical state	
Through 100-mesh sieve	100%

375 Channel Black. This standard conforms to the following requirements:

Loss at 100° C.	2.00% maximum
Ash at 550° C.	0.15% maximum
Physical state	
Retained on 325-mesh sieve	0.10% maximum
Retained on 30-mesh sieve	0.001% maximum

376 Light Magnesia. This standard conforms to the following requirements:

Magnesium oxide	91.0% minimum
Loss on ignition	7.0% maximum
Calcium oxide	1.0% maximum
Water solubles	1.0% maximum
Acid insolubles	0.4% maximum
Fe_2O_3 and Al_2O_3	0.1% maximum
Manganese	0.004% maximum
Density	10 lb./cu. ft. maximum
Physical state	
Retained on 325-mesh sieve	0.1% maximum

377 Phenyl-beta-Naphthylamine. This standard is distilled phenyl-beta-naphthylamine conforming to the following requirements:

Phenyl-beta-naphthylamine	99.25% minimum
Loss at 105° C.	0.25% maximum
Ash	0.25% maximum
Beta-naphthol	0.10% maximum
Benzene insolubles	0.10% maximum
Melting point	107° C minimum
Physical state	
Retained on 100-mesh sieve	0.10% maximum

378 Oil Furnace Black. This standard conforms to the following requirements:

Loss at 100° C	1.0% maximum
Ash at 550° C	0.5% maximum
Physical state	
Retained on 325-mesh sieve	0.1% maximum
Retained on 30-mesh sieve	0.005% maximum

379-382. 379 Conducting Black, 380 Calcium Carbonate, 381 Calcium Silicate, and 382 Gas Furnace Black. These standards are commercial materials supplied through ASTM Committee D-11 so that no requirements for composition have been established.

383 Mercaptobenzothiazole. This standard conforms to the following requirements:

Mercaptobenzothiazole	99.0% minimum
Moisture	0.3% maximum
Ash	0.3% maximum
Melting point	179° C. minimum
Physical state	
Retained on 100-mesh sieve	0.1% maximum

385 Natural Rubber. This standard conforms to the following requirements:

Rubber hydrocarbon	92.0% minimum
Volatile matter	0.5% maximum
Ash	0.5% maximum
Dirt (retained on 325-mesh sieve)	0.05% maximum
Copper	0.0004% maximum
Manganese	0.0005% maximum

386 SBR-1500. This standard conforms to the following requirements:

Volatile matter	0.75% maximum
Ash	1.50% maximum
Rosin acid	5.00 to 7.25%
Soap	0.50% maximum
Stabilizer	1.00 to 1.75%
Bound styrene	22.5 to 24.5%

387 SBR-1000. This standard conforms to the following requirements:

Volatile matter	0.50% maximum
Ash	1.50% maximum
Fatty acid	4.00 to 6.25%
Soap	0.75% maximum
Stabilizer	1.00 to 1.75%
Bound styrene	22.5 to 24.5%

Appendix B

Design for Vulcanization Tests

The design of test selected for determining the uniformity of a standard for rubber compounding with respect to the vulcanization characteristics of the rubber compound depends on the number of portions comprising the sample, which usually is between 8 and 13. Further, the design must accommodate tests in groups of four because four compounds are vulcanized simultaneously. Also, experience indicates that four compounds should be prepared from each portion in the sample in order to attain the desired precision for evaluating the standard. The following designs fulfill these requirements:

Sample Size	Design*
8	(3) page 142, design Sr 7
9	(3) page 186, design R 8
10	(3) page 232, design T 12
11	None available
12	(3) page 188, design R 15
13	(4) page 145, table 13.6

* These publications give instructions for analyzing these designs.

For illustration, the following design was used recently to evaluate NBS Standard Sample 371c of sulfur:

Order of Mixing	Day of Mixing											
	a	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*	*k*	*m*	*n*
A	4	1	9	8	12	10	11	2	5	7	6	3
B	5	3	10	12	1	11	4	7	8	6	9	2
C	1	6	5	2	7	8	12	10	3	11	4	9
D	2	10	12	6	9	1	3	4	7	5	8	11

The numerals correspond to the twelve portions in the order in which they were taken from the lot. The following table lists the times in minutes for incipient cure, t_5, measured in the Mooney viscometer at 150° C.

Portion	A	B	C	D	Observed Mean
1	8.26b	8.78e	8.46a	8.43f	8.482
2	8.45h	8.57n	8.55d	8.49a	8.515
3	8.60n	8.39b	8.43i	8.31g	8.432
4	8.45a	8.49g	8.48m	8.46h	8.470
5	8.28i	8.45a	8.70c	8.50k	8.482
6	8.58m	8.58k	8.47b	8.57d	8.550
7	8.58k	8.52h	8.56e	8.47i	8.532
8	8.25d	8.36i	8.38f	8.63m	8.405
9	8.23c	8.43m	8.57n	8.56e	8.448
10	8.32f	8.40c	8.69h	8.48b	8.472
11	8.52g	8.52f	8.54k	8.58n	8.540
12	8.33e	8.56d	8.40g	8.51c	8.450
					8.482

An analysis of variance following the procedure given in Table 1.0 (*3*, page 5) gives the following results:

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square
Portions	11	0.0936	0.0085
Days	11	0.2000	0.0182
Order	3	0.0987	0.0329
Error	22	0.2663	0.0121

The mean square for portions is less than that for error indicating no detectable difference among portions. The mean square for error corresponds to a standard deviation for a single measurement of 0.11 minute. The variability arising from day and order is small so that this design of test offers no advantage over a completely random design in this instance. Frequently, there is an appreciable variability arising from day and order. In such cases, the above designs have advantages in detecting heterogeneity in the lot.

The following tabulation lists the mean squares for portions and error calculated from the results for the various tests, and the minimum and maximum means for the 12 portions corrected for day effects.

Tests	Mean Square		Portions	
	Portion	Error	Min.	Max.
Incipient cure, t_5, min.	0.0085	0.0121	8.37	8.55
Cure index, $t_{35}-t_5$, min.	0.0052	0.0040	3.08	3.23
Strain at 400 p.s.i., %				
15-min. cure	41	67	300	309
30-min. cure	3.25	2.47	170	172
60-min. cure	2.48*	0.80	141	143
Stress at 300%, p.s.i.				
15-min. cure	583	363	467	516
30-min. cure	237	675	1169	1200
60-min. cure	243	553	1557	1585
Stress at failure, p.s.i.				
30-min. cure	6938	27218	4189	4333
Elongation at failure, %				
30-min. cure	63	188	623	640
Resistivity, megohm-cm.				
60-min. cure	52	54	59	71

* This value is significantly greater than that for error. However, the error mean square usually obtained for this compound is above 2. Further, there is no evidence of any trend in the portions. In view of no other evidence of heterogeneity, it is concluded that the lot of sulfur is uniform.

REFERENCES

(1) Roth, F. L., Decker, G. E. and Stiehler, R. D., "Temperature Control During Mixing of Rubber Compounds," *Rubber World* 132, 482 (1955); *Rubber Chem. and Technol.* 28, 1157 (1955).

(2) McKinney, J. E. and Roth, F. L., *Ind. Eng. Chem.* 44, 159 (1952).

(3) Bose, R. C., Clatworthy, W. H., and Shrikhande, S. S., *N. Carolina Exptl. Sta. Tech. Bull.* 107, August 1954.

(4) Brownlee, K. A., "Industrial Experimentation," Chemical Publ. Co., Brooklyn, N. Y., 1949.