RUBBER GRADE CARBON BLACKS

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Over the years, many materials have been used as fillers in rubber compounds. In this sense, filler is a diluent and is used primarily to lower volume cost. With use, all fillers modify certain physical properties of the compound in addition to lowering cost. Therefore, lower cost is generally achieved at the expense of other desirable properties and all compounds are compromises with various trade-offs considered and balanced by the compounder. Elastomer systems respond to the addition of a few fillers, termed reinforcing agents, in a way that enhances certain properties. Among such substances used in rubber compounding, carbon black is unique in its ability to significantly enhance the properties of nearly any base elastomer system while lowering cost. It is truly more than a simple filler.

Buried within the generic term carbon black are many variations on a theme. There are so many facets to carbon black, each altering a rubber compound in its own subtle way, that the number of possible products is almost limitless. Recognition of some of these facets has, in many instances, been easier than devising corresponding testing methods, which would allow process control and exploitation as new products. Indeed, product refinement in the carbon black industry is probably hampered more by lack of definitive testing methods than by any other single problem. Still, a vast amount of progress has been achieved by the industry to the point that carbon black is doubtless the most refined and best-controlled commodity available to the rubber industry.

Basic Chemistry

In the simplest terms, carbon black is essentially elemental carbon in the form of extremely fine particles having an amorphous molecular structure. Buried within the amorphous mass is an infrastructure of microcrystalline arrays of condensed rings. These arrays appear to be similar to the layered condensed ring form exhibited by graphite, which is another form of carbon. The orientation of the arrays within the amorphous mass appears to be random, consequently a large percentage of arrays have open edges of their layer planes at the surface of the particle. Associated with these open edges are large numbers of unsatisfied carbon bonds providing sites for chemical activity. In use, particles remain largely intact and many of the useful properties of carbon black stem from their morphological characteristics while others result from surface activity.

Other than carbon, also present are very small quantities of other elements such as oxygen, hydrogen, and sulfur occurring in various functional groups bound to the carbon mass. In addition, small quantities of condensed hydrocarbons are adsorbed onto the particle surface of most rubber grade carbons.

Extraneous materials originating from the manufacturing process and equipment are typically also found in carbon black, for example: moisture, refractory dust, metallic oxides, coke, and water soluble salts. The levels of these materials are controlled within specified limits and are usually not significant in the final rubber product.

The Manufacturing Process

Carbon black is a product of incomplete combustion. It is the dark component of smoke and in fact all carbon black processes start with the production of a "smoke." In the process, the first step is to produce an intensely hot combustion zone with a convenient fuel. After combustion is complete, a hydrocarbon feedstock in excess of stoichiometric quantities is injected into that intensely hot zone. With this injection, carbon black will be produced, the art comes with assuring that the required properties are attained, the volume adequate and the cost supportable. Following the feedstock injection, the reaction is stopped by either injection of water or by allowing the temperature to decay with time. All furnace grades are made in a continuous process while thermal grades are made in a cyclical process. The carbon particles thus produced are separated from the process gas stream or "smoke" by conventional means and pelletized to increase the bulk density.

Although not all hydrocarbons lend themselves to economical production, essentially any combustible hydrocarbon could theoretically be used as a feedstock to produce carbon black.

Morphology

Morphology is a term having to do with the form and structure of an entity. Although not a common word, it certainly has been aptly applied in discussions of carbon black technology since the properties of carbon black, to a large extent, depend upon form and structure.

Industry Conventions for Particles and Aggregates

In the carbon black industry, the convention has been to refer to the smallest individually distinct unit of carbon as an aggregate. This convention contrasts with that of other pigment industries in which the smallest distinct unit of material is referred to as a particle. The carbon black industry convention, however, refers to the component parts of aggregates as particles.

The distinctions between particles and aggregates are readily observable with the aid of electron microscopy. Fig. 1, shows a sample of N351 at 150,OOOX magnification; both a particle and an aggregate are labeled. Note that clusters of fused particles make up aggregates.

Average particle size and average aggregate configuration play major roles in determining the utility of a given carbon black grade in a rubber formulation. In fact, the major differences between grades result from control of these averages, but such averages are difficult to assess with the limited sample size observable with an electron microscope. Fortunately, there are other methods available to quickly assess these fundamental characteristics.

Particles

The average particle size of commercially available rubber type carbon black grades ranges from about 10 to 500 nanometers. Within this fifty to one spread exists the possibility of a very large number of grades, each providing the rubber formulation a unique set of properties. In general, the larger the particle size, the lower the cost and the poorer the reinforcement potential of the material.

Just as the average particle size is important so also is the distribution of particle sizes. Distributions of particle size can be narrow or broad or even bimodal, each type influencing the rubber properties in its own subtle way. To further confuse the picture, broad distributions may occur, for example, as narrow distributions within single aggregates, but as a broad distribution in the grade. Such distributions are easily produced if the products of one or more reactors operated under differing conditions are blended. Yet a different type distribution occurs when a range of particle sizes exists within single aggregates. To date, convenient means of measuring all types of distributions do not exist; however, the manufacturer can exercise a degree of control, as suggested by the example just mentioned, through astute manipulation of various process factors and conditions.

Aggregates

As is apparent in Fig. 1, individual carbon black aggregates occur in what appear to be random constructions of randomly sized particles, but when dealing with aggregates, enormous numbers are involved and it is the mean effect of all these individual entities that must be controlled.

The morphology of aggregates is just as complex as that of particles. Aggregate sizes can vary as can the distribution of those sizes. They can occur as semi-spherical groupings of particles or they can occur as groupings with a distinctly long dimension. Aggregates can be of a very dense, solid construction or of an open lattice-like configuration. This last parameter can be termed aggregate density and will have a direct bearing upon aggregate count per unit mass. Aggregate count can be envisioned as a primary factor in many of the observed changes in rubber compounds with changes in carbon black morphology. As the count per unit mass increases, aggregate interstitial spacing is reduced, which affects the mobility of that portion of elastomer that bridges the space. Again, convenient methods for distinguishing between many of these aggregate characteristics have not as yet been devised.

In general, those properties of aggregates, which are independent of particle size, have been lumped into the term "structure." For a higher structure, these would include the propensity of aggregates to have a higher particle count and for particles to be joined into more chain-like clusters, having a narrow core. The cores can include random branching.

Surface Activity

In addition to particles and aggregates, a third major parameter of carbon black is what has become known as "surface activity." It can be shown experimentally that a given carbon black sample possessing a high reinforcement potential, upon being subjected to sufficient heat, will lose some of its ability to reinforce rubber. Since its morphology is changed very little with this treatment, such a sample can be described as having lost "surface activity." The loss of reinforcement is evidenced by a reduction in cure rate, modulus, tensile strength, abrasion resistance, tread wear and other physical properties. The degree of change will depend upon the severity of treatment. This, in a negative but practical way, demonstrates what is meant by "surface activity": which is that portion of reinforcement due to chemical linkages at the rubber/ carbon interface as opposed to morphological construction. This surface effect is what makes carbon black more than just a filler.

Over the years, technologists studying "surface activity" have identified a range of chemical groups associated with the surface of carbon blacks. It was thought for a time, that these groups must play a crucial role in surface activity. A great deal of effort was expended trying to gain a better understanding of how the surface, including these groups, reacted chemically with the rubber compound. The subject has proven to be very intractable, and more than limited understanding of these reactions has yet to be widely achieved. Practical applications of such work have not materialized in the carbon black industry.

Modern evidence suggests, however, that surface activity is more likely a function of the number of open edged layer planes exposed at the surface along with the associated unsatisfied carbon bonds than it is a function of the chemical groups that might exist there. This theory fits empirical observations with the process.

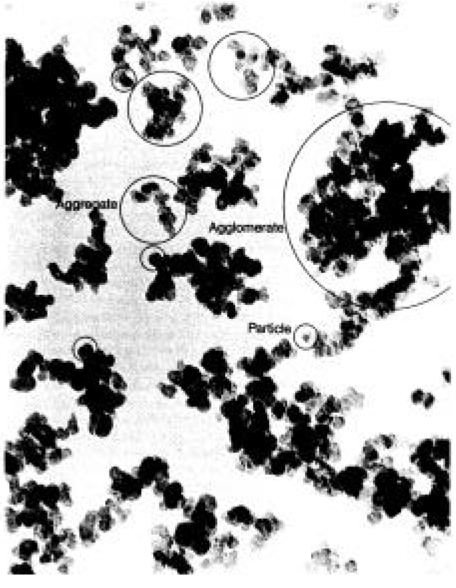
The carbon blacks that provide the highest reinforcement to surface area ratio are those that have been produced using the shortest reaction time. The evidence is that the immediate precursor of finished carbon black includes a very rough surfaced particle composed of fused microcrystalline arrays. These arrays should first appear joined in a totally random fashion with a large percent of them oriented in such a way that the ends of planes are exposed along with a large number of unsatisfied carbon bonds. This is the most active surface that can be obtained.

It has been demonstrated that with sufficient heat treatment these arrays will rearrange themselves in such a way that the layered graphitic planes will lie with only planes at the surface, thereby effectively satisfying the largest possible number of bonds as carbon-carbon linkages. In fact, thermal blacks exhibit such structure resulting from the extremely long reaction time used to produce these materials. Consequently thermal blacks exhibit a uniquely low reinforcement potential.

In addition to the heat effect, oxidation reactions are an unfortunate fact of life in the final stages of all carbon black production reactions. All these surface oxidation reactions are equally deleterious to the carbon black particle surface.

So there exists a continuum of surface activity delineated by these two extremes and, unless some unusual chemical treatment has been utilized, all carbon blacks can be expected to lie somewhere on this continuum. The best of the modern carbon blacks are produced with much shorter reaction times than has been the historical precedent and consequently exhibit a better balance of properties than the older materials. How far the possible improvement can be carried is dependent upon the expertise of the manufacturer.

Fig. 1, Carbon Black Morphology



Agglomerates

A fourth basic concept is agglomeration. For fundamental reasons, carbon black aggregates tend to coalesce with physical agitation. This propensity for association is the characteristic that allows formation of pellets. In Fig. 1, an agglomerate is also labeled. Agglomerates consist of loosely bound but not fused aggregates.

The degree with which agglomeration takes place directly impacts the ability of the end user to disperse a carbon black in his formulation, be it rubber or some product such as ink. Even with the high intensity ultrasonic agitation with which the sample of Fig. 1 was prepared, complete agglomerate disassociation apparently was not realized. With perhaps the single exception of conductive compounds, ultimate physical properties are achieved only with complete dispersion of agglomerates into their constituent aggregates. In the real world, however, this desirable condition is rarely achieved.

Environmental Health

Carbon black is manufactured in highly specific processes under controlled conditions and differs markedly from soots and other naturally occurring forms of carbon. Most naturally occurring forms of carbon have either a hard, glassy structure or crystalline structures and occur as rather large sharp edged particles when broken down to dust. Such materials generally also have a large hydrocarbon component. Coal and soot from wood fires are typical examples. Both of these must be handled with care due to health hazards associated with long-term exposure to their dusts. These same hazards do not seem to exist with manufactured carbon blacks, apparently because the form of the particles is not a body irritant, the very small size and rounded nature of the particles allow the body, with time, to slough off accumulations of the material. Also, any hydrocarbons present appear to be so tightly bound to the carbon black surface the human body cannot elute them, effectively blocking assimilation.

Based on a large body of studies performed under the auspices of the Carbon Black Industry Committee for Environmental Health, manufactured carbon black can be considered as a nuisance dust in the working environment. Dust protection should be worn if the time weighted 8-hour exposure exceeds 3 Mg/ m3.

Nomenclature

The nomenclature currently used for the rubber grade carbon blacks was instituted by the D 24ASTM Committee On Carbon Black in 1968. It consists of a prefix letter followed by a three-digit number. The prefix, either N or S indicates whether the grade is a (N)ormal or a (S)low curing material. When the system was developed channel blacks were still commonly used and were slow curing. Afterwards, a fifty-fold increase in natural gas price ended rubber grade channel black production. For a time furnace grades treated to emulate the cure characteristics of channel were available. These too have largely disappeared leaving little need for or use of the "S" prefix letter. Consequently, most (if not all) currently active rubber grades carry the prefix "N".

The first of the three digits is used to provide a coarse measure of the mean particle diameter of the grade as determined by electron microscope and expressed in nanometers. The possible particle diameters were arbitrarily grouped as shown in Table 1. Shown also are typical Iodine Numbers for each group. In a very general way, both manufacturing costs (prices) and rubber reinforcement potential (abrasion resistance) increase with smaller numbers in the first digit.

ASTM D 24 assigns the second and third digits to new products as the various manufacturers develop them. When a competitor matches a new product it normally carries the same "N" number as that provided the originator. In general, lower structure blacks have been assigned lower numbers; higher structure blacks, higher numbers. However, there are exceptions and structure values are not always proportional to the assigned second and third digits.

This system could perhaps be improved upon, but is a large improvement over the confusion of individual trade names that it replaced.

Characterization Testing

As inferred in the foregoing discussion of the fundamentals, characterization of carbon blacks is difficult based on the complexities of the material. It is made even more so because of the limitations of the standard characterization tests. A key problem is that not a single ASTM approved test defines an exact morphological characteristic. Interactions exist in each with two or more characteristics influencing the results. These limitations allow carbon blacks of very similar specification properties to provide quite different results when compounded in a rubber stock and performance is tested. As a result, rubber data from selected recipes are commonly used in conjunction with analytical properties for specifications. This too has its limitations, with repeatability high on the list. The shortcomings of, or lack of definitive characterization tests lead to what is often called the "black art", meaning simply that the manufacturer of carbon black is forced to use empirically derived information to control the process in a way that assures an acceptable product.

If the carbon black manufacturer is hampered by lack of definitive testing methods, so is the compounder. Carbon black, in many rubber compounds, has an influence second only to the polymer on compound properties and volume cost. If one is to intelligently choose which carbon black(s) to use for the best balance of cost and properties in a product, it is essential to have an understanding of the utility and limitations of characterization data. Table 2 gives an overview of the ASTM methods available for characterizing carbon black.

Surface Area Measurements as Estimates of Particle Size

As previously discussed, average particle size is one of the distinguishing characteristics of any carbon black grade. Since measurement procedures with electron microscopy are both cumbersome and subject to considerable sampling error, indirect methods of assessment are used based on the fact that surface area per unit weight varies inversely with particle size. Resulting from this relationship the industry has standardized on the convention that particle size effects are related directly to surface area. Any sound procedure for surface area analysis can be used. Three methods are currently approved by ASTM D 24 and in order of utilization they are:

Iodine Adsorption Number

Iodine Adsorption is one of the oldest analytical procedures used in assessing carbon black quality yet is still reliable with most carbon black grades. Since the procedure is based on classical "wet" chemistry, care must be exercised when assessing the merits of grades that contain a high residual feedstock component because the residual oil interferes with the wetting of the surface of the carbon black and produces lower than normal values for a given particle size. Such residual material may result from very short reaction times in the carbon black manufacturing process. The net effect is improved reinforcement for a given iodine value. This anomaly was exploited in producing the so called "New Technology" tread blacks of the early 1970's: N339 and N351 are in this group. The coarser furnace blacks, particularly of the N700 series, also exhibit a similar bias. Indications of such deviations may be assessed by examining the toluene discoloration, ASTM D 1618, for low transmittance (high extractables) at both the 425 and 338 nm wavelengths coupled with Nitrogen Surface Area values several points higher than Iodine values.

Surface Area by Nitrogen Adsorption

Most classical grades have surfaces that are relatively "clean" regarding residual feedstock and have not been overexposed to oxidation in their manufacture. For these grades, Nitrogen Surface Area values are very nearly identical with Iodine Number: N330, N347 and N220 are good examples.

For those grades that contain significant feedstock residual, and that includes most of the newer grades, Nitrogen Surface Area is the best indicator of relative average particle size and hence reinforcement potential.

When the surface of the carbon particles is oxidized in the manufacturing process, surface pitting occurs which disturbs the relationship between particle size and Nitrogen Surface Area. The interior surface of the pits or micropores can significantly increase the Nitrogen Surface Area leaving the particle size relatively unchanged. Such oxidation is indicative of a very long reaction time for a given particle size and is always accompanied by slow cure rates and low modulus values: early manufacture of N660, N550, and N 1 10are good examples. Since such oxidation results in a loss of carbon yield, few if any, modern rubber grades will exhibit such oxidation. Possible exceptions are extremely high surface area grades of the N100 series.

CTAB Surface Area

The CTAB Surface Area test was designed to overcome both the problems mentioned for the Iodine Number and Nitrogen Surface Area tests, in that the molecule to be adsorbed, cetyltrimethylammonium bromide, is far larger than the nitrogen molecule and is also a very effective wetting agent. In practice, however, the CTAB test is still affected to a degree by hydrocarbon residual and is more difficult to perform than either Iodine or Nitrogen Surface Area tests. Since little or no additional information is gained from that available with Iodine Number and Nitrogen Surface Area, this test has not been universally adopted as a specification value.

Structure Measurements

The second carbon black fundamental is structure. As previously mentioned, carbon black particles tend to fuse together, during the course of the manufacturing reaction, in a rather random fashion to form aggregates.

As with particle size measurements, direct measurement of structure has proven to be impractical if not impossible, therefore, secondary methods of analysis are again utilized.

Dibutyl Phthalate (DBP) Absorption Number

One of the earliest tests to be devised for carbon black was to determine the relative amount of oil that carbon blacks could absorb. Although the oil used as the absorbate and the end point definition have been changed, oil absorption is still the most commonly used measure of structure. In the current form of test, dibutyl phthalate (DBP) is used as the absorbate and is titrated into a given mass of carbon black as it is worked in a specially devised mixing chamber. As the test proceeds the mixture begins to change from an incoherent solid toward becoming a very viscous paste. During the transition, the machine torque required for mixing increases very rapidly. The end point is defined as attainment of a certain torque value.

Void Volume

As stated above, structure interferes with the packing of aggregates creating voids in the carbon black mass and a consequent decrease in apparent density. For the past 25 years or so this density change with structure has been recognized by carbon black technologists and attempts to use this relationship as a basis for developing a suitable measure of carbon black structure have been attempted by several with some degree of success. The generally proposed scheme is to measure the apparent volume under a specified pressure, followed by subtraction of the assumed volume of solid carbon. Most schemes appeared to offer promise as test procedures although ASTM has adopted no standard. At the time most of this work was done the mechanical aspects of the apparatus were very cumbersome. Now, however, electronic load transducers and micro computers allow design of very cost effective test apparatus, and have created renewed interest in this measurement scheme.

DBPAbsorption Number of Compressed Samples

It can be observed that DBP values will decrease in nearly all cases if mechanical work is applied to carbon black samples. Apparently, such work progressively breaks the bridging occurring between particles beginning with the weakest. It has been postulated that some of the bridges are so weak, in fact, as to be vulnerable to breakage or disruption in the process of being dispersed into a rubber matrix. These "weak" elements of structure lead to what has been called "transient structure," that is structure measured with the DBP test but not extant in the final rubber compound. Such structure again arguably leads to discrepancies between DBP data and measured compound properties.

In order to more closely approximate the structure remaining after mixing, a test was devised wherein the carbon black sample is compressed four times at 24,000 psi prior to the normal DBP test procedure. Whether the DBP or the CDBP (compressed) procedure better predicts rubber compound properties is still debated. However, the procedure does discriminate between carbon samples and doubtless the inclusion of both DBP methods in quality specifications has led to more uniform carbon blacks from both single and multiple sources.

Aggregate Size Measurements

As previously discussed, carbon black aggregates are synonymous with particles to the rest of the scientific community. Any method for testing particle size of solid materials that will measure accurately in a range from about 10 to 500 nanometers can be used to measure aggregate size. Two methodologies are being used in the industry for these measurements. One is a variation of classical sedimentation using an ultracentrifuge, wherein the rate of settlement is a function of the particle size.

The other, less dirlable. The light scattering devices are very easy to use, are fast, and the average values are very reproducible but they do not measure aggregate size distribution with the definition provided by the ultra centrifuge techniques.

To date there are no standard ASTM methods for aggregate size measurements with carbon black and no size standards exist. Since any method used must make assumptions regarding shape, density, and degree of dispersion levels obtained, level of results from the different instruments may vary considerably; however, comparisons using a given method can still be of value in assessing the relative merits of products in any particular group.

Indirect Measurements

Tint Strength

Since carbon black was first used as a pigment rather than reinforcing agent, it was soon discovered that certain carbon blacks produced a deeper black tint than others. No doubt this observation led to the development of a procedure to test this property, as an aid in developing more uniform pigmented products. As carbon black began to be used in rubber, systematic changes in rubber properties with tint strength were noted and control of tint strength of carbon black for use in rubber was developed as well.

The first methods depended upon dispersing zinc oxide and carbon black into linseed oil thereby producing a typical gray paint and comparing the degree of jetness developed by the different carbon black samples. The carrier liquid has been changed and the value now read electronically, but otherwise it is the same test used from the very earliest times and the data developed still correlate well to the reinforcing properties the carbon black imparts to the rubber compound.

Modern carbon black theory relates tint strength inversely to aggregate diameter. In an unpublished study, comparison of measured tint strength to mean aggregate diameter values across a broad range of carbon black parameter suggested that most (about 90%) of the variation in tint strength was accounted for by variation in mean aggregate diameter. Still, tint strength is very highly indicative of ultimate reinforcement potential, which in many instances, is not indicated by other accepted test methods including aggregate diameter.

Indicators of Surface Activity

No direct means of surface activity measurement exists. Two relatively simple indicators, however, are available for oil furnace grades particularly tread grades. One is to subtract the Iodine Number from the Nitrogen Surface Area. The very highly active carbon black samples will normally give a positive number which, depending upon the surface area level, can be as much as 10 to 15 units or even more. As NSA minus Iodine becomes negative, rubber reinforcement can be expected to progressively deteriorate. The second indicator is the Toluene Discoloration Test.

Extractables, Toluene Discoloration

From the time of the very earliest carbon black production it was noted that completeness of reaction could be judged by the depth of color of the solvent after performing an extraction on a sample of carbon black. During the early days of oil furnace production, reactor control was monitored by a simple chloroform extraction followed by a colorimeter reading. The commonly chosen colorimeter filter produced a wavelength of 425 nm. Later this test became a way for consuming industries to judge the likelihood that feedstock residual from the carbon black might migrate into adjoining stocks, for example from a tread stock into a white wall extrusion. It therefore, became a common specification property with minimum values above 85 generally being specified. With the advent of solvent exposure restrictions the solvent has been changed to toluene.

Studies of extractables with scanning spectrophotometers indicate that absorption peaks also occur at shorter wavelengths. A significant absorption occurs at 338 nm and is measurable with relatively inexpensive apparatus. If, while manufacturing a carbon black, the reaction time is short for a given surface area, a low reading will be obtained at this wavelength which can approach zero and still meet 425 nm specifications. Carbon blacks that exhibit low percent transmission values at 338 nm will usually be found highly active, having been subjected to minimum heat treatment and oxidation.

Pellet Properties

In its fluffy form as it originates at the carbon black reactor, carbon black agglomerates easily with agitation. This propensity is employed in the formation of pellets from the fluffy material, In the most common method called the "wet process", the fluffy black is mixed with water, followed by high speed agitation as a mass to form pellets and then passed through a dryer. With this method pellets are formed which for most rubber grades are too soft for bulk rail shipments. For these grades, a binder containing a sugar component is commonly premixed into the pelletizing water. Moderate usage is necessary because such binders can create very hard, tough pellets.

Although pellet properties are not used as a guide for choosing the grade of carbon black to be used in a given compound, depending upon the mixing characteristics of the compound, they can certainly have a direct bearing on the achievement of ultimate properties and upon batch to batch uniformity.

Individual Pellet Crush Strength

Pellet crush strength, or pellet hardness as it is commonly termed, is a simple concept but as indicated by the repeatability estimate, is one that is difficult to define, specify, and measure with precision. There are several sources of variability that methods to date do not address well.

Microscopic examination of typical carbon black pellets will quickly demonstrate that they are far from being round. This means that when crushed on a flat plate there will be a variable supporting footprint depending upon the specific shape of the individual pellet being examined. Consequently a range of values can be expected even with pellets consisting of the same mass strength of the internal carbon matrix and of the same size. It is the strength of this internal carbon matrix on which dispersibility in rubber depends. Technicians are instructed to choose the most spherical pellets. This leads to operator bias and can also lead to a "hard" bias since a binder is used to increase the hardness of most carbon black pellets and binder influences the sphericity of pellets.

For pellets of the same internal matrix there is a direct relationship between size and hardness; therefore, pellet size must be specified when discussing pellet hardness. It is common to specify the cut between two screens to narrow the range of pellet sizes to an acceptable level. Pellets that pass through US # 12 sieve and are retained on a US # 14 are widely used. Even with this narrow cut, the range of possible diameters can account for ± 6 grams at an average hardness of 40. This, no doubt, contributes a great deal to the poor repeatability estimates for this procedure.

Recent work has demonstrated that the speed with which force is applied to a pellet during the crushing test influences the test value significantly. With the current apparatus this speed is operator controlled and very difficult to maintain with precision. Directed toward elimination of the operator altogether, several groups are currently developing new methods of carrying out the actual crushing in which the rate of force application is totally machine dependent. To date none of these has become standard.

Sampling error is another implacable factor. The ASTM procedure calls for crushing a total of 20 pellets from which the high and low are picked and the average calculated. These 20 pellets are expected to represent the average of those in a sample, which in the case of a hopper car shipment, may total 25 trillion pellets. Also, the test is destructive and results can never be exactly repeated under any circumstance.

Regardless of the testing deficiencies mentioned, pellet hardness as it relates to the strength of the internal matrix of the pellet has an important bearing on dispersibility of the carbon black in a compound. Hardness becomes critical if the viscosity of the compound is low or if plasticizer oil content is very high. Typical problem compounds are butyl tubes, low durometer low cost EPDM extrusions, and extruded sponge. Such compounds may require a pellet hardness of less than 30 grams maximum (through 12 on 14). A dilemma can develop if the bulk handling equipment at the consuming plant is aggressive toward pellets because such soft pellets break up very easily into fines. Thirty grams average is softer than most bulk handling systems can tolerate and levels of 45 to 60 are more common for bulk consumers.

Carbon Black, Pelleted - Fines Content

Sampling error can again influence repeatability since fines tend to segregate in bulk handling equipment, especially when flowing in and out of storage tanks. Non-uniform pockets of fines can randomly form which are difficult to find.

Fines in carbon black are undesirable for several reasons, not the least of which are the associated housekeeping problems usually accompanying dusty material. Variable bulk flow characteristics are associated with higher fines content and this can create non-uniform discharge problems in automatic weighing equipment and consequently poor batch uniformity. Dust tends to coat the internal surfaces of mixing equipment preventing immediate wetting of the metal surface with the polymer and slowing the progress of the mix. Apparently dust pockets can form in the mix, which are harder to disperse than pellets and can lead to unsatisfactory dispersion, depending of course upon the compound and mixing equipment.

Carbon Black, Pelleted - Pellet Attrition

Poor pelletizing and poor control of drying processes can create high attrition values in pellets which in turn lead to rapid fines build-up in handling systems. Fines content can be low as shipped as a result of either a sound process or from fines removal prior to shipment, but if attrition is high the consumers' bulk handling equipment can still create enough fines to cause problems. Generally, attrition values of 1 % or less are excellent and up to 3% adequate for most bulk handling installations.

Pour Density of *Pellets*

Pour density is listed as a pellet property which it is to an extent, but only within the narrow range of structure represented by a single grade. However, across a range of grades and even within a grade specification, pour density also varies inversely with structure. As indicated by their correlation coefficients, structure, as measured by DBP Absorption, accounted for about 9396 of observed density variation in a recent unpublished study. Included in the study was a group of 150 experimental samples encompassing a broad range of properties produced at a single location.

The pelletizing process influences density in two major ways: First an increase in the unit work applied in the pelletizing equipment squeezes the aggregates into more compact mass displacing water in the process. After drying, this leaves less void within the pellet and an increased density. However, this increase in work also results in a decrease in structure as measured by the DBP Absorption test, again demonstrating a clear relationship between structure and density. If the manufacturer, at this point, adjusts reactor operations to bring DBP Absorption back to the original target value while leaving the increased work in place, the density can be expected to decrease from the level obtained with the increased work but to remain higher than the original value.

The second effect of the pelletizing process on pour density involves pellet size distribution. It is a long established principle that with spherical objects, a broad range of diameters will pack more densely than will spheres of the same diameter. This same phenomenon is exhibited by carbon black pellets; however, examination of the size distributions of a large number of carbon black samples indicates that distributions among grades, plants, and suppliers are remarkably similar and this impact on density can be expected to be small, except perhaps where an unusually high fines content exists.

Density exerts an economic impact on shipping and storage costs, since with bulk grades these costs are, to an extent, based on volume. The lighter materials are associated with higher costs and higher densities are therefore economically desirable. However, outside a range of about ± 1.5 lb/ft3, density is a function of other specification properties (e.g. DBP) and not independently controllable by the manufacturer.

Compounding With Carbon Black

Compounding with carbon black usually comes down to two fundamental decisions: the choice of carbon black grade and of loading. The variety of ways the balance of properties can be modified by the compounder with these parameters is nearly unlimited. These two decisions will depend upon the properties required in the final product. Sometimes these requirements are very well defined but in many instances the compounder is faced with making his own judgments as to the suitability of any given compound for a given purpose. Since carbon black has such a major impact on the ultimate properties of a compound, the success of the rubber product may well depend upon the skill of the compounder in manipulating these two factors.

Choosing the "Right Stuff'

When choosing a carbon black grade, one must recall that the fundamental characteristics of carbon blacks are particle size and structure level. These will differentiate between most grades and also influence compound properties more than other characteristics. Table 3 provides a list of grades commercially available to the rubber industry at the time of the writing of this article. Included in the table are typical iodine numbers and DBP values which are most generally used to assess the particle size and structure of rubber grade carbon blacks.

This mix of grades has evolved over time as needs of compounders have been identified. It covers the large majority of compound requirements very well, but all grade possibilities are by no means exhausted. Innovations are constantly under evaluation as possible new products to bring into the market place and most carbon black suppliers have contributed innovations when market volume appeared sufficient to justify an additional grade. Open discussion with carbon black suppliers regarding required properties are often fruitful, resulting in suggestions for alternate grades or even the development of a new grade. Such discussion allows suppliers to keep pace with new demands placed on rubber products as they evolve.

Choosing a Particle Size

Among the commonly used fillers and reinforcing agents, carbon black offers the most potential reinforcement. However, there is such a broad range of grades available that there are areas of overlap with other materials such as the kaolin clays and precipitated silicas.

Since particle size or surface area is the primary determinant of reinforcement perhaps the logical starting point in choosing a carbon black is to assess the level of reinforcement which will be required and based on these considerations pick a surface area range with which to start. Compound requirements such as tensile strength, abrasion resistance, tread wear and tear resistance must be considered, bearing in mind that as these properties are improved by choosing a higher surface area, other changes occur: viscosity and compound cost will increase while dispersibility and "snap or feel" as indicated by rebound and other dynamic properties will be reduced. Referring again to Table 3, typical types of compounds in which each grade has found application are also listed. Consideration of the general harshness of service for these typical applications can serve as a guide for the surface area level likely to be required of other potential rubber products.

To illustrate rubber property changes that occur with particle size, a group of carbon blacks encompassing the available range of iodine numbers has been tested in a simple SBR compound, shown as recipe A in Table 4. Major rubber properties have been assessed and values are shown in Table 5. Grades tested are shown ranked in descending order of iodine value.

It must be recognized that the levels of these properties will change depending upon other compound components, basic of which is the exact elastomer being used in the compound. Fortunately for the compounder, ranking reversals of carbon black grades for any particular property rarely occur when other compound components are changed. For example, if carbon black A has a higher modulus than carbon black B in a given compound and the polymer is changed, black A can still be expected to have the higher modulus after the change.

Choosing a Structure Level

The second parameter one must choose when deciding what carbon black grade to use is the structure level.

Carbon black structure as indicated by DBP absorption inhibits the elasticity of a compound in much the same way as reinforcing steel inhibits the elasticity of reinforced concrete. Essentially spherical aggregates loaded in a compound will inhibit the elasticity of a compound to a degree, but when these aggregates have a certain shape factor, that is have a long dimension, they act as if they were very short fibers and interfere with the elastic mobility of the polymer in which they are dispersed. This stiffening effect is, therefore, more pronounced with structure than with particle size.

Increased structure manifests itself in many related ways: viscosity, modulus, stiffness, hardness, conductivity, and dispersibility are all increased while extrusion surface imperfections and swell, and tear strength are decreased. As a general rule, increased structure has little impact on compound costs since high and low structure blacks are usually priced similarly. Fig. 2 presents graphs showing trends that can be expected when structure is changed at a given particle size. The carbon blacks used in these illustrations were experimentally produced samples controlled to 92 ± 2 Iodine Number and serve well to demonstrate structure change. The recipe is the same as used to illustrate changes with particle size.

Occasionally compounds are too soft to disperse adequately the most common carbon black grade of a required surface area. In such instances, it is often possible to change to a higher structure, perhaps at a slightly reduced loading, and achieve an improved balance of reinforcement and dispersion. This technique has led to increased utilization of the finer grades in rubber products. Most of the newer fine grades are of a high structure level and the trend is to even higher structure levels.

Compounding to a Given Hardness

Many commercial rubber compounds are developed to a given hardness specification. Since hardness changes with both particle size and structure, changes in carbon black grade are usually accompanied with adjustments in carbon black and/or plasticizer loading. Choosing the optimum balance in carbon black and plasticizer loading can be a time consuming process since nearly every compound property, as well as compound volume cost, is affected to some degree by these two factors.

A useful exercise is to design an evenly spaced grid covering the possible carbon black and plasticizer loadings of interest, then mix and test each resulting compound. Since compounds respond to changes in these two ingredients in mathematically predictable ways, development of isopleths or even equations for each property is therefore possible. Such graphs provide an immediate understanding of possible trade-offs and promote fast, accurate optimization.

Graphs from an example of this type of compounding study are provided in Figs. 3 and 4. The specific carbon black shown is a low hysteresis grade having an Iodine Number of 80 and a DBP Absorption Number of 132. The compound is a **typical SBR/NR/BR** tire tread formulation as shown as recipe B in Table 4.

If the graphs are examined carefully, it becomes apparent that adding carbon black and pasticizer oil in increments such that the hardness remains a constant can provide a tool to reduce compound volume cost with minimum deleterious effect on other properties. This technique is widely utilized. Note that if a hardness line is overlaid with modulus, for example, the result is almost a constant. Some properties are shown to form a peak. Abrasion resistance as measured by tread wear is an example. Depending upon where the exercise is initiated it may be possible to decrease compound costs and even obtain improved properties by studied manipulation of these two variables.

Another typical compounding exercise is to examine an existing compound for possible cost savings while maintaining other factors. Sometimes a change to a higher structure carbon black makes an easy improvement. This is accomplished by taking advantage of the hardness increase, which is then offset with added plasticizer. Higher structure carbon blacks have the capability to absorb the incremental plasticizer with little detrimental effect on other properties and the net change is simply a reduced cost. Because of this compound cost advantage, consumption of high structure carbon black grades has steadily grown over the past twenty years or so and now, as a group, represents the major volume. In contrast, trying to gain a cost advantage utilizing the hardness increase due to a decrease in particle size is seldom successful because most properties, as well as carbon black price, change very rapidly with particle size.

Processing Carbon Black Loaded Compounds

Just as the carbon black grade chosen for a given compound can have a very large influence on the properties of that compound, it can also have a very large impact on the methods used to process the compound. The two processes particularly sensitive to the grade of carbon black are mixing and extrusion. In fact, often problems with these two processes will materially influence the decision regarding which grade to ultimately use.

Mixing

In order to achieve the full potential of any rubber compound a high degree of dispersion of the ingredients in the polymer matrix must be realized. This sounds easy but it is not always so, especially when mixing time is important. Since the primary mixer can be the major factor limiting plant capacity, mixing time is nearly always an important consideration.

With carbon black there are three key properties that significantly influence dispersibility: particle size, structure and pellet hardness. The degree of difficulty in achieving suitable dispersion becomes worse as both particle size and structure are decreased. In fact, exceedingly poor dispersibility has prevented the commercialization for use in rubber of very fine, low structure carbon blacks even though the properties they could provide would otherwise assure a market for such a grade.

The best mixing technique to use in any given situation depends upon so many factors that generalizations are difficult to draw. A rule of thumb is like the old sailors admonition "any port in a storm" or whatever works! Nevertheless, certain trends are observable. For any carbon black grade and polymer system a certain minimum batch viscosity must be achieved for a given length of time in the mixer to obtain a given level of dispersion. Trade-offs between time and viscosity are possible. Increasing levels in these two factors can be expected requirements as particle size and structure decrease if adequate dispersion is to be maintained. For example, with the thermal blacks, which have uniquely large particles, very good dispersion is readily attained in nearly any compound. In contrast, reaching the same dispersion level with N110, which has very fine particles, can be very difficult and may require as many as three or more passes through the mixer.

Certain situations tend to prevent attainment of one or another of the two necessary conditions. A low viscosity polymer can prevent obtaining the necessary viscosity with the carbon loading used. In such an instance, the carbon black loading can be increased to achieve the dispersion followed by an addition of polymer in a second pass to realize the desired final loading. Perhaps a better trade-off would be to simply increase the mixing time either with a second pass or by remaining in the first pass for a longer period of time.

A high loading of plasticizer can prevent achieving the necessary viscosity for an adequate period of time. Depending upon the level of plasticizer, this can be a very difficult problem. The general approach is to hold back as much plasticizer as possible until dispersion is achieved then adds the final increment of plasticizer. Another approach is to add all the carbon black and oil initially to the mixer followed by the polymer. With this technique, the carbon black absorbs a fair amount of the oil that stays on the carbon black until the first dispersion is achieved. This technique has been used with varying degrees of success but is usually a poor compromise at best as judged by the ultimate dispersion of such batches. With either of these methods the exact timing of additions of materials becomes critical because dispersion is usually limited by the risk of over lubricating the mixer surfaces and "putting the batch to sleep."

To achieve dispersion of the very small particle size carbon blacks, a high compound viscosity is required which must be maintained for a relatively long period of time. Since these stiff batches generate heat at prodigious rates, the necessity of dumping such batches before the necessary work input has been achieved is often a fact of life. The only solution is generally multiple passes with adequate cooling and aging between. In any event, it is possible that the only point in the mixing cycle in which the viscosity is sufficient enough to gain further dispersion is at the initial breakdown of the cold batches.

As previously mentioned, pellet hardness can contribute to poor mixing and dispersion. Since the economics of mass production dictates that most carbon black consumers handle the material in bulk, pelletizing is a necessity. All pelletizing is simply agglomeration on a large scale and the job of the rubber mixer is to break up these agglomerates to attain the desired dispersion. In addition, it is common practice to add binder to the pellets of many grades in order to assure that the pellets are hard enough to handle well in existing bulk handling equipment. The more tightly the pellets are knitted together the better they handle and the more likely they are to mix poorly. The carbon black manufacturer is, therefore, continually treading the line between sufficiently good bulk handling and enough friability to assure dispersion. In some installations, improved bulk handling equipment could contribute materially to improving overall mixing efficiency by allowing pellet hardness specifications to be reduced. Also, if the volume of a difficult-to-disperse grade is such that it allows receiving the material in bags instead of bulk, often much softer pellets can be provided which again can materially contribute to the desired dispersibility.

Many attempts to improve carbon black dispersibility with various additive treatments have been tried but with limited success. The economics of this approach is usually poor since the prices of most chemical additives are far higher than that of carbon black. Also the dosages required to achieve a significant level of improvement, when it can be achieved at all, are significant. With most such systems, if they are successful in loose carbon black they are equally successful when added to the rubber batch during mixing. Considering the usual logistics problems of additional carbon black grades, the rubber mixer is the most feasible place to add the material and not at the point of manufacture of the carbon black.

Extrusion

Most elastomers exhibit, in the uncured state, a phenomenon termed elastic memory. Elastic memory simply stated is the propensity of the material to try to return to its original shape after that shape has been distorted by application of an outside force. This is the phenomenon that produces swelling after a rubber stock passes through an extruder die. Most fillers, including carbon black, inhibit this elastic property by interfering with the mobility of the elastomer molecules. This interference is a function of the loading of the filler.

Table 1

First Digit Assignment by ASTM

In Carbon Black Nomenclature System

First Digit	Typical Average Particle Size, nm
0	1 to 10
1	11 to 19
2	20 to 25
3	26 to 30
4	31 to 39
5	40 to 48
6	49 to 60
7	61 to 100
8	101 to 200
9	201 to 500

Comparing the extrusion properties of carbon black grades will demonstrate that extrusions tend to improve to a degree with increasing surface area, but to a much larger degree with increasing structure. The difference between both the extrusion swell and the smoothness of surfaces is very dramatic if one compares for example N326 and N358. The differences in swell values to be expected are indicated in Fig. 4. In many products the structure level has been chosen based solely on the desirable extrusion characteristics offered by the higher structure grades.

Table 2

Test Methods for Carbon Black

	ASTM Method	Range of Values	Single Operator Repeatability	Lowest Black	Highest Black
Particle Size					
Iodine Adsorption	D1510	8-145g/kg	± 0.5 g/kg	N990	N110
Nitrogen Adsorption	D3037	8-143 m^2/g	± 2.00%	N990	N110
CTAB	D3765	8-132 m^2/g	± 1.6 m^2/g	N990	N121
Structure					
DBP Adsorption	D2414	43-150 cm^3 /100g	± 0.80%	N990	N358
DBP Compressed	D2493	42-112 cm^3/g	± 0.7 cm^3/g	N990	N358
*Agregate Size **					
Tint Strength	D3265	17-125 tu	± 0.9 tu	N990	N234
Surface Activity					
Toluene Discoloration	D1618	98-75	± 2.30%	N351	N110
Pellet Properties					
Crush strength	D3313	20-80 g	± 22%		
Fines Content	D1508	5-15%	± 36%		
Pellet Attrition	D4324	2-5%	± 67%		
Pour Density	D1513	18-40 lb/ft^3	± 0.1 lb/ft^3	N358	N990

* = Centrifugation and light scattering are direct measurements of aggregate size, but have no standardization ASTM method. Tint strength is an indirect measure aggregate size.

Table 4

Compound Formulations Utilized

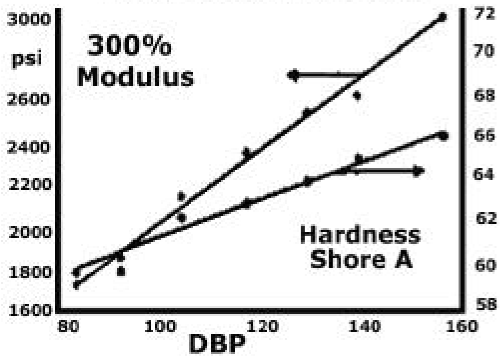
	A	B
BBR 1500	100.0	
Solution SBR		45.0
Natural Rubber		35.0
Polubutadiene		20.0
Carbon Black	50.0	Variable
Napthenic Oil	10.0	Variable
Zinc Oxide	3.0	3.0
Stearic Acid	2.0	2.0
AGERITE STAOITES	1.0	
ANTOZITE 67P		2.0
AGERITE RESIN D		0.8
VANAX NS	1.0	
AMAX		1.5
Sulfur	2.0	1.8
	169.0	Variable

Table 5

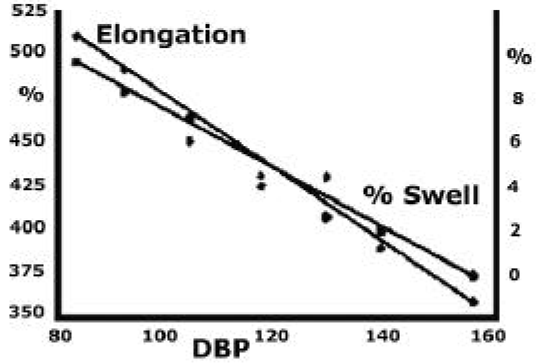
Carbon Blacks Compared in SBR

Carbon Black	N110	N220	N339	N351	N550	N660	N762	N990
Mooney at 100°C (212°F)								
Viscosity, (ML1+4)	65	64	62	59	60	52	48	46
Die Swell, 0.25" diam. Die								
45 rpm, 70°C (150°F)								
% of swell	9.6	8.0	6.4	7.2	4.0	4.4	6.0	5.6
Physical Properties								
300% Modulus, Mpa	13.2	12.9	15.5	14.3	12.3	9.9	7.9	3.7
(psi)	1920	1870	2240	2070	1790	1440	1140	530
Tensile Str. Mpa	27.4	27.5	25.6	25.2	20.2	21.4	22.5	12.6
(psi)	3960	3990	3700	3670	2920	3110	3260	1820
Elongation, %	500	530	440	470	480	540	630	730
Hardness, Shore A	60	61	60	59	57	53	50	44
Tear, Die C, kN/m	36	37	35	33	35	33	34	26
(pli)	205	210	200	190	200	190	195	150
Dynamic Testing								
Rebound, Zwick, %	44	46	50	53	58	60	61	63
Heat Buildup, °C	137	134	116	117	112	107	108	104
Firestone, (°F)	278	273	242	245	233	224	226	220
E', Mpa	9.8	8.7	8.2	7.6	6.6	5.8	5.2	4.4
(psi)	1420	1265	1190	1100	965	845	760	645
E", Mpa	2.4	2.1	1.7	1.4	1.1	0.9	0.8	0.6
(psi)	355	300	250	210	160	130	115	90
Loss Factor, tan δ	0.25	0.24	0.21	0.19	0.17	0.15	0.15	0.14

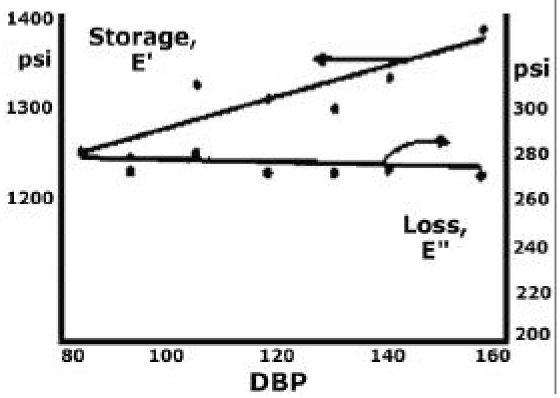
Base Compounds: SBR recipe A from Table 4



Modulus and Hardness



Elongation and Die Swell



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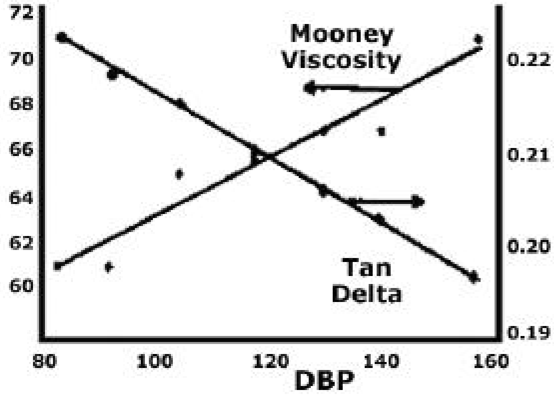
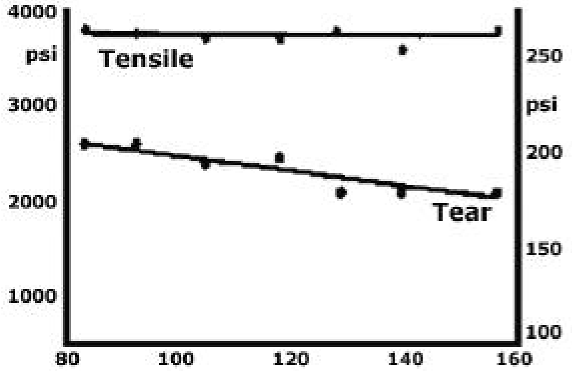
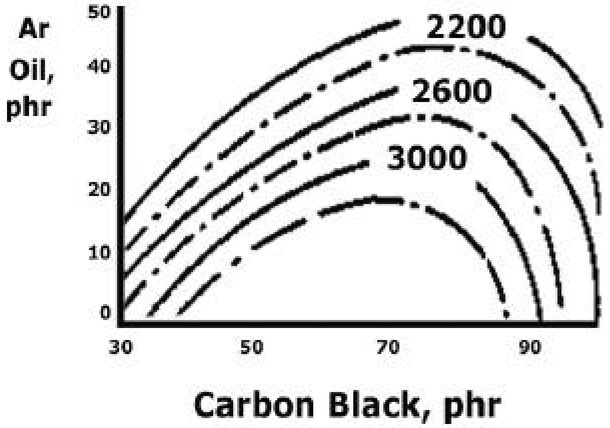


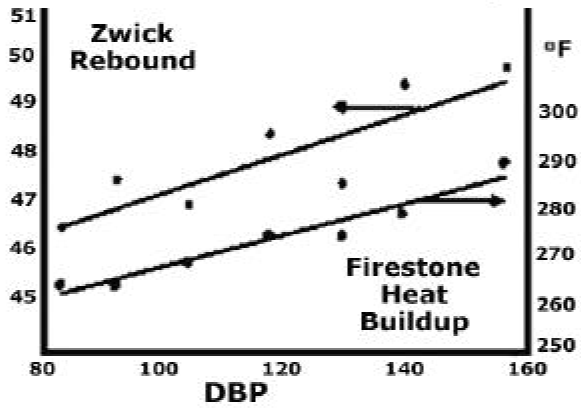
Viscosity and Loss Factor



Tensile Tear Strength



Tensile Strength, psi



Rebound and Heat Buildup