9

Recycled Rubber

by Krishna C. Baranwal[1]

9.1 DEFINITIONS AND RUBBER RECYCLING PROCESSES

ACCORDING TO ASTM STANDARD CLASSIFICATION for Rubber Compounding Materials—Recycled Vulcanizate Particulate Rubber (ASTM D 5603-01):

- *Recycled rubber* is defined as recyclable, vulcanized rubber that has been processed to give particulates or other forms of different shapes, sizes, and size distributions.
- *Parent Compound:* original compound used in rubber product.
- *Vulcanizate:* cured (vulcanized) rubber.

Various techniques are used to generate recycled rubber. Major processes are briefly discussed below.

9.1.1 Reclaiming

This is done by a chemical digestion process. Aryl sulfides and other chemicals are added to rubber, and then the mixture is chemically digested. This process does not produce crumb rubber. Rather, it generates coherent chunks or lumps that can be shipped in the bale form. Over the years, there have been significant decreases in use of reclaim rubber. Currently, consumption is significantly curtailed and only two companies in the United States are in the rubber reclaiming business, one dealing with butyl reclaim and the second with VMQ, EPDM, and other specialty reclaim rubbers. Another international company sells low-odor reclaim rubber from whole tire, NR, and butyl rubber.

9.1.2 Ground Rubber

Here, vulcanized scrap rubber is first reduced to approximately 2.5-cm

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by 2.5-cm to 5 cm by 5-cm chips by shredding. This material is further reduced in size by use of ambient grinding mills. The finer the particle size needed, the longer the rubber must be milled. Multiple grinds reduce the particle size. Any fiber is removed by air and metal is removed by magnetic separation. The production rate is about 550 kg/h for 30 to 40 mesh size crumb rubber. The heat generated in this process can degrade rubber if the product is not cooled properly before storage or shipping.

9.1.3 Cryogenic Ground Rubber

In this process, small rubber chips or crumb rubber, 10 to 20 mesh, are cooled by a chiller using liquid nitrogen and then put through a grinding mill. For finer particles, multiple cooling and grinding are usually needed. A typical production rate is 1800 to 2700 kg/h for 60 to 80 mesh material. Little heat is generated in the process, thereby decreasing possible degradation of the rubber. All fiber and steel are separated by freeze-grinding to give a higher yield of usable product.

9.1.4 Wet Ground Rubber

Here ground rubber is produced by passing a water suspension of rubber particles through a flour-grinding-type mill. Mesh sizes from 60 to 120 are typical.

9.1.5 "Devulcanization" Process

In sulfur-accelerator vulcanization of diene rubbers, sulfur-sulfur bonds are formed. "Devulcanization" is the reverse process in which either via external energy (ultrasonic) or by the addition of chemicals some of the sulfur-sulfur bonds are broken. There may also be cleavage of some C-S and C-C bonds in these processes.

In ultrasonic "devulcanization" [1,2], a crumb rubber is exposed to ultrasonic vibrations. Presumably, the energy absorbed by the rubber breaks the sulfur-sulfur bonds. The resulting devulcanized rubber can be compounded as is, or mixed with virgin rubber and recured. Chemical "devulcanization" involves addition of certain accelerators and sulfur to the crumb rubber on a mill or in a Banbury.®[2]

9.1.6 Need for Standards

Since recycled rubber is produced using different processes, it is important to have standards for different particle sizes and chemical tests for characterization.

[2] Farrel Corporation, Ansonia, CT.

In early 1995, ASTM Subcommittee D11.26 on Recycled Rubber was formed. By late 1996 ASTM approved two standards: ASTM Standard Classification for Rubber Compounding Materials—Recycled Vulcanizate Particulate Rubber (ASTM D 5603-96) and ASTM Standard Test Methods for Rubber Compounding Materials—Determination of Particle Size Distribution of Recycled Vulcanizate Particulate Rubber (ASTM D 5644-96) developed by the subcommittee. These standards were revised and reissued as D 5603-01 and D 5644-01.

ASTM D 5603-01 includes classification of crumb rubber based on parent compounds, specifications for the first two screens for particle size determination for particles 100 mesh and larger, limits on chemical test results and maximum limits for fiber and metal content. ASTM D 5644-01 describes a mechanical sieve shaker technique to determine particle size and particle size distribution of crumb rubber for coarser particles and ultrasonic and light optical microscope technique for 80 mesh or finer particles.

In late 1997, the Chicago Board of Trade [3] (CBOT) published a document on definition of terms, chemical tests, and particle size specification based on ASTM D 5603-96 for buying and selling crumb rubber. Thus, there are now specifications available for recycled rubber that vendors and customers should use to ensure material quality.

9.2 STORAGE, QA SAMPLING, AND TEST PLANS

9.2.1 *Material and Safety Data Sheets (MSDS)*

Recycled rubber processors should provide MSD sheets to their employees and to the end-users. Information for MSDS can be generated at either the processor's laboratory or at an independent laboratory. An MSDS should include information on chemical reactivity, storage, disposal, and physical hazards.

9.2.2 *Crumb Rubber Storage*

Recycling rubber from whole tires into chips and crumbs can generate heat up to 115°C in the ambient grinding process. This can, on storage, without sufficient cooling, lead to spontaneous combustion. The presence of iron (Fe) in natural rubber compounds, can catalyze the oxidation process, causing rubber degradation. This degradation is accelerated with heat. During processing, generation of crumbs and storage, volatiles and hot fumes may be generated.

Thus, the materials must be sufficiently cooled, either by water or air, to avoid spontaneous combustion. Crumbs should be stored at ambient temperatures in dry areas, but not in tin sheds or tin roof warehouses.

9.2.3 Sampling and Test Plans

Each rubber recycling plant may have its own sampling procedures. A typical sampling procedure is given here. Two samples, about 125 g each of each skid (1000 to 1200 kg), are taken by the bagger at the time of bagging recycled rubber. Random samples are taken by the laboratory personnel for quality checks. Frequency and sampling procedures may vary, but should be agreed upon between vendor and customer.

After sampling, the following tests, described in ASTM D 5603-01, are carried out: % extractables, % ash content, % moisture (heat loss), % natural rubber, % rubber hydrocarbon, and % carbon black. Two samples per truck load (five skids) are tested for % moisture. The remaining tests are one sample per truck load shipment. All these tests are carried out according to ASTM D 297. For ambient ground materials, moisture content and bulk density measurements are made on every skid because of possible moisture content variation in feedstock. Fiber and metal contents should be reported as agreed upon between vendor and customer.

Particle size and particle size distribution measurements are made according to ASTM D 5644-01. ASTM D 5603-01 should be used to determine if the material meets the size specification for the top two screens.

Analysis results are shipped along with the materials meeting customer's specifications.

9.3 TEST METHODS

ASTM D 5603-01 defines classification of crumb rubber based on parent compounds (see Table 9.2). Below is a summary:

- *Grade 1* Crumb rubber from passenger car, truck, and bus tires from which metal and fibers have been removed.
- *Grade 2* Crumb rubber from tread only from passenger car, truck, and bus tires.
- *Grade 3* Crumb rubber from tread and shoulder area buffing (in retreading operation) from passenger car, truck, and bus tires.
- *Grade 4* Crumb rubber from passenger car, truck, and bus tire retreading where the buffing from tires includes tread, shoulder area, and sidewalls.
- *Grade 5* Crumb rubber from off-the-road tires, large equipment tires, industrial tires, forklift tires, and farm implement tires. This excludes car, bus, and truck tires.
- *Grade 6* Crumb rubber from nontire rubber products.

9.3.1 Particle Size (PS) and Particle Size Distribution (PSD)

PS and PSD measurements are made according to the procedure described in ASTM D 5644-01 using six screens and a mechanical sieve shaker,

TABLE 9.1—Recycled Rubber Product Designation (ASTM D 5603-01).

NOMINAL PRODUCT DESIGNATION	EXAMPLE ASTM D 5603 DESIGNATION	ZERO SCREEN μm	PERCENT RETAINED ON ZERO SCREEN	SIZE DESIGNATION SCREEN μm	MAXIMUM PERCENT RETAINED ON DESIGNATION SCREEN
10 Mesh	Class 10-X	2360 (8 Mesh)	0	2000 (10 Mesh)	5
20 Mesh	Class 20-X	1180 (16 Mesh)	0	850 (20 Mesh)	5
30 Mesh	Class 30-X	850 (20 Mesh)	0	600 (30 Mesh)	10
40 Mesh	Class 40-X	600 (30 Mesh)	0	425 (40 Mesh)	10
50 Mesh	Class 50-X	425 (40 Mesh)	0	300 (50 Mesh)	10
60 Mesh	Class 60-X	300 (50 Mesh)	0	250 (60 Mesh)	10
70 Mesh	Class 70-X	259 (60 Mesh)	0	212 (70 Mesh)	10
80 Mesh	Class 80-X	250 (60 Mesh)	0	180 (80 Mesh)	10
100 Mesh	Class 100-X	180 (80 Mesh)	0	150 (100 Mesh)	10
120 Mesh	Class 120-X	150 (100 Mesh)	0	128 (120 Mesh)	15
140 Mesh	Class 140-X	128 (120 Mesh)	0	106 (140 Mesh)	15
170 Mesh	Class 170-X	106 (140 Mesh)	0	90 (170 Mesh)	15
200 Mesh	Class 200-X	90 (170 Mesh)	0	75 (200 Mesh)	15

TABLE 9.2—Properties for Recycled Rubber (Grades 1–6) (ASTM D 5603-01).

PROPERTY	%	TEST METHOD
(a) *Grade 1–4*		
Acetone Extractables	8–22	D 297, Sec. 17,18, 19
Ash, max	8	D 297, Sec. 34, 35, 36, 37
Carbon Black	26–38	D 297, Sec. 38, 39
Loss on Heating, max	1	D 1509
Natural Rubber	10–35	D 297, Sec. 52, 53
Rubber Hydrogen Content (RHC), min	42	D 297, Sec. 11
(b) *Grade 1–6*		
Metal Content, max	0.1	See 7.3.2
Fiber Content, max (Grades 1, 4, 5, 6)	0.5	See 7.4
Fiber Content, max (Grades 2, 3)	Nil	See 7.4

usually the Ro-Tap sieve shaker. The first two top screens, zero screen and designation screens, are defined in ASTM D 5603-01 for sizes 10 to 200 mesh. The remaining four screens for these sizes can be agreed upon by vendor and customer.

In a PS and PSD test, screens are stacked on a shaker in order of increasing mesh size with the coarsest mesh screen on top and the finest mesh at the bottom. Approximately 100 g of crumb rubber is mixed with talc powder, about 5 g of talc for coarser than 50 mesh, and 15 g for finer particles. The mixture is put on the zero screen and the shaker started. After the specified time, the shaker is stopped, and the material retained on each screen is weighed. The weight percent retained on a designated screen determines the crumb size (see Table 9.1). Weight percents retained on all six screens when plotted as a function of screen size gives the particle size distribution.

The mechanical shaker is suitable for coarser particle sizes. For 80 mesh and finer particles, it is recommended that the ultrasonic and light microscope technique, described in Section 12 of ASTM D 5644-01, be used.

9.3.2 Particle Size Classification (ASTM D 5603-01)

Table 9.1 defines particle size classification of crumb rubber for sizes 10 to 200 mesh. The crumb rubber size designation is the mesh size based on the size of designation sieve screen, which allows a range for the upper limit of material retained on that screen. No crumb rubber is retained on the zero screen.

The overall classification of recycled crumb rubber is based on particle size distribution and origin (Grades 1–6, previously listed). Other size designations, not listed in Table 9.1, can be agreed upon by vendor and customer.

9.3.3 Chemical Analysis (ASTM D 5603-01)

Table 9.2 lists properties, their limits, and ASTM test methods for crumb rubber.

Based on ASTM procedures, the following are brief descriptions of test methods.

9.3.3.1 Percent Extractables (ASTM D 297, Section 19) About 2 g of crumb rubber is extracted with hot acetone for 16 h. Acetone is evaporated from the extract over a steam bath and the dried extract is weighed. Percent extract is calculated based on the original mass of the samples.

9.3.3.2 Percent Ash (ASTM D 297, Section 35) A known amount of sample is heated at 550 ± 25°C in air for 1.5 h or until all carbonaceous material is burned off to give residue or ash. Ash may be due to zinc oxide, silica, clay, or some other inorganic material in crumb rubber.

9.3.3.3 Percent Carbon Black (ASTM D 297, Section 39) A known amount (X g) of crumb rubber is extracted with solvent, usually acetone. Extracted rubber is pyrolyzed at 800 to 900°C in nitrogen in an electrically heated tube furnace. It is then cooled and weighed (Y g). The pyrolysis sample is then heated at 800 to 900°C in air in a muffle furnace for 2 h. The resulting material is cooled and weighed (Z gms).

$$\text{Percent carbon black is} = \frac{Y - Z}{X} \times 100 \tag{1}$$

9.3.3.4 Percent Moisture Content (ASTM D 1509–2000) or Heating Loss About 2 g of weighed recycled rubber is heated at 125°C for 1 h, cooled, and weighed. Percent mass loss is the moisture content. Typically, moisture content in crumb rubber is less than 1 %, which is the current accepted maximum level.

Too much moisture can cause caking and may inhibit free flow in processing. Anti-caking agents such as calcium carbonate can be used. Moisture buildup can lead to acidic conditions, giving slower cure rates in compounds.

9.3.3.5 Percent Natural Rubber Content (ASTM D 297, Section 53) A known amount of cured rubber is extracted with hot methyl ethyl ketone and dried in an oven at 100°C for 1 h. The extracted rubber is digested in chromic acid solution to quantitatively oxidize the rubber, resulting in acetic acid formation. The acetic acid is separated by distillation. It is then aerated to remove carbon dioxide. The amount of acetic acid is determined quantitatively by titration with 0.1 M, NaOH solution. A blank titration should also be determined. Percent isoprene is calculated as:

$$\text{Isoprene Polymer \%} = \frac{9.08\,(A - B)M}{C} \tag{2}$$

where

A = volume of NaOH solution required for titration of the specimen.
B = volume of NaOH solution required for titration of the blank.
M = molarity of NaOH solution.
C = grams of specimen used.

This procedure is currently used for reclaimed rubber, even though it has been found to give consistently lower than previously accepted estimates of the isoprene polymer content.

9.3.3.6 Percent Rubber Hydrocarbon (ASTM D 297) By determining percentages of extractables, ash, moisture, and carbon black, rubber hydrocarbon (RHC) can be calculated as:

$$\begin{aligned}\text{\% RHC} = 100 - (&\text{\% Extractables} + \text{\% Ash} \\ &+ \text{\% Moisture} + \text{\% Carbon Black})\end{aligned} \tag{3}$$

9.3.3.7 Iron and Fiber Content (ASTM D 5603-01, Section 7) Crumb rubber may contain metal particles remaining from recycling radial tires, wire-reinforced hoses, belts, etc. To determine iron content, about 100 g of crumb rubber is weighed and spread on a flat nonmagnetic surface. A small horseshoe magnet is passed over the specimen for 60 s to pick up iron particles. All iron fragments are removed and weighed. The percentage of iron is then calculated.

Loose fiber in crumb rubber may come from recycling fiber-reinforced tires, hoses, belts, etc. Fiber content determination can be made after normal mechanical shaker sieve analysis procedure according to ASTM D 5644-01. After sieve analysis, any free fabric would result in the form of "fabric balls," which can be removed from each screen. "Fabric balls" are weighed and fabric content is calculated as percentage of initial sample mass used for sieve analysis.

9.4 EVALUATION OF RECYCLED RUBBER IN COMPOUNDS

Recycled rubber is blended with virgin rubber compound in two ways: (1) the total elastomer content from the virgin compound plus recycled rubber is kept at 100 phr (parts per hundred rubber) or (2) the recycled rubber is added on top of the virgin compound, whereby the total elastomer content becomes more than 100 phr. W. Dierkes [5] found that at more than 20 phr natural rubber reclaim, tensile strengths are higher when reclaim rubber is added on top of 100 phr than when elastomer content of the blend is constant at 100 phr. This is according to expectations. Higher elastomer content can lead to more crosslinked rubber and, hence, can give higher tensile strength.

The amount of recycled rubber used in a rubber compound must be optimized. Experiments can be used to determine the effects of varying amounts of recycled rubber on desired properties. Table 9.3 shows the effects

TABLE 9.3—Effect of Cryogenically Ground Butyl Rubber on Innerliner Compound[a] Properties [6].

PROPERTIES		GROUND BUTYL[b] ADDED, %			
		0 (CONTROL)	5	10	15
Masterbatch, phar		188.0	178.6	169.2	159.8
Cryo Ground Butyl, phar		...	9.4	18.8	26.2
Cure Time t90, min	ASTM D 2084	47.5	46.3	47.0	46.5
Cure Rate, lbf in./min	ASTM D 2084	0.59	0.58	0.55	0.56
Tensile Strength, psi	ASTM D 412	1410	1350	1290	1280
300% Modulus, psi	ASTM D 412	1120	1040	1000	950
100% Modulus, psi	ASTM D 412	415	410	365	365
Air Permeability[c], Q		4.71	4.70	4.47	4.16

[a] Formulation: Butyl HT-1066, 80.0; RSS No. 1, 20; N-650 Carbon Black, 65.0; Mineral Rubber, 4.0; Durez 29095, 4.0; Sunthene 410, 8.0; Stearic Acid, 2.0; Zinc Oxide, 3.0; Devil A Sulfur, 0.5; MBTS, 1.5. Total recipe = 188.0.

[b] 80 mesh.

[c] $Q \times 10^3$ (cubic ft/0.001 in./°F psi/day).

of 0 (control), 5, 10, and 15 phr cryogenically ground butyl rubber on tensile properties [6].

In this case, the virgin rubber compound, formulation given at the bottom in Table 9.3, was mixed, cured, and cryogenically ground. The ground recycled rubber was added to the virgin rubber compound at different levels. It appears that 5 phr ground butyl rubber content (or 9.4 phr cryo-ground) is the optimum level. At 10 and 15 phr, tensile properties and air permeability are reduced significantly. Because of the addition of ground butyl rubber, air permeability of a compound is reduced, which is desirable.

Phake, Chakraborty, and De [7] observed that natural rubber compound containing 30 phr recycled rubber had shorter scorch time, higher cure rate, and lower maximum torque than the control compound with no recycled rubber. In a more recent study, Gibala and Hamed [8] got similar results for SBR compounds. Based on experimental results, they proposed that migration of sulfur takes place from the matrix to the recycled rubber giving, overall, lower torque, and that migration of accelerator from the recycled rubber to the matrix, causes shorter scorch time and faster cure rate.

Therefore, when compounding with recycled rubber, curatives should be adjusted accordingly.

REFERENCES

[1] U.S. Patent 5,258,413, Ultrasonic Devulcanization, assigned to: A. Isayer, University of Akron, November 1993.

[2] Boron, T., Roberson, P., and Klingensmith, W., "Ultrasonic Devulcanization of Tie Compounds," pp. 82–84; and Sekhar, B. C. and Kromer, V. A., "The DeLink Concent," pp. 87–88, *Tire Technology International*, 1996.

[3] "Crumb Rubber (Tire or Non-Tire)," Rubber/Polymer Type, Particle Size Distribution, by Chicago Board of Trade, 1997.

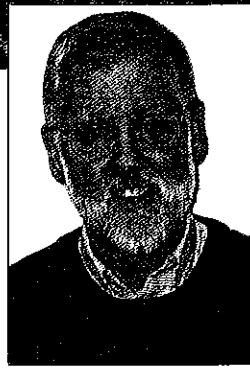
[4] Klingensmith, W. K. and Baranwal, K. C. "Best Practices in Scrap Tires and Rubber Recycling, Clean Washington Center," June 1997.

[5] Dierkes, W. in *Tire Technology International*, 1998, p. 170.

[6] Klingensmith, W. K. and Smith, F., "Cryofine Butyl Rubber in Tire Innerliners," technical bulletin, Midwest Elastomers, Inc., 1986.

[7] Phadke, A., Chakraborty, S., and De, S., *Rubber Chemistry & Technology*, Vol. 57, 1984, p. 19.

[8] Gibala, D. and Hamed, G. R. in *Rubber Chemistry & Technology*, Vol. 67, 1994, p. 636.



ABOUT THE EDITOR

John Dick has over 30 years of experience in the rubber industry. He was with BF Goodrich and later Uniroyal Goodrich Tire Co. as a Section Manager and Development Scientist in R&D until 1991 when he joined Alpha Technologies (formerly Monsanto's Rubber Instruments Group) as a Senior Marketing Technical Service Specialist. Mr. Dick has authored over 45 journal and magazine publications and three books on polymer technology. He received the Monsanto Master Technical Service Award in 1994, the American Chemical Society Rubber Division "Best Paper Award" in 1995, and a University of Akron Appreciation Award in 1998 for Teaching Polymer Compounding Courses in their Continuing Education Program. He is a Fellow in ASTM International, receiving the Award of Merit in 1990. Also he has represented the United States as a delegate to the International Standards Organization (ISO) for the last 20 years. He was appointed in 1992 to be the leader of the U.S.A. Delegation to ISO TC-45 on Rubber. He teaches rubber technology courses at both University of Akron and University of Wisconsin Continuing Education Departments. He is a member of American Chemical Society, Society of Rheology, and the American Society for Quality with a CQE. He is also a representative to the RMA. Mr. Dick received his B.S. degree from Virginia Polytechnic Institute in 1970 and an M.A. from the University of Akron in 1979. His hobbies include photography and amateur radio.

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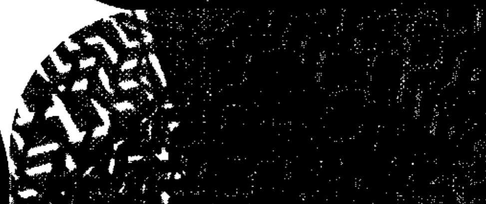

Selecting Methods for a Rubber Test Program

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