

# Advances in structure measurements of carbon black.

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The carbon black industry has been using a term known as "structure" since the 1940s to describe one of the most important properties of carbon black. Structure, a term that describes the fusion of primary particles that make up aggregates of carbon black, strongly affects the properties of filled rubber compounds, including processability and reinforcement. In the early 1960s, carbon black structure was directly estimated using a manual oil absorption method borrowed from the coatings industry, and a compression method that was proposed as a quality control test by Medalia (ref. 1). In addition, structure measurements based on compound extrusion shrinkage were widely used at this time.

In 1965, ASTM D24 adopted a new mechanical oil absorption test as a standardized measure of structure. This structure test was shown to have a linear relationship to compound die swell, and was selected over other structure tests primarily due to the automatic end-point provided by the mechanical oil absorptometer (ref. 2). The industry named this oil absorption test "DBP," due to the use of dibutyl phthalate oil; however, it is now referred to as an oil absorption number or "OAN." OAN and iodine number are the two target properties used to manufacture and sell carbon black products globally.

In 2004, ASTM International D24.11 Committee on Carbon Black Structure Methods concluded that the industry needed an improved structure measurement. Key deficiencies cited with the mechanical oil absorption test were that OAN is not a measure of an intrinsic characteristic of the carbon black (i.e., primary structure) and offers little insight into aggregate reduction, which is known to occur during the mixing or dispersion cycle (refs. 3-5). Carbon black studies from 1965 indicated that mechanical oil absorption numbers are strongly related to compound processability, but also found that OAN is influenced by bulk density. Bulk density is a characteristic that may vary between producing plants or production units, resulting in different relationships between oil absorption numbers and application properties for the same ASTM grades.

One of the most important concepts pertaining to carbon black structure is the occlusion of rubber within the aggregate void space (ref. 6). An example of aggregate void space is depicted with the carbon black aggregate shown in figure 1. This complex aggregate was sampled from a high structure carbon black that would occlude a large volume of polymer.

Good estimates of carbon black aggregate void volumes are needed to reliably predict

compound properties. Therefore, an improved structure test is one that provides specific estimates of intra-aggregate void volume and correlates well to end-use applications, including compound processability and reinforcement properties. Other improvements would include a faster and cleaner test, and elimination of solid-liquid interactions which are known to influence DBP oil absorption numbers.

Patel studied compressed void volume as an improved structure measurement through the 1990s and concluded that void volume, nitrogen surface area and volume fractions could describe the reinforcement nature of filled rubber compounds (ref. 7). A recent study concluded that compressed void volume (VV) offers a significant improvement in carbon black structure measurement when compared to oil absorption methods (ref. 8). Those conclusions were based on improved relationships to compound processability and reinforcement properties. The VV quantity is derived from apparent volume measurements as a function of applied pressure and expressed per unit mass. Once a critical density is achieved through application of pressure, VV is an intrinsic characteristic that is not influenced by bulk density, which is a product attribute purposely increased through the carbon black manufacturing process. Recently a new generation dynamic void volume analyzer (DVVA) has been commercialized as the result of a joint development with a world-class instrument company. The subject of this article focuses on the investigation of an improved structure measurement based on dynamic void volume.

## Experimental

### Carbon blacks

A broad range of furnace carbon blacks from very low ( $\sim 35$  [cm<sup>sup.3</sup>]/100 g) to very high ( $\sim 175$  [cm<sup>sup.3</sup>]/100 g) OAN are included in this study. The carbon blacks include a variety of Statex, Furnex and other experimental furnace carbon blacks from Columbian Chemicals, along with Standard Reference Blacks (SRB) from ASTM International which are produced by various manufacturers. Modeling sample sets also included low-density powder blacks collected from reactor ports or bag collectors, along with corresponding pelletized products. Several hundred samples were included within the various analyses discussed in this article. The colloidal space encompassed by the samples in this study is shown in figure 2, and represents a majority of commercially important rubber carbon blacks.

[FIGURE 1 OMITTED]

### Dynamic void volume analysis

Early literature of void volume studies reported use of single-pressure equilibrium measurements where the compressed volume was typically reported at a constant applied pressure (refs. 9 and 10). Piston height measurements at several pressure points were common in order to develop multi-point compression curves. In the 1990s, Titan Specialties produced an experimental dynamic compression analyzer, or DCA, capable of faster experiments, but it was never adopted by the industry. Another compression analyzer developed by Patel was based on a modified capillary rheometer (ref. 11). Compressed void volume experiments were reported in 2005 using an equilibrium VV analyzer from Jaron Technologies where multiple single-point experiments were combined to develop multi-point compression curves (ref. 8). These experiments required a new

sample aliquot for each compression point, resulting in a slow test method; however, the conclusion from this recent study was the motivation for development of a more advanced dynamic void volume analyzer.

In the present study, dynamic scan experiments are investigated on carbon blacks using a new dynamic void volume analyzer, DVVA 4000, from Micromeritics. The DVVA 4000 consists of a vertical load frame supporting a load cell and linear actuator which controls piston travel through a sample cylinder, measuring force and displacement. The sample cylinder is located below the actuator where the piston applies an axial or normal force to the sample. The bottom of the cylinder is a motorized anvil that is stationary during sample compression and opens for automated removal of the compressed sample. The DVVA sample cylinder is 1.27 cm (0.500 inch) in diameter and approximately 13.6 cm in length (5.75 inches), and designed for a sample mass of 1 gram to accommodate low-density powders or pelleted products. A block diagram of the DVVA with major components is shown in figure 3.

The DVVA records displacement or axial position of the piston tip, force and time. The force applied to the piston is measured with a load cell, while sample height measurements are accomplished using a linear transducer attached to the piston. Calibration of height measurement is achieved using steel calibration plugs. Hysteresis in the measurement system and friction between the piston tip and cylinder wall are removed from the sample data by subtracting a blank run from the sample experiment.

[FIGURE 2 OMITTED]

Experiments within these studies used a data acquisition rate of 5 Hertz. Apparent volumes were calculated over applied pressures of 0 to 210 MPa using a scan-rate controlled experiment at 69 MPa/min., and an ambient temperature of 23 [+ or -] 2 [degrees]C. This scan rate resulted in a total experimental time of seven minutes for both blank and sample scans; low-density powders have slightly longer analysis times. The data collection and scan rates were experimentally optimized with the objectives of reducing the total experimental time, but also maintaining data equivalence with both equilibrium and stepped-scan compression experiments.

Calculation of the measured-compressed void volume,  $[VV.sub.M]$ , is shown in equation 1 (ref. 12):

$$[VV.sub.M] = ([V.sub.a] - [V.sub.t])/m \cdot 100 \quad (1)$$

where  $[V.sub.a]$  is equal to the apparent volume of the sample in  $[cm.sup.3]$ ,  $[V.sub.t]$  is equal to the theoretical volume of the solid sample in  $[cm.sup.3]$ , and  $m$  is the sample mass in grams. The unit of measure for  $[VV.sub.M]$  is  $[cm.sup.3]/100 \text{ g}$ . The apparent volume,  $[V.sub.a]$ , is defined by equation 2:

$$[V.sub.a] = h \times [\pi][D.sup.2]/4 \quad (2)$$

where  $h$  equals the measured sample height in cm, and  $D$  is equal to the cylinder diameter in cm. The theoretical solid sample volume,  $[V.sub.t]$ , is defined by equation 3:

$$[V.sub.t] = m/[\rho].sub.t] \quad (3)$$

where  $m$  is the sample mass in grams and  $[\rho]_{\text{sub.t}}$  is the true or skeletal density of carbon black, commonly accepted as 1.9 g per  $[\text{cm}]_{\text{sup.3}}$  for many carbon blacks (ref. 13). The DVVA software has several input fields, including one for measured skeletal densities.

The measured sample height,  $h$ , at an applied pressure is determined by the axial position of the piston tip,  $z$ . Calibration of the piston tip displacement is achieved by measuring at least two axial reference positions, a zero height reference at the bottom of the cylinder, and one or more reference positions based on the height of the steel calibration plugs.

[FIGURE 3 OMITTED]

#### Application and predictive modeling

In this study, the modeling variables make use of the large amounts of data available from dynamic scanning using the DVVA. Void volumes at common pressure intervals along with other calculated compression properties were collected into arrays as discrete modeling variables. This approach was taken to include modeling variables that can describe the shape of the compression curves, since many carbon blacks exhibit unique compression profiles. Numerical quantities which can describe the shape of the compression curves include differential void volumes, absolute void volumes at applied pressures, and combinations of both. Discrete variables and combinations of variables were included in the advanced linear and non-linear modeling to analyze millions of possible models to determine optimum relationships to OAN measurements and compound properties.

#### Other carbon black testing

Carbon black samples were also analyzed for typical colloidal properties. Nitrogen surface areas were measured per ASTM D6556 at 77[degrees]K using a Micromeritics TriStar 3000 where the sample free space was calculated based on skeletal densities obtained with a Micromeritics AccuPyc 1330. Oil absorption numbers (OAN) were obtained per ASTM D2414 using a Hitec DABS absorptometer with stainless steel mixing chamber using dibutyl phthalate oil. Oil absorption numbers of compressed samples (COAN) were obtained per ASTM D3493. COAN samples were prepared with a Titan carbon black press and compressed to 165.5 MPa (24,000 psi) a total of four times prior to testing the oil absorption. Pour densities were obtained on the pelleted blacks per ASTM D1513. Colloidal properties for the SRB blacks were obtained from ASTM D4821 or ASTM International laboratory proficiency rating system (LPRS) studies.

#### In-rubber testing

A variety of rubber carbon black products was analyzed for in-rubber rheometer and dynamic properties using an Alpha Technologies Rubber Process Analyzer 2000 (RPA) per ASTM International D6601. Test compounds included styrene-butadiene rubber (SBR) and natural rubber (NR) formulations per ASTM D3191 and D3192, respectively. The rheometer properties were obtained at 150[degrees]C using 30 minute cures, and dynamic properties at 100[degrees]C at 1 Hz and 1%, 10% and 50% single strain amplitude (SSA).

Compounds were also prepared in the ASTM NR D-3192 formulation for stress-strain

properties. Tensile stress measurements were made with a United Testing System per ASTM D412, and reported as delta IRB-7.

## Results

### OAN predictive modeling from D VVA data

The carbon black and rubber industry have used mechanical oil absorption as the basis for carbon black structure measurement for the past 43 years. In the course of developing a new structure method, it is recognized that a number of years will be required to achieve industry acceptance, even with a superior method; therefore, there is a present need to predict OAN numbers from dynamic void volume measurements such that OAN can continue to be reported even when the testing is discontinued. With this objective in mind, the task of determining how to accurately model oil absorption data from DVVA void volume-pressure scans was studied in great detail. The following discussion summarizes the information learned from OAN predictive modeling from analysis of hundreds of carbon black samples within multiple modeling sample sets.

A predictive model for oil absorption numbers should have a standard error equal to or less than the OAN test reproducibility standard deviation (OAN SR), since this analysis is a comparison of the variation between samples, not replicates within a single sample. According to ASTM D2414, the pooled OAN SR is 1.4 [cm.sup.3]/100 g (ref. 14). Initial predictive modeling of OAN made use of large sample sets containing a variety of carbon blacks. Initial studies indicated that universal OAN prediction models from void volume data did not appear feasible since the model standard errors were quite large.

Subsequent studies methodically limited the sample sets to specific types of products for predictive modeling. This process of categorization of sample sets ultimately led to modeling specific carbon black production lines in order to determine the best relationship between OAN and DVVA data. The chart in figure 4 summarizes the progression of predictive modeling from highest to lowest standard error.

The chart in figure 4 begins with a universal OAN model with the highest standard error of 6.7 [cm.sup.3]/100 g, as shown in figure 5. As indicated earlier, this dataset included multiple producers, standard and specialty blacks, and powder and pelleted samples.

The next modeling data set included samples from multiple producers including ASTM tread and carcass products, and powder and pelleted samples, but excluded all specialty carbon blacks. This data set resulted in a model that provided a standard error of only 4.3 [cm.sup.3]/100 g, as shown in figure 6. Although a standard error of 4.3 [cm.sup.3]/100 g is still large, the improvement in the model due to elimination of specialty blacks resulted in a 36% reduction in the model standard error. An interpretation of this observation is that the OAN values for many of these specialty carbon blacks are not consistent with standard grades, and are most likely influenced by non-structure related product characteristics, such as microporosity in the case of racing blacks.

[FIGURE 4 OMITTED]

The next step in this modeling process was to analyze sample sets specific to each of the reactor types, including tread and carcass (hard and soft blacks). This resulted in another

large reduction in model standard error from 4.3 to 2.5 and 2.2 [cm.sup.3]/100 g, respectively, for tread and carcass models, as shown in figures 7 and 8.

The standard errors for these models are only slightly higher than the OAN SR. The logical reason for the model improvement is due to bias in OAN values between tread and carcass blacks. OAN testing requires use of two different sets of ASTM standards to nonnormalize the measured OAN results, one set of standards for tread and another set of standards for carcass grades. Secondly, the preferred ASTM measurement method for tread blacks is different than for carcass blacks (D2414 Methods A and B). The combined effect of different measurement methods and normalization standards introduces bias in OAN testing. The standard error in the individual tread and carcass prediction models should be similar to the standard error of the combined sample set if bias did not exist between the carcass and tread OAN testing. Unlike oil absorption, the void volume analysis uses a common test method for all carbon blacks.

[FIGURE 5 OMITTED]

[FIGURE 6 OMITTED]

Additional modeling sample sets were collected that restricted samples to a single producer and single production facilities. Modeling combined carcass lines produced a standard error of 1.1 [cm.sup.3]/100 g, while a prediction model for a single carcass line resulted in a standard error of only 0.55 [cm.sup.3]/100 g. Each of these sample sets from a single production facility produced OAN prediction models with standard errors well below the OAN SR. An example of measured and predicted OAN data from a single carcass production line is shown in figure 9.

[FIGURE 7 OMITTED]

[FIGURE 8 OMITTED]

The carcass line product analysis in figure 9 includes products at three different structure levels where the OAN was measured and also predicted (POAN) from a model based on differential void volumes. This OAN prediction model is defined in equation 4.

$$\text{OAN} = -23.1642 + 0.11099 \times [\text{VV.sup.2}] @ 19 \text{ MPa} - 0.19485 \times [\text{VV.sup.2}] @ 32 \text{ MPa} + 0.17652 \times [\text{VV.sup.2}] @ 102 \text{ MPa} \quad (4)$$

This three-term model is specific to the sample set from a single carcass production line and has a standard error of 1.1 [cm.sup.3]/100 g.

OAN predictive models are not limited to the product physical form. Loose powder and pelleted samples were included within the modeling sample sets such that a single model is useful for analyzing product from reactor ports or bag collectors and finished-pelletized product. An example of within-grade OAN prediction of loose black and pelletized product is shown in figure 10.

Figure 10 is an example of in-process sampling and structure analysis of two carbon black products. The POAN data in figure 10 are from a single OAN prediction model based on DVVA analysis of loose and pelletized blacks. The first product's pelletized samples have

OAN and predicted OAN levels near the target of 130 [cm.sup.3]/100 g and loose black samples (from reactor ports) in the range of 137-140 [cm.sup.3]/100 g. The second product exhibits OAN and POAN levels slightly higher than the target of 121 [cm.sup.3]/100 g for pelletized product, while the loose black samples exhibit OAN levels of approximately 130 [cm.sup.3]/100 g. Figure 10 demonstrates just one of the complications from use of the OAN structure method, which is that loose black samples always exhibit higher OAN levels than corresponding pelletized samples; however, there is no evidence of reduction in primary structure due to the pelletization process.

[FIGURE 9 OMITTED]

[FIGURE 10 OMITTED]

OAN measurements are known to be influenced by bulk density, and loose blacks exhibit much lower bulk densities and higher OAN than pelletized blacks. Wampler prepared SBR compounds containing N299 at various levels of density from powder to pelletized product and demonstrated that pelletization has no effect on the carbon black primary structure as indicated by compound physical properties and COAN measurements (ref. 15).

A direct structure analysis of N650 loose black and pelletized samples was performed to provide an example of OAN and DVVA data. Dynamic void volume-pressure curves shown in figure 11 indicate the loose black sample exhibits a higher level of void volume than pelletized black at very low applied pressures, and this difference is a reflection of the bulk density of these samples. At applied pressures of approximately 55 MPa and greater, the two curves converge, indicating an equivalent level of primary structure for the loose black and pelletized samples. OAN and DVVA data for these N650 samples are shown in table 1. This analysis offers further support that the primary structure of this N650 furnace carbon black is unaffected by the pelletization process. The relationship between the carbon black primary structure, as measured by DVVA, and compound properties is discussed later.

Modeling samples from a single tread line using a two-term model resulted in a standard error of 0.7 [cm.sup.3]/100 g, a level which is half the OAN SR of 1.4 [cm.sup.3]/100 g. Observed versus predicted OAN data for the single tread line sample set are shown in figure 12. This two-term model, shown in equation 5, includes 70 samples in the range of approximately 100 to 130 [cm.sup.3]/100 g.

$$\text{OAN} = -27.3769 + 8.4943 \times \text{VV} @ 141 \text{ MPa} - 6.5465 \times \text{VV} @ 204 \text{ MPa} \quad (5)$$

Interpretation of the OAN predictive modeling leads to some interesting hypotheses. First, it was observed that the ASTM carcass model based on standard grades from multiple producers had a standard error of 2.2 [cm.sup.3]/100 g, while the carcass model for a single production facility with two lines has an error of only 1.1 [cm.sup.3]/100 g. This suggests that product OAN from multiple producers contains more error as compared to a single producer. In other words, products from different producers with equal OAN can have varying levels of primary structure as measured by void volume. To a lesser extent, it was observed that the same issue can exist within a producing plant with two or more tread or carcass production lines.

The modeling example of one production facility with two carcass lines produced a

combined model with a standard error of 1.1 [cm.sup.3]/100 g, while a model representing only one production line has a standard error of 0.55 [cm.sup.3]/100 g. In this example, the modeling indicates that products produced on different lines within the same production facility may exhibit equivalent OAN, but the primary structure of those products can vary between the producing lines. The authors believe that much of the variation found in product performance between producers or between producing lines within a production facility can be attributed to use of the OAN test method. Based on modeling of sample sets produced on different production units, OAN prediction models with the least standard error are specific to production lines and not suitable for general use. Further analyses of the best OAN prediction models from different production lines are needed to better understand how applicable these models and DVVA variables are between production lines.

### Modeling SBR and NR compound properties

The basis for selecting the DBP oil absorption structure measurement in 1964 was a linear relationship to extrusion die swell or shrinkage (ref. 2), which is a measure related to factory performance. This ASTM test method utilized linear and mass measurements following a rest period to calculate extrusion shrinkage. Today's laboratories are equipped with a variety of rheometers and dynamic test equipment capable of precisely measuring processability and reinforcement properties with established relationships to carbon black properties, including structure. An assessment of a new structure method should include a critical comparison to performance properties, including processability and vulcanizate properties.

[FIGURE 11 OMITTED]

Compound properties, including viscosity and shear modulus from RPA analysis at low strain levels, were recently reported (ref. 8) as the basis for assessing structure measurements, including OAN, COAN and void volume. The carbon blacks used in this study included ASTM furnace grades, thermal black and racing blacks. The strength of the model relationships between the structure measurements and application properties in SBR and NR compounds clearly indicated that void volume was a superior structure measurement compared to oil absorption methods. The same set of carbon black samples previously studied was re-analyzed with the DVVA.

The processability and vulcanizate properties of SBR and NR compounds were modeled with the three structure measurements, including OAN, COAN and DVVA. The best predictive models observed for the SBR compounds using single and two variable terms are shown in figures 13-17. The best single-term predictive model for the SBR compound minimum rheometer torque, S' min, was the squared term of void volume, [VV.sup.2] and is shown in figure 13 and equation 6.

$$\text{SBR MinS' (ML)} = 1.16817 + 0.56335E - 3 \times [\text{VV.sup.2}] @ 90 \text{ MPa (6)}$$

[FIGURE 12 OMITTED]

[FIGURE 13 OMITTED]

A direct comparison of the single-term models for each of the three structure tests for the

SBR compound  $S'$  min is shown in figure 14. The chart in figure 14 is a plot of the model [R.sup.2] values and displayed as a function of applied pressure for the DVVA data, but is a constant for OAN and COAN. This chart indicates the void volume data exhibits a stronger relationship to compound viscosity as compared to COAN or OAN. At low applied pressures, the DVVA data have a similar level of [R.sup.2] as COAN, and then improve with pressures up to about 50 MPa, whereas OAN exhibits the weakest relationship of the three structure methods.

A similar comparison is made to the SBR compound shear modulus,  $G'$  @ 1% SSA, using a single-term model, and is shown in figures 15 and 16. Figure 15 is a chart of observed and predicted shear modulus. The single-term void volume model shown in equation 7 and figure 16 exhibits a stronger relationship to the shear modulus than COAN, and OAN exhibits the weakest relationship of the three structure methods.

$$\text{SBR } G' \text{ @ 1\% SSA} = 673.1012 + 0.6840 \times [\text{VV.sup.2}] \text{ @ 204 MPa (7)}$$

[FIGURE 14 OMITTED]

[FIGURE 15 OMITTED]

The best two-term predictive model for the SBR compound  $G'$  @ 1% SSA is shown in equation 8 and figure 17. This predictive model is based on dynamic void volume using differential void volumes. This model has a standard error of 73.7 kPa, as compared to the single-term model, which has a standard error of 92.2 kPa and describes the variation in modulus across these SBR compounds much better than the oil absorption methods.

$$\text{SBR } G' \text{ @ 1\%} = 686.9372 - 8.03221 \times [\text{VV.sup.2}] \text{ @ 164 MPa} + 8.84914 \times [\text{VV.sup.2}] \text{ @ 170 MPa (8)}$$

Comparisons of the single-term models for each of the three structure tests for the NR compound properties, including the  $S'$  min and  $G'$  @ 1% SSA, are shown in figures 18 and 19 and equations 9 and 10.

$$\text{NR Min}S' \text{ (ML)} - 1.0022 + 0.0012 \times [\text{VV.sup.2}] \text{ @ 204 MPa (9)}$$

$$\text{NR } G' \text{ @ 1\% SSA} = 544.6472 + 0.7205 \times [\text{VV.sup.2}] \text{ @ 208 MPa (10)}$$

[FIGURE 16 OMITTED]

[FIGURE 17 OMITTED]

At low applied pressures, where the carbon black sample has not been sufficiently compressed to bring the aggregates close together to minimize inter-aggregate void space, the DVVA data provide a similar relationship as COAN to the viscosity and shear modulus properties. At pressures above 35-50 MPa, the void volume models exhibit a stronger relationship to these compound properties than COAN. As previous comparisons have shown in the SBR compounds within this study, the OAN structure test exhibited the weakest relationship for these NR compound properties.

The best two-term predictive model for the NR compound  $G'$  @ 1% SSA is shown in

equation 11 and figure 20. This predictive model is based on dynamic void volume using differential void volumes. This model has a standard error of 83.6 kPa as compared to the single-term model, which has a standard error of 92.2 kPa, and describes the variation in modulus across these NR compounds much better than the oil absorption methods.

NR  $G'$  @ 1% SSA =  $546.1192 - 5.5279 \times [VV.\text{sup.}2] @ 41 \text{ MPa} + 5.9890 \times [VV.\text{sup.}2] @ 44 \text{ MPA}$  (11)

[FIGURE 18 OMITTED]

[FIGURE 19 OMITTED]

In summary, comparisons between structure tests and compound properties known to be strongly influenced by carbon black structure confirm prior studies in which void volume is observed to be an improved structure measurement.

#### Modeling NR compound stress-strain

Another compounding and modeling study was undertaken to observe the predictive capability of DVVA structure data to describe the tensile stress (modulus) at 300% elongation of NR vulcanizates using the ASTM D3192 formulation. Compound modulus at 300% elongation ([DELTA] IRB-7) was measured for 35 tread samples and 41 carcass samples of various ASTM rubber grade carbon blacks. Non-linear void volume differentials, including the square of the void volumes at pressures between 144 and 198 MPa, were observed to be the best measures for describing the effect of tread carbon black structure on the cured NR compound modulus. The best measure for describing the effect of carcass black structure on the cured NR compound modulus utilized differential void volumes between 114 and 170 MPa applied pressure. The actual and predicted properties for these tread and carcass NR compounds are shown in figures 21 and 22, respectively.

[FIGURE 20 OMITTED]

[FIGURE 21 OMITTED]

Each of the actual and predicted data sets includes error limits set at [+ or -] 0.5 MPa, which is approximately the repeatability of the test. The predictive model for the tread samples has a standard error of 0.28 MPa and carcass model standard error is only 0.16 MPa. A summary of the model features is shown in table 2.

These data demonstrate that carbon black structure, as measured by dynamic void volume, is strongly related to compound reinforcement, as measured by the tensile stress at 300% elongation in this NR formulation. The use of differential void volumes from DVVA analysis at specific applied pressures describes the change in modulus for the different samples of tread and carcass blacks with a precision level that rivals the in-rubber measurement. As appropriate models are established, structure dependent compound properties can be predicted and reported along with OAN and COAN data from a single DVVA compression scan of carbon black.

#### Summary

A new dynamic void volume analysis has been shown to be an improved structure measurement of carbon black compared to oil absorption methods based on processability and reinforcement properties of SBR and NR compounds. DVVA and OAN data have been modeled and used to predict OAN data within a production process with accuracy equal to or better than the precision of the oil absorption testing. Interpretation of this modeling also led to the observation that the use of OAN testing in the carbon black industry has led to structure variation between producers' products, and to a lesser extent, within producing lines of a production facility. The advancement in structure measurement offered by dynamic void volume should facilitate the replacement of oil absorptometers in the carbon black industry, and ultimately replace product structure specifications based on oil absorption methods.

[FIGURE 22 OMITTED]

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Table 1--structure analysis of N650 loose and pelletized black

Sample	OAN D2414 [cm.sup.3]/ 100 g	VV @ 1 MPa [cm.sup.3]/ 100 g	VV @ 55 MPa [cm.sup.3]/ 100 g	VV @ 100 MPa [cm.sup.3]/ 100 g
Loose black	130.9	152.0	58.8	48.5
Pelletized	122.2	125.9	58.8	48.6

Table 2--predictive models for NR compound tensile stress at 300% elongation

Model	n	Standard error MPa	Minimum DVVA pressure MPa	Maximum DVVA pressure MPa	Variables
Tread	35	0.28	144	198	VV, [VV.sup.2]
Carcass	41	0.16	114	170	VV

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