Improved framework for particle analysis based on ASTM D3849

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Executive summary

ASTM D3849 is the only recognized standard method for the digital measurement of carbon black particle size statistics via transmission electron microscopy (TEM). The method makes use of fractal geometry to derive particle size statistics for both aggregates and primary particles, using only the measured values of aggregate perimeter and area. Despite the sophistication of ASTM D3849, there has been disagreement in the industry regarding its utility and inter-laboratory reproducibility, especially with regard to smaller grades of carbon blacks. As a leader in third-party testing, Smithers recently developed a methodology based on ASTM D3849 that seeks to address these issues and improve identification of recovered carbon black obtained from mixed rubber samples.

Carbon black is one of the most important raw materials in the rubber industry. It is a form of elemental carbon produced through the incomplete combustion of hydrocarbon oils under controlled conditions. When mixed with rubber, carbon black acts as a filler to reduce cost and reinforce the bulk compound. Carbon black is used to tailor rubber performance properties such as tensile strength, abrasion resistance and conductivity.

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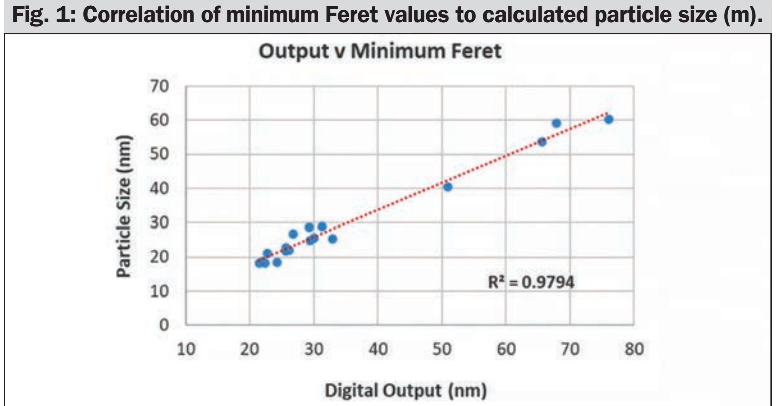
At the macroscopic level, carbon black is a soot-like substance, a black powder. However, its microscopic characteristics largely determine application performance. At the sub-micron level, carbon black exists as discrete particles called aggregates that are often described as "grape-like clusters," a conglomeration of ellipsoidal primary particles (nodules) covalently fused together. Primary particles range in diameter from 5 to 300 nm, while aggregates are usually between 50 to 1,000 nm in size. The production of carbon black is a dynamic process that can be controlled to produce aggregates of varying size and complexity of shape. Shape complexity is referred to as structure. Greater deviation from an ideal sphere and a higher degree of branching correspond to higher structure. Aggregates also form higher order structures called agglomerates that are held together by weak intermolecular attraction. These structures are largely broken down during rubber mixing.

Table 1: Standard ASTM grade carbon blacks used for external calibration.

Carbon Black Grades			
N1XX	N2XX	N3XX	N5XX+
N110	N220	N326	N550
N115	N231	N330	N660
N120	N234	N339	N762
N134	N299	N347	N774
		N351	
		N358	

Fig. 1: Correlation of minimum Feret values to calculated particle size (m).



Carbon black and rubber performance

Both aggregate surface area and structure are important to rubber performance properties such as abrasion resistance, conductivity and, for tires, rolling resistance. Surface area is measured using techniques that involve adsorption of small molecules to the surface of the carbon black, most commonly iodine (I_2), nitrogen (N_2), and cetyltrimethylammonium bromide (CTAB). Surface area correlates well with primary particle size. Structure, on the other hand, is measured by oil absorption, typically using dibutyl phthalate. When mixed with carbon black, oil molecules fill the void space between aggregates. Highly structured carbon blacks absorb more oil since aggregates of complex and irregular shape cannot pack as tightly as aggregates of simple shape. Iodine number and oil absorption number are the two most widely used metrics to characterize grades of carbon black.

Carbon black particle measurement via TEM

Transmission electron microscopy (TEM) is an alternate method used to study and characterize carbon black at the nanoscopic level. Primary particle and aggregate size statistics can be calculated by direct measurement of the 2D projection of carbon black aggregates captured in electron micrographs. Originally this was accomplished through analog measurements of minimum Feret values of individual particles. Now digital image analysis has made the process almost entirely automated, as advanced image analysis software has become available on the market.

ASTM D3849 is the only recognized standard method for the digital measurement of carbon black particle size statistics. Carbon black aggregates are self-affine, fractal structures; the ASTM method makes use of fractal geometry to derive particle size statistics for both aggregates and primary particles, including frequency and weight mean particle size, electron microscope surface area and heterogeneity index. The only measurements required are aggregate perimeter and area.

Particle analysis at Smithers—Akron Labs

Despite the sophistication of ASTM D3849, there has been disagreement regarding its utility and reproducibility. Characterization of structure is beyond the scope of the method, and it provides no correlation of calculated properties to the standard evaluation metrics commonly used in the industry (i.e. I2 and OAN). As a leader in third-party testing within the tire industry, Smithers recently developed an improved methodology based on the principles of ASTM D3849 that seeks to address these issues and improve identification of carbon black obtained from mixed rubber samples. Criteria that informed method development included 1) suitability for routine, expedited production; 2) improvement of method accuracy; and 3) modeling of bulk properties.

Base method

External calibration was established using 18 grades of commercially available carbon black (**Table 1**) with a wide variety of sizes and structures. Micrographs were taken at a resolution of 2.23 nm/pixel, and enough were taken so that approximately 2,000-4,000 aggregates were captured. Digital image processing was carried out with a commercially available software package that allows for tailored recipes, which automatically apply the processing techniques outlined in ASTM D3849, such as contrast adjustment, thresholding and background correction. Particle size distributions for each carbon black reference grade also were determined by manually measuring minimum Feret values for about 2,000 primary particles. The frequency means obtained from these measurements served as the reference values for the mean particle size (m) output from the ASTM Method (**Fig. 1**). Additional data treatment was applied for normalization and to correct for outliers. EMSA data was correct-

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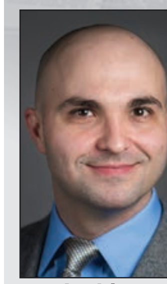
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Table 2: Mean particle size (m) and EMSA values generated by external calibration of the base control set.

	Digital Output (nm)	Minimum Feret (nm)	m, calc (nm)	%RSE	EMSA (m^2/g)	ASTM STSA (m^2/g)	EMSA, calc (m^2/g)	%RSE
N110	24.3	18.5	21.7	-17.30	132.8	115	105.0	8.70
N115	22.4	18.2	20.1	-10.44	146.1	124	117.2	5.51
N120	22.0	18.7	19.7	-5.35	146.8	113	117.8	-4.26
N134	21.5	18.3	19.3	-5.46	152.3	137	122.9	10.30
N220	25.6	22.7	22.6	0.44	129.5	106	101.9	3.91
N231	25.7	21.9	22.8	-4.11	125.8	107	98.4	7.99
N234	22.7	21.2	20.4	3.77	142.2	112	113.6	-1.41
N299	26.1	22.0	23.0	-4.55	127.6	97	100.2	-3.30
N326	32.9	25.4	28.5	-12.20	97.7	76	63.6	16.36
N330	31.3	28.9	27.1	6.23	107.0	75	72.5	3.29
N339	26.8	26.7	23.5	11.99	125.3	88	93.9	-6.71
N347	29.4	24.9	25.6	-2.81	116.2	83	82.6	0.43
N351	30.1	25.5	26.2	-2.75	110.8	70	76.5	-9.36
N358	29.3	28.7	25.5	11.15	114.4	78	80.4	-3.14
N550	50.9	40.5	42.8	-5.68	65.9	39	40.5	-3.94
N660	65.7	53.6	54.5	-1.68	51.2	34	32.9	3.36
N762	67.9	59.2	56.0	5.41	45.2	28	30.2	-7.93
N774	76.1	60.3	62.9	-4.31	43.4	29	29.4	-1.43
			av	6.42			av	5.63
			stdev	4.41			stdev	3.95
			95% conf	15.24			95% conf	13.52

Table 3: Comparison of particle size values (m) obtained by Donnet et al. and Smithers.

	Minimum Feret	Donnet et al	%RSE	Smithers	%RSE
N110	18.5	18	2.70	21.7	-17.30
N220	22.7	21	7.49	22.6	0.44
N234	21.2	20	5.66	20.4	3.77
N299	22.0	24	-9.09	23.0	-4.55
N326	25.4	27	-6.30	28.5	-12.20
N330	28.9	30	-3.81	27.1	6.23
N339	26.7	26	2.62	23.5	11.99
N351	25.5	32	-25.49	26.2	-2.75
N358	28.7	30	-4.53	25.5	11.15
N550	40.5	56	-38.27	42.8	-5.68
N660	53.6	67	-25.00	54.5	-1.68
N774	60.3	79	-31.01	62.9	-4.31
		av	13.50	av	6.84
		stdev	12.70	stdev	5.14

Analysis

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ed in accordance with ASTM D3849 section 8.2.1. using STSA values published in IARC Monographs Volume 93.

The resulting values for mean particle size, m, and EMSA are compiled in **Table 2**. Relative Standard Error (RSE) for calculated particle size values averaged 6.42% (sd=4.41%) resulting in a %RSE at a 95 percent confidence interval of 15.3 percent. The average RSE for the calculated EMSA data set was 5.63% (sd=3.95%) with a %RSE at a 95 percent confidence interval of 13.5 percent.

These values were benchmarked against those obtained by Donnet et al (1993), one of the most reliable sources for ASTM D3849 data, to validate proof of concept. When compared with Donnet et al, the Smithers method resulted in a 50-percent reduction in the RSE of calculated particle size **(Table 3)** and a 35-percent reduction in the RSE of calculated EMSA values **(Table 4)**.

Table 4: Comparison of EMSA values obtained by Donnet et al. and Smithers.

	ASTM STSA	Donnet et al	%RSE	Smithers	%RSE
N110	115	138	-20.00	105.0	8.70
N220	106	121	-14.15	101.9	3.91
N234	112	124	-10.71	113.6	-1.41
N299	97	107	-10.31	100.2	-3.30
N326	76	87	-14.47	63.6	16.36
N330	75	80	-6.67	72.5	3.29
N339	88	96	-9.09	93.9	-6.71
N351	70	77	-10.00	76.5	-9.36
N358	78	84	-7.69	80.4	-3.14
N550	39	41	-5.13	40.5	-3.94
N660	34	35	-2.94	32.9	3.36
N774	29	29	0.00	29.4	-1.43
		av	9.26	av	5.41
		stdev	5.41	stdev	4.29

Modeling of bulk properties

Upon achieving such a marked increase of accuracy using the base method, efforts were turned to the development of proprietary models to relate size and shape parameters to the common industry metrics of iodine and oil absorption values. The parameters used included those in ASTM D3849 and others defined elsewhere, all of which were automatically measured by the image analysis program.

At the onset, calculated particle size values (m) of the controls were plotted against known iodine values **(Fig. 2),** and were found to be as accurate as literature data—20% RSE at a 95-percent confidence interval. The relationship, however, between particle size and iodine number is exponential. Therefore, a surface area factor was developed to establish a linear relationship to iodine values and avoid the pitfalls associated with exponential modeling **(Fig. 3)**. The model was shown to predict iodine values with the same level of accuracy as particle size (m). N351 was omitted as an outlier. To model the oil absorption number, a structure factor was developed and correlated to the known OAN values of the controls **(Fig. 4)**. RSE of the model was 13.0 percent at a 95-percent confidence interval. N351 and N358 were omitted as outliers.

Model validation

The iodine and oil absorption models were validated using two additional sets of carbon black controls (**Table 5**) obtained from the open market. The first set from Supplier 1 was comprised of standard ASTM grades N121, N220, N347, N550, and N772. The second set from Supplier 2 was comprised of non-standard ASTM carbon blacks similar to ASTM grades N1XX, N2XX, N3XX, N5XX, N7XX. Particle size (m), oil absorption number, and iodine number were calculated for all 10 controls for a total of 30 measurements. Twenty-seven of 30 (90 percent) values were within 15% RSE or less of the true values, while 23 of 30 (75 percent) were within 10 percent of the true values, demonstrating the efficacy of the surface area and structure factors to accurately calculate bulk properties from two dimensional micrographs.

Table 5: Validation of iodine and oil absorption models using standard and non-standard grades of carbon black.

ASTM Blacks (Supplier 1)	Particle Size, m	*m*, calc	%RSE	OAN, Actual	OAN, Calc	%RSE	I2, Actual	I2, Calc	%RSE
N121	21.9	21.7	0.91	132.0	122	7.58	121.0	125	-3.31
N220	21.3	23.2	-8.92	116.3	119	-2.32	119.8	114	4.84
N347	24.6	25.2	-2.44	124.0	107	13.71	90.0	101	-12.22
N550	35.5	37.8	-6.48	122.1	105	14.00	44.2	48	-8.60
N772	51.2	53.3	-4.10	65.0	63	3.08	31.0	33	-6.45
Non-ASTM Blacks (Supplier 2)	**Particle Size, m**	***m*, calc**	**%RSE**	**OAN, Actual**	**OAN, Calc**	**%RSE**	**I2, Actual**	**I2, Calc**	**%RSE**
N1XX	18.8	19.7	-4.79	113.0	120	-6.19	144.0	135	6.25
N2XX	19.9	20.4	-2.51	113.9	110	3.42	120.3	130	-8.06
N3XX	25.6	24.5	4.30	140.3	113	19.46	75.9	104	-37.02
N5XX	36.0	39.0	-8.33	119.3	103	13.66	42.4	49	-15.57
N7XX	50.6	52.8	-4.35	50.4	54	-7.14	30.6	32	-4.58

Summary

As a leader in third-party testing, Smithers developed an improved methodology based on ASTM D3849 for the determination of recovered carbon black particle statistics using transmission electron microscopy. Using a large library of controls, the Smithers method has been demonstrated to calculate primary particle size (m) to within no more than 15 percent relative standard error at 95 percent confidence and EMSA to within 14 percent relative standard error at 95 percent confidence.

When compared to values determined by Donnet et al., this represents a 50-percent and 35-percent reduction in error for particle size and EMSA, respectively. Smithers also developed proprietary models by which to calculate iodine value and oil absorption number from measured particle data to within 20 percent and 13 percent relative standard error at 95 percent confidence, respectively. With this comprehensive data, the Smithers method not only is able to provide more accurate IDs for recovered carbon black, but can even discriminate between some N100 and N200 series blacks.

Fig. 2: Calculated particle size (m) correlated to iodine value.

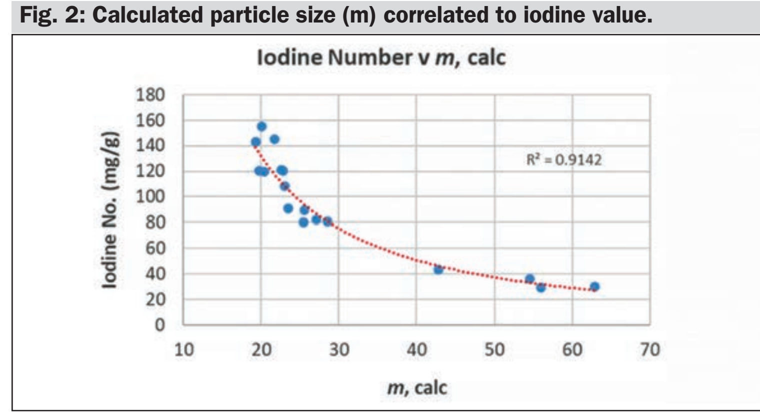

Fig. 3: Surface area descriptor correlated to iodine number. N351 is omitted as an outlier.

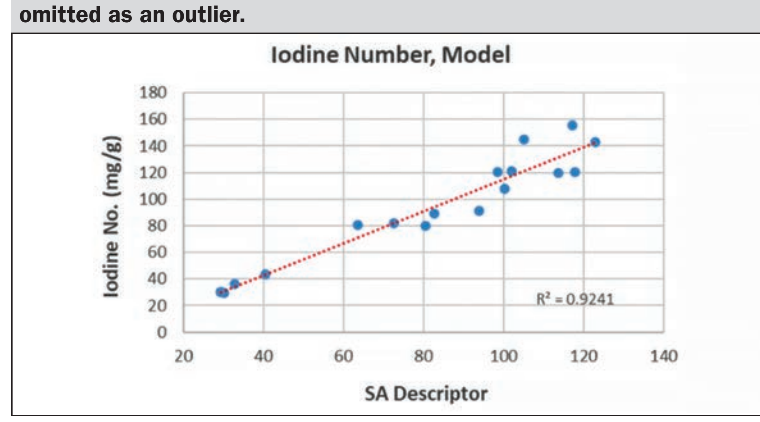

Fig. 4: Structure factor correlated to oil absorption number. N351 and N358 are omitted as outliers.